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Fragilisation des aciers par le zinc liquide à haute température et conséquences

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RENAUD FRAPPIER

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Liquid zinc embrittlement of steels at high temperature and consequences

RENAUD FRAPPIER

Fragilisation des aciers par le zinc liquide à haute température et conséquences

RENAUD FRAPPIER

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Introduction

Les procédés métallurgiques existent depuis les débuts de la technologie humaine. Dans son histoire, l'humanité a développé sa connaissance des métaux, en particulier pour la mise en œuvre du fer et des aciers, pour rendre possible la réalisation de projets très ambitieux. Aujourd'hui, les sidérurgistes et constructeurs automobiles maîtrisent les procédés de soudage pour assembler des pièces d'acier à haute résistance revêtu d'une fine couche de zinc. De cette manière ils fabriquent les caisses des voitures, des objets de hautes technologies. La recherche en métallurgie apporte les connaissances de base pour les développements à venir de l'ingénierie des aciers.

Les aciers avancés à haute résistance (HR) ont été développés par les sidérurgistes depuis 20 ans pour la construction automobile dans le cadre de l'allégement des structures, qui représente une des principales problématiques de l'industrie des transports. Des compositions chimiques et des traitements thermomécanique innovants ont permis d'obtenir des microstructures multiphasées, par exemples les aciers biphasé martensite-ferrite (DP, pour *dual phase*) ou les aciers à plasticité induite par transformation (TRIP, pour *transformation-induced plasticity*). Ces matériaux sont un compromis aux exigences apparemment contradictoire de l'obtention:

- d'une forte résistance mécanique (haute limite d'élasticité),
- d'une formabilité suffisante (grand allongement avant striction),
- d'un bas cout.

Pour être utilisés comme pièces de structure dans la caisse automobile, les aciers doivent être revêtus d'une couche de protection anticorrosion. La galvanisation à chaud et l'électro-galvanisation (EG) sont deux procédés mis en œuvre dans les lignes de traitement continu des aciers et permettent de déposer une couche de zinc à la surface de la tôle. Le produit « acier » final est caractérisé par sa microstructure de base, sa résistance à la traction, son épaisseur et son revêtement. Par exemple un produit nommé DP600 1mm EZ est un acier électrozingué de microstructure DP, d'épaisseur 1 mm, avec une résistance de 600 MPa. Il est ainsi vendu par le sidérurgiste au constructeur automobile.

Dans l'industrie automobile, le principal procédé d'assemblage est le soudage par résistance par point (RSW pour *resistance spot welding*). A la suite de retour d'expérience des constructeurs automobiles, l'équipe de recherche et développement (R&D) en soudage du centre de recherche ARCELORMITTAL de Maizières-lès-Metz, France, a observé que certains points soudés pouvaient présenter des fissures à leurs surfaces remplies du zinc provenant du revêtement de galvanisation. Le zinc est *a priori* à l'état liquide dû aux hautes températures impliquées dans le soudage. Les produits non-revêtus ne fissurent pas. L'effet détrimental du zinc à l'état liquide à la surface de l'acier a alors été étudié.

Le phénomène de fragilisation par les métaux liquides (FML, ou LME pour *liquid metal embrittlement*), documenté dans la littérature scientifique, a été identifié comme la cause de l'apparition du défaut au cours du soudage. La FML se traduit par une perte de ductilité importante d'un métal solide lorsqu'il est déformé en contact avec un autre métal à l'état liquide. Identifié et étudié depuis des dizaines d'années, ce phénomène est encore sujet à de nombreux débats dans la communauté scientifique. Plusieurs critères empiriques et mécanismes théoriques ont été proposés mais ils sont souvent contradictoires et ne semblent pas décrire l'ensemble des observations expérimentales présentes dans littérature. D'autre part l'étude bibliographique

n'avait jusqu'alors pas permis de trouver de solutions technologiques simples au problème rencontré par les industriels.

Aujourd'hui, la fissuration induite par le zinc liquide peut être supprimée par un bon contrôle des procédés de mise en forme. Néanmoins, un effort important est réalisé par les services de R&D du groupe ARCELORMITTAL pour décrire les causes du phénomène, les mécanismes de fragilisation et pour expliquer la sensibilité des différents produits développés. Ceci est effectué dans le but de permettre le développement de compositions chimiques et de microstructures résistantes à la FML.

Cette étude a été menée entre 2011 et 2014 dans le cadre d'une *Convention industrielle de formation par la recherche* (CIFRE) entre le centre de recherche *ArcelorMittal Maizières* et l'*Institut des Matériaux Jean Rouxel* (IMN) à Nantes.

Ce rapport de thèse résume les investigations sur la fragilisation par le zinc liquide et la fissuration de surface pendant le soudage par résistance par points de tôles galvanisées. Elle a été principalement menée sur trois nuances d'aciers HR. La problématique suppose une étude scientifique et technique. Ce manuscrit questionne donc le sujet de manière fondamentale mais aussi du point de vue ingénierie et développement industriel. Il donne des éléments de réponse aux questions suivantes :

- Comment décrire l'occurrence de la FML dans le cas du système acier/zinc ? Peut-on s'inspirer des mécanismes décrits dans la littérature pour d'autres systèmes métal solide/métal liquide ? (Chapitre I)
- Quelles sont les causes de la fissuration pendant le soudage par résistance par point? Peut-on décrire un scénario pour la fissuration qui soit en accord avec la description des mécanismes de la FML? (Chapitre II)
- Peut-on observer des différences de sensibilité entre les différentes nuances? La description des mécanismes et l'explication des différences entre les nuances permettent-elles de concevoir des solutions pour supprimer le phénomène de fissuration? (Chapitre III)

Ce manuscrit est divisé en trois chapitres. Au vu de l'environnement industriel et scientifique de cette thèse, la plupart des investigations, discussions et rapports ont été réalisés en langue anglaise. C'est pourquoi les Chapitres I et II sont rédigés en anglais. Les résumés de ces deux chapitres en français sont proposés en annexes. Le Chapitre III et la conclusion sont rédigés en français.

Chapter I Occurrence and mechanisms of embrittlement

This first chapter aims to describe the occurrence of liquid zinc embrittlement of steels: temperature range, critical stress/strain for cracking, influence of the steel grade (microstructure and composition). Fundamental mechanisms will also be discussed: crack velocity, cracking path and atomic scale mechanism of propagation. This knowledge is supposed to be the basis for a better understanding, in order to identify materials parameters that should influence cracking extent. Numerous metals and alloys can be embrittled by other liquid metals. For examples, low-alloy steels can be embrittled by cadmium [ARA1982], by sodium [HIL1995], and by zinc particularly during the galvanizing process [CAR2009][CAR2010][KIN2004]; chromium martensitic steels by tin, lead, bismuth, or the eutectic lead-bismuth [LEG2000][NIC2001][SER2006][AUG2008][HAD2009][VAN2010][DIN1976]; austenitic stainless steels by zinc [COT1976][ALL1992][BRU1992] and by gold [FAV2011]; nickel alloys by bismuth [FUN1982][MAR2000][MAR2001][WOL2001][WOL2002]; aluminium and its alloys by gallium [GOG1964][GUO1999][BRE2002]; and copper by bismuth and by the eutectic lead-bismuth [WOL2001][WOL2002].

LME fundamental's still puzzles the scientific community. For example, two recent papers [MAL2013][GLI2011] described contradictory fundamental mechanisms. The first excludes any diffusive phenomenon because it is supposed to be unable to explain high crack velocity; the other describes a diffusion-based mechanism with a complicated reaction chain involving dissolution/diffusion/redeposition, and also proves high kinetics. Other contradictory facts can be found about empirical description of the occurrence of LME. For example it was almost admitted that low mutual solubility [FER1996] between solid metal (SM) and liquid metal (LM) is a condition for embrittlement. The present case is in contradiction with that! Indeed it is known that the mutual solubility of Fe and Zn is large (several percents) compared to many other systems [RAG2003]. Experimental conditions, such as strain rate in tensile tests or surface oxidation, can have a large influence on the detection of the embrittlement [FER1996]. This is supposed to produce errors and misunderstanding.

First, LME mechanisms described in the literature are summarized. For that, the penetration mechanism of LM into the microstructure of SM without external stress is reviewed. In the case with external stress, existing models for liquid-metal induced crack propagation are reviewed. In each case the constitutive hypotheses of the model and its kinetic predictions are described. In a second time, data about the steel/Zn and Fe/Zn systems are given: equilibrium phase diagram, diffusion data, and reports about LME detection. In the third section, preliminary characterization of the galvanized steels of the study is described: composition, microstructure, phase transition temperature, initial state of the coating, etc. In the fourth section, the experimental characterization of the embrittlement is described: loss of ductility in tensile tests at high temperature, microstructural description of the cracks. In the fifth section, the experimental characterization of the (stress-free) contact between steel and Zn is described: GB wetting and penetration at the steel/coating interface, penetration and dissolution during long time contact in sealed quartz tube. To finish results are discussed in terms of practical information about the embrittlement of steels, and of fundamental description of the atomic-scale mechanism of crack propagation.

1. Literature review: LME mechanisms

Liquid metal embrittlement (LME) occurs when a solid polycrystalline metal (SM) is strained in intimate contact with other liquid metal (LM). Fracture path is usually intergranular. In interface science, intimate contact refers to the description of surface wetting. In the case of a polycrystalline material, the wetting of the surface and the emerging grain boundary (GB) induces GB boundary diffusion and grooving due to the chemical potential (composition) gradient. The mass transport of LM atoms in the SM microstructure appears preferentially along GBs and is named GB penetration. This review focuses first on basic phenomena for GB penetration. In a second time the behavior of the GB is discussed when thermodynamic parameters such as composition or temperature may significantly vary. For example, GB composition is modified during mass transport by GB penetration. By analogy to the bulk, phase transitions or complexions transitions can be observed and described. The consequences of such transitions for GB properties are reviewed. Then some models giving a phenomenological and kinetic description of GB penetration are described. To finish, what is named in the literature “pure LME” or “LME itself”, i.e. models for fracture and crack propagation induced by the presence of the LM, is reviewed.

1.1. Basic phenomena for GB penetration

In a situation of macroscopic mechanical equilibrium, i.e. no or low external stress application (at the opposite, a situation where external stress leads to crack propagation is described in the paragraph 1.4), the contact between a solid polycrystalline metal (SM) A and the liquid metal (LM) B induces matter flow of B in A. Matter transport driven by chemical potential gradient, is achieved by “volume” diffusion, but also along “short circuit” paths: grain boundaries (GBs). GB diffusion can be several orders of magnitude faster than volume diffusion.

Diffusion usually involves small quantity of matter. For example, GB diffusion can be viewed as a monoatomic layer of matter penetrating GBs. But GBs take also part in macroscopically observable phenomena of penetration like so-called GB grooving or wetting.

1.1.1. GB diffusion

GB diffusion has been experimentally evidenced in the early 1950's by radiotracer methods. Fisher's model [FIS1951] is the most famous mathematical model and constitutes the basis of the further phenomenological models. Phenomenological models are often discussed at the level of atomistic analyses, since it was pointed out that coupling phenomenological and atomistic approaches is the basic way to understand grain boundary diffusion [ADD1966] [LEC1963]. Experimental and fundamental facts were reviewed and compiled in the 1990's and 2000's [KAU1989][KAU1995][MIS1999]. These papers are the principal source for the reminders about grain boundary diffusion given in this paragraph. Readers should refer to these papers for complete information. The original work of classical authors about GB diffusion models are also of high interest: Fisher [FIS1951], Whipple [WHI1954], Shewmon [SHE1963], and Suzuoka [SUZ1961].

GBs are “short-circuits” paths

GBs are considered as transition zones between misoriented crystals of the material. This hypothesis involves that the GB structure and properties may depend on the relative orientation of the two adjacent crystals. Thus the GB is usually defined by five parameters, three for the misorientation of adjacent crystals (Euler angles), and two others for the orientation of the GB plane. Low angle GBs can be geometrically described by simple operation (rotation and torsion). The energy γ_{gb} of low angle boundaries can be calculated, for example from the misorientation angle for a simple flexion boundary. In industrial materials, most GBs are general boundaries, *i.e.* high angle boundaries. Due to the complex structure associated with these boundaries, no models give any fully-admitted description of high angle boundaries.

For the properties of the polycrystal, GBs are of high interest because of their excess free energy γ_{gb} compared to the bulk. Atomic transport along grain and interphase boundaries is of great importance in the analysis of numerous metallurgical processes, such as creep, sintering, recrystallization or embrittlement, since diffusion along GBs can be several orders of magnitude faster than in the crystal.

Fundamental description of GB diffusion

In the present study, the solute B diffuses along the GBs between crystals of metal A. According to the Fischer’s model [FIS1951], it can be described as a single boundary perpendicular to the surface as displayed in the figure 1. Based on Fick’s equations for diffusion, this process is described by a couple of equations:

$$\frac{\partial c_v}{\partial t} = D \left(\frac{\partial^2 c_v}{\partial x^2} + \frac{\partial^2 c_v}{\partial y^2} \right). \quad (1)$$

where $|x| > \delta/2$, and:

$$\frac{\partial c_{gb}}{\partial t} = D_{gb} \frac{\partial^2 c_{gb}}{\partial y^2} + \frac{2D}{\delta} \left(\frac{\partial c_v}{\partial x} \right)_{x=\delta/2}. \quad (2)$$

Here c_v and c_{gb} are the concentration of the diffusive species in the volume and in the GB, respectively. x and y are spatial coordinates defined in the figure 1, and t the time. These equations represent diffusion in volume and along the grain boundary, respectively. The second term in equation 2 takes into account the diffusion from the GB to the volume corresponding to a leakage of atoms B from the GB.

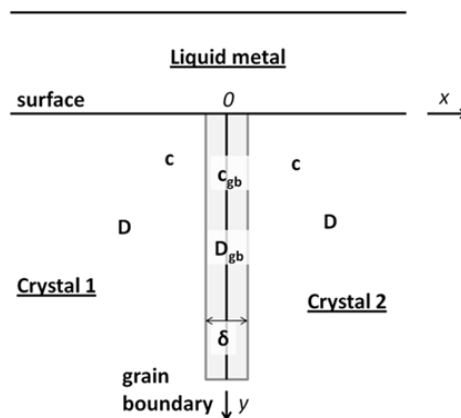


figure 1 : Schematic geometry for GB diffusion analysis. LM (considered as B solute in Fick's equations) diffuses in the SM (considered as A matrix) GB

The complete mathematical description needs to define the boundary and initial conditions. The simplest boundary condition is the constant source condition at the surface, as initially proposed by Fischer. This condition will be used in this introduction paragraph to GB diffusion (an alternative boundary condition is the instantaneous source proposed in [SUZ1961]).

$$c(x, 0, t) = c_0 = \text{const.}$$

The diffusion of B, considered as an “impurity”, along the boundary may involve a coupling conditions to describe the discontinuity between $c_{gb}(y, t)$ and $c_v(y, t) = c(x, y, t)_{x \rightarrow \delta/2}$. It is actually related to the second term of the equation (2). This condition considers the segregation factor s defined as follows.

$$c_{gb}(y, t) = s c_v(y, t) \quad (3)$$

The theoretical description of the segregation factor is not detailed here. It involves segregation regime and for examples consideration about the concentration dependence of s . It practically means that when s is high enough the loss of B atoms from the GB to the bulk can be neglected. The solutions for the single perpendicular boundary were also applied to the polycrystal. All these descriptions should be considered as approached or simplified exact solutions that were discussed according to experimental results, but also atomistic considerations. As this thesis is not explicitly devoted to grain boundary diffusion analysis, these theoretical considerations are not detailed. The implication of this theoretical work on the processing of diffusion profile is described in the paragraph below.

Deducing the GB diffusivity D_{gb} from penetration profile

Experimentally a concentration $\bar{c}$ of B atoms is measured at different distances from the surface. It is the measurement of both GB and surrounding bulk concentrations. This layered average concentration can be measured by means of radioactive activity measurement on a layer sectioned at constant depth, or by EDX line scans. The function $\bar{c}(y)$ contains the information about GB diffusion parameters. The mathematical analysis of the problem is able to discriminate bulk and GB contributions. It comes that the part of the function $\bar{c}(y^n)$ corresponding to the grain boundary diffusion becomes a straight line when $n = 6/5$, as shown in the figure 2.

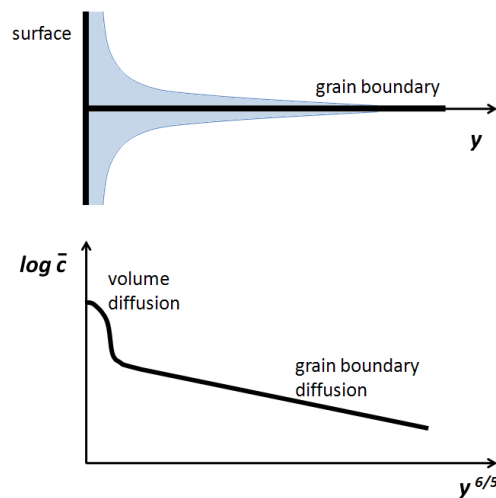


figure 2 : Schematic concentration profile associated with grain boundary diffusion experiments

According to authors cited in [MIS1999], the following analysis shall be conducted to extract information from the experimental function. It was found in the case of the constant source that the triple product $s\delta D_b$ can be calculated according to:

$$s\delta D_{gb} = 1.322 \left(\frac{D}{t} \right)^{1/2} \left(-\frac{\partial \bar{c}}{\partial y^{6/5}} \right)^{-5/3} \quad (4)$$

The volume diffusion coefficient D is supposed to be known from other measurements and $\frac{\partial \bar{c}}{\partial y^{6/5}}$ is graphically determined. This result is valid only if the following conditions are met.

$$\beta > 10 \quad (5)$$

$$\alpha < 0.1$$

Here these two parameters are

$$\beta = \frac{s\delta D_{gb}}{2D(Dt)^{1/2}} \quad (6)$$

$$\alpha = \frac{s\delta}{2(Dt)^{1/2}} \quad (7)$$

To discriminate each parameter of the triple product and to finally calculate D_{gb} it is generally accepted (see previous references for GB diffusion models) that the boundary width $\delta = 0.5$ nm is a very reasonable value in metals, in particular regarding high resolution transmission microscopy observations. This value is widely used in grain boundary diffusion interpretation. The estimation of s is more difficult, in particular because s is temperature dependant like D_{gb} . Measurements and interpretation in a wide temperature range is a way to discriminate D_{gb} and s . As an empirical rule, grain boundary coefficient follows an Arrhenius-type temperature-dependence.

$$D_{gb} = D_{gb0} \exp\left(-\frac{E_{gb}}{RT}\right) \quad (8)$$

Here D_{gb0} is the preexponential factor, E_{gb} the activation energy and R the gas constant.

A simplified solution for GB diffusion

Several mathematical solutions of the problem have been calculated from both analytical and numerical resolutions. The simplified Fisher's exact solution for the C regime is considered, i.e. in the case where $D_{gb} \gg D$, meaning that there is no contribution of the volume diffusion (mathematically: $c_v = 0$, $D = 0$):

$$c_{gb}(y, t) = c_0 \operatorname{erfc}\left(\frac{y}{\sqrt{2D_{gb}t}}\right). \quad (9)$$

Here erfc is the complementary error function. A numerical example of equation (9) is shown in figure 3. The time dependence of the penetration depth y measured for a constant value of c_{gb} follows $t^{1/2}$ and is also shown in figure 3. According to equation (9) this curve can be fitted by

$$y = \sqrt{2D_{eff}t}, \quad (10)$$

with

$$D_{eff} = D_{gb} \left(\operatorname{erfc}^{-1} \left(\frac{c_{gb}}{c_0} \right) \right)^2. \quad (11)$$

If the equation (11) is applied for the present numerical values, namely $c_{gb} = 0.1$ and $c_0 = 1$, it gives $D_{eff} \approx 1.82D_{gb}$.

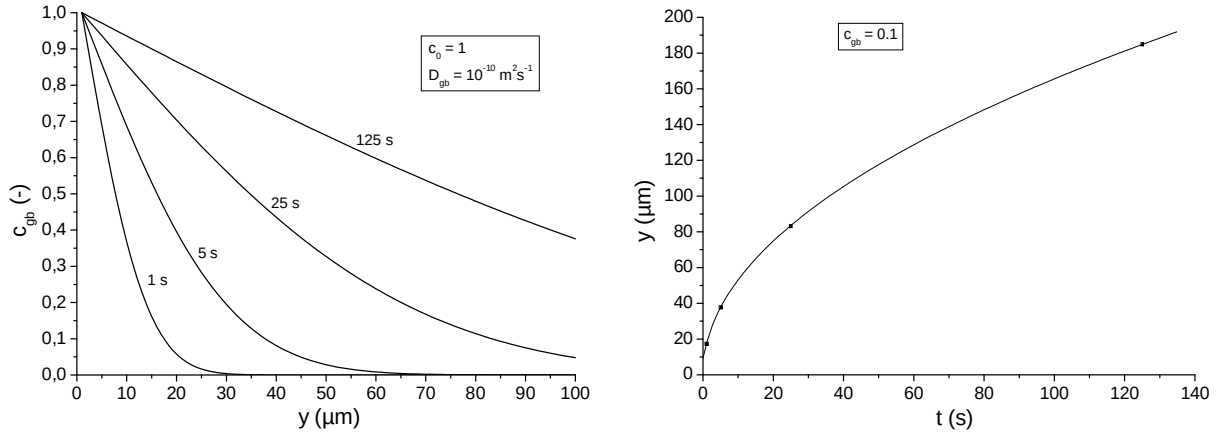


figure 3: Penetration profile according to equation (9) (left), and time-dependence of the penetration depth for $c_{gb}=0.1$ (right)

1.1.2. GB grooving

Mullins GB grooving

Thermal grooving refers to a diffusion process that tends to form a “groove morphology” at the surface at the position of the GB. The thermodynamical equilibrium of interfacial energies during the experimental process of thermal treatment in air or inert environment was described by Mullins [MUL1957]. The kinetic law to reach the equilibrium is also described.

This theory can be applied to a LM environment as shown in the figure 4. It is rigorously relevant only if a chemical equilibrium exist at the initial stage, i.e. if the liquid B is saturated by A atoms. The following equation gives the wetting angle θ_0 as a function of interfacial energies of the system.

$$\theta_0 = 2 \cos^{-1} \left(\frac{\gamma_{gb}}{2\gamma_{SL}} \right) \quad (12)$$

Here γ_{gb} is the grain boundary energy and γ_{SL} the solid/liquid interfacial energy. Equation (12) described only the local equilibrium morphology at the groove root. To keep this equilibrium, the groove penetrates the GB. In the case of LM grooving Mullins shows that the controlling kinetic mechanism is the dissolution-condensation mechanism: dissolution of SM atoms around the groove root, transport by diffusion in the LM, redeposition on the surface (formation of two bumps at the surface). The limiting step is the diffusion of solid metal atoms in the liquid. In this case the penetration depth d scales with $t^{1/3}$.

$$d = \left(1.01 \cot \left(\frac{\theta}{2} \right) \right) \left(\frac{D_L \gamma_{SL} C_0 \Omega^2}{k_B T} \right)^{1/3} t^{1/3} \quad (13)$$

Here D_L is the diffusion coefficient of SM atoms in the LM, C_0 the solubility limit of SM atoms in the LM, Ω the atomic volume of the SM, and k_B the Boltzman constant.

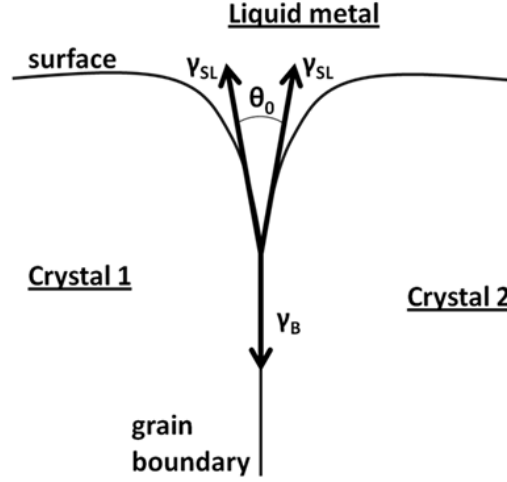


figure 4: Schematic grain boundary grooving morphology

Limitation of the Mullins' model

The evolution of θ_0 based on equation (12) has been represented in the figure 5. The following conditions may be considered:

$$\frac{d\gamma_{SL}}{dT} < \frac{d\gamma_{gb}}{dT} < 0.$$

It means that the S/L interfacial energy decreases faster than the GB energy as temperature increases. A temperature T_{wet} can be found, such as

$$\theta_0 = 0 \leftrightarrow 2\gamma_{SL} = \gamma_{gb}. \quad (14)$$

T_{wet} is called the wetting transition temperature [WOL2002][WOL2008][STR2004][CAN2013]. For temperature above T_{wet} complete wetting (or perfect wetting) should occur. The grain boundary is thermodynamically instable and should be replaced by the liquid phase, *i.e.* by two solid/liquid interfaces. It is also possible to find a GB concentration for which a similar transition occurs at constant temperature [STR2004]. Wetting transitions can be described in the framework of “GB phase transitions”, or “GB complexion transitions” [CAN2013][KAP2013]. This will be detailed in section 1.2 of this chapter.

It is admitted that, above T_{wet} , the penetration channel does not show Mullins-like surface curvature, as pointed out for example in [GLI1999]. In other words, it is impossible to apply Mullins theory for temperature above the wetting transition. It has also to be noticed that in most cases of interest, the liquid metal is not saturated in SM atoms. This is another concern to explain why Mullins's groove theory is difficult to be applicable.

Models were developed to find a kinetic model of the fast non-Mullins penetration of thin liquid channel in GBs and will be described in the section 1.3.

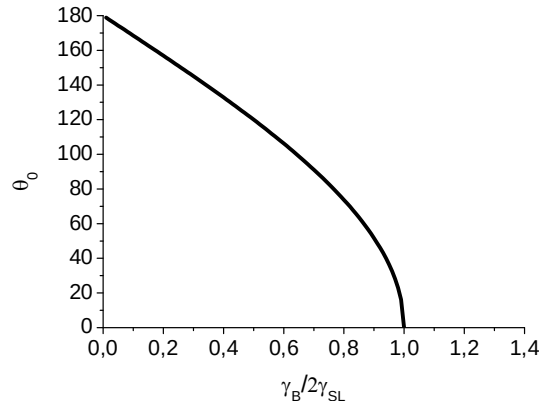


figure 5: Contact angle vs. interfacial energies. GB wetting transition occurs when θ_0 drops to zero.

1.2. “GB complexion transitions” [CAN2013]

1.2.1. Definition

GB wetting channel is a type of GB complexions

Analog definition to bulk phase transitions is proposed by Cantwell, et al. for GBs and named complexion transitions [CAN2013]. This paragraph is based on the conceptual analysis and experimental results reviewed in this paper. Readers should refer to this study and references therein. As already mentioned, the GB has an excess (interfacial) energy γ_{gb} . It depends upon the following parameters: geometry (relative misorientation and translation of adjacent grains, boundary plane, and residual crystallinity), temperature T , pressure P , chemical potential of atoms μ (or concentration c). As γ_{gb} is a continuous function of these thermodynamical parameters, a GB complexion transition occurs when there is a discontinuity in the first derivative of γ_{gb} as a function of one of the parameters (1st order transition) or in the second derivative (2nd order transition). A complexion transition can affect structure or thickness of the boundary but also composition, chemical bonding, roughening and/or atomic construction of the boundary. A classification of the complexions transitions can be found depending upon the parameter that they affect. It gives the framework for the analysis and definition of GB faceting and GB wetting transition.

So GB wetting transitions at T_{wet} (all other thermodynamical parameters being fixed) defined by the equation (14) can be identified in this classification. Others exist which can be 1st order, 2nd order or continuous transitions. In pure materials, GB premelting transitions have been observed for temperatures significantly below the melting point of the bulk, for example by observing high “liquid-like” diffusivity of Cu GBs at high temperature. In non-pure materials, adsorption (segregation) along GBs causes the GB composition to differ from the bulk. GB complexion transition results in drastic modification in the adsorption behavior of GBs. Classical segregation theory describes fraction of monolayer adsorbed along GBs while GB complexions result in the presence of multilayers or nanometer-thick amorphous or liquid films. The thermodynamical analyses predict premelting and prewetting transitions as the formation of intergranular films (IGFs) of finite thickness, i.e. without the presence of bulk liquid phase.

Adding GB complexion transitions to bulk binary phase diagram

In a binary system A-B, complexion transitions can be added to the 2D bulk equilibrium diagram as shown in figure 6, if pressure and geometrical parameters are considered constant. The premelting transition lines for three different GB orientations $\Delta\theta$ (energies) are plotted: $\Delta\theta_1 < \Delta\theta_2 < \Delta\theta_3$. The influence of the energy of the “dry” GB on the premelting (premelt), prewetting (prewet) and wetting (wet) transition temperatures is pointed out. Above the premelting or prewetting transition, a multilayer complexion or IGF should be observed along the GB of interest, while it is monolayer or fraction of monolayer below it. Since the dispersion of GB orientations and GB energies can be high in a polycrystal, it would be impossible, and also not helpful, to indicate a complexion transition line for all GBs. A transitions line should actually be added when a significant amount of GBs are affected by GB complexion, and consequently when macroscopic material properties are significantly affected. A “real” example of bulk equilibrium diagram with GB complexions for $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ [CAN2013] is shown in figure 7.

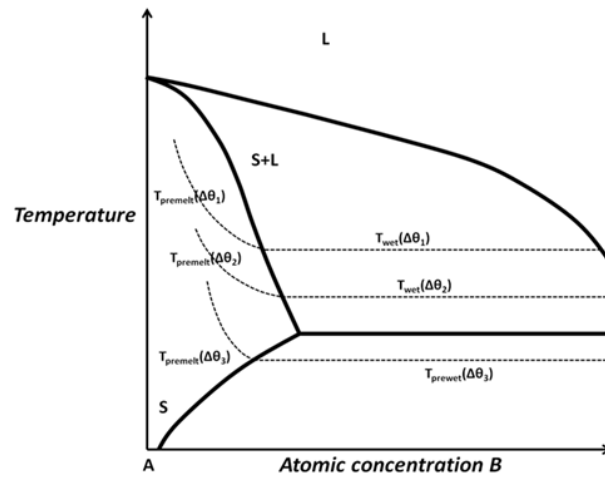


figure 6: Eutectic equilibrium diagram with lines of GB phase transitions

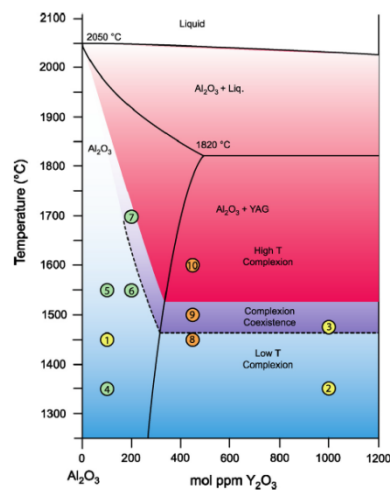


figure 7: Experimental complexion diagram for $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ showing premelting-type and prewetting-type complexion transitions. The complexion diagram has been made according to measurement of grain boundary mobility. Reprinted after [CAN2013]. See references therein

1.2.2. Practical consequences

Discrete complexions: from sub-monolayer to bulk liquid film

Innovation in high resolution microscopy allows the observation of grain boundary complexions. It comes that several discrete complexions with an equilibrium finite thickness exist. As shown in the figure 8, they are categorized according to their thickness, from clean GB to arbitrary-thickness wetting layer, increasing the atomic disorder. For example, the bilayer complexion of GBs after Bi penetration was directly observed in Cu and Ni [LUO2011][KUN2013] as shown in figure 9.

So passing across the premelting (premelt) or prewetting (prewet) lines of the equilibrium phase diagram (figure 6) by increasing the temperature or the chemical composition would make the GB to experience different GB complexions.

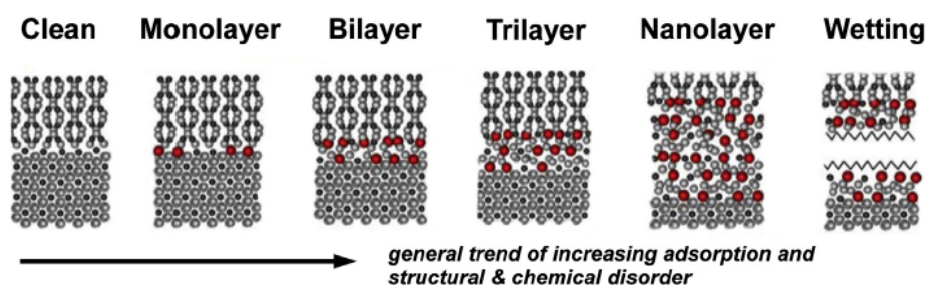


figure 8: Schematic representation of discrete complexions, named Dillon-Harmer complexions. Reprinted after [CAN2013]

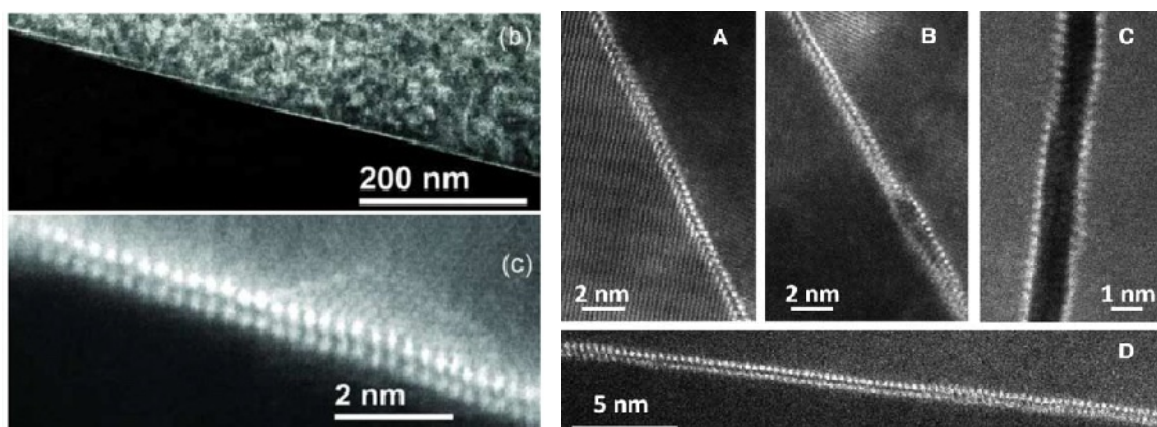


figure 9: Intergranular penetration of Bi in Cu at 700°C [KUN2013] (left), and Bi in Ni [LUO2011] (right). Bi atoms appear lighter than the SM matrix. Atomic bilayer complexion of Bi was identified to be very embrittling

Diffusivity and mechanical properties of complexed GBs

Complexion transitions cause a drastic change in GB properties. For example the triple product (m^3s^{-1}) of complexed GBs of Fe-Si-Zn alloys increases by two or three orders of magnitude [RAB1991]. Figure 10

shows the example of the Cu-Bi system. The transition from bilayer to multilayer complexion would lead to a jump of two orders of magnitude in the GB diffusivity.

The mechanical properties of GBs are also affected since the complexion transition increases the atomic disorder. Indeed the bilayer complexion in Cu-Bi and Ni-Bi has been identified as the embrittling step in the study of the embrittling GB penetration of Bi (figure 9). Indeed Bi-Bi atomic strength is calculated to be low compared to Cu-Cu and Ni-Ni strength. The correlation between LME and GB complexions was explicitly described in the Luo, et al. paper published in *Science* [LUO2011].

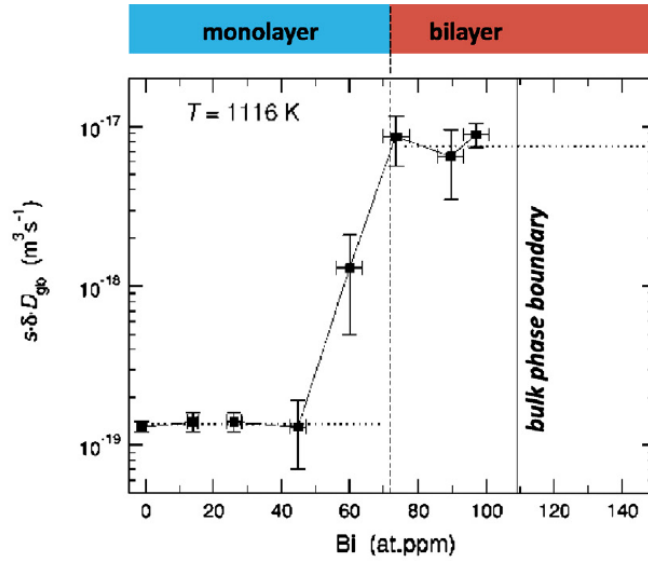


figure 10: At 1116 K, a transition from Bi monolayer complexion to Bi bilayer complexion along Cu GBs occurs at $c = 70$ ppm and corresponds to a jump of two orders of magnitude in the GB diffusivity

1.3. Grain boundary penetration models

1.3.1. Observation of non-equilibrium angle

The case where conditions for the thermodynamical complete wetting (equation(14)) are achieved is discussed in this paragraph. But $\theta_0 = 0^\circ$ is in practice impossible. Because the thickness of the channel is not zero, a “dynamic” angle $0 < \theta_d < 90^\circ$, as named by Glickman and Nathan [GLI1999], is observed at the root of the penetration channel. Actually $\theta_0 = 0$ predicted by the equation (14) just indicates that quasi-parallel walls should be observed for the penetration channel. In this case the solid GB is not equilibrated with the liquid metal phase. In other words, the imbalanced capillarity force creates a “pressure” at the root of the channel.

Modeling grain boundary penetration (GBP) needs to provide kinetic description regarding the out-of-equilibrium root described by θ_d , material properties, and the driving force ($\gamma_{gb} - 2\gamma_{SL}$). Models in agreement with linear kinetics of penetration are first described, then those with parabolic kinetics.

1.3.2. Linear kinetics of penetration

Faceting-induced linear penetration

As mentioned by Bernardini, et al. [BER2002] and Chatain, et al. [CHA2001], there is some undersaturation of the solid GB by the LM atoms. These authors proposed a model for propagation induced by the faceting at the root of the real GB groove, as shown in figure 11.

No solid diffusion (GB or bulk), nor liquid diffusion is directly taken into account for the analysis of the kinetics. The migration of the facets is attributed to an interfacial reaction and the migration rate is hypothesized to be proportional to the driving force associated with the non-equilibrium shape of the root, i.e. a function of θ_d and $(\gamma_{gb} - 2\gamma_{SL})$. The migration of the facets CD and DE (figure 11), characterized by the mobility M_{CD} , occurs by “lateral propagation of steps” from the triple line seen as “a natural site for the heterogeneous nucleation of steps”. The mobility of the walls is assumed to be negligible compared to M_{CD} .

The equation given here is simplified according to the arguments of the discussion conducted in [BER2002].

$$l = \frac{M_{CD}(\gamma_{gb} - 2\gamma_{SL})}{a \sin\left(\frac{\theta_d}{2}\right)} t \quad (15)$$

Here a is the width of the channel and θ_d the dynamic angle. Both need to be determined from experimental observations. The analysis proves a linear kinetics of penetration.

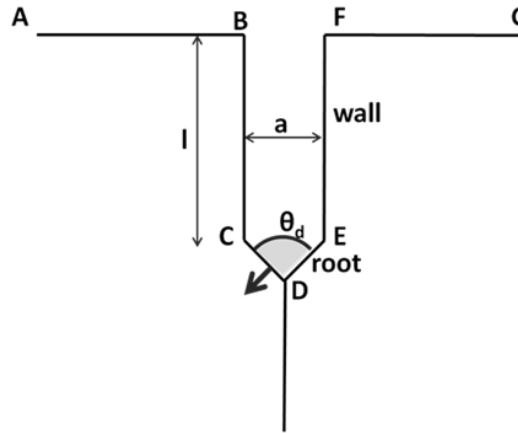


figure 11: Schematic representation of the faceted channel analyzed by Bernardini, et al. [BER2002]. The black arrow indicates the direction of migration of the facet CD of the root of the channel.

Coupled GB diffusion and liquid diffusion for linear penetration

Glickman and Nathan [GLI1999] assume that imbalanced forces at the root of the channel with concave curvature surface should impose a compressive stress and cause SM atoms from the bulk to diffuse along the GB and to be deposited on the GB further from the root. The flux I_{gb} “drains” atoms from the root and causes the groove extension. To balance this flux, a flux I_{gb} of solid metal atoms via fast diffusion mass transfer through the liquid metal is necessary. A linear dependence for the penetration rate is found.

$$l = \left(\frac{\gamma_{gb}^2 \left(1 - \frac{\cos(\theta_d/2)}{\cos(\theta_0/2)} \right) \Omega}{D_L \gamma_{SL} C_0 Z^2 T} \right) D_{gb}^2 t \quad (16)$$

Here Z is the characteristic distance between dislocation-like defects.

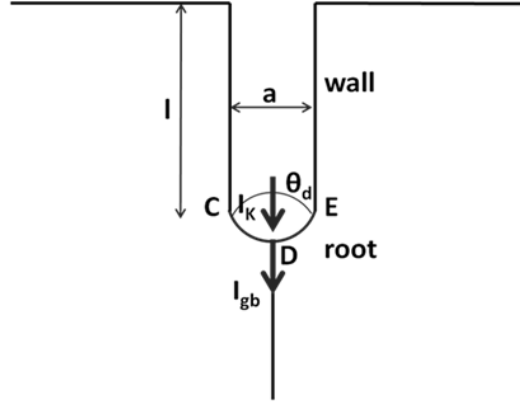


figure 12: Schematic representation of finger-like channel, characteristic of GB penetration according to Glickman [GLI1999]

Stress-induced GB adsorption/diffusion for crack-like linear penetration

Brechet, et al. [BRE2002] supposed that the difference in atomic radii causes elastic deformation after GB diffusion. First, in a simplified continuum mechanics analysis, they calculated this stress field and the distance at which a dislocation will be emitted. According to the authors the emission of the dislocation corresponds to a cracking event that may propagate the liquid channel. Then the atomic jump frequency Γ (around $10^3 - 10^4 \text{ s}^{-1}$) is estimated from the diffusion coefficient of the LM atoms in the SM grain boundary by

$$\Gamma = \frac{D_{gb}}{\Delta^2}. \quad (17)$$

Δ is the atomic jump length. A simplified equation based on Brechet's arguments can be derived as follow:

$$l = \frac{2\Gamma\mu(r_{SM} - r_{LM})}{\sigma_y} t. \quad (18)$$

Here μ is the shear modulus of the SM, σ_y the yield stress, r_{SM} and r_{LM} are the atomic radii of the SM and the LM, respectively. This simple analysis gives a linear propagation rate in the range of 10^{-6} m s^{-1} for the Al-Ga couple. This model is supported by Klinger [KLI2010] who finds using numerical calculations that tensile stress associated with GB diffusion is high compared to the yield stress of pure ductile metal. According to Brechet, et al. this crack-like model could also be used for crack propagation under external stress.

1.3.3. Square root kinetic penetration

Chen and Huang [CHE1995] proposed a kinetic law with a square root time dependence, and diffusion in the liquid as the limiting step.

$$l^2 = \frac{2C_0 D_L V_{SM}^S}{(1-C_0) V_{LM}^L} \left[\exp \left(\frac{\gamma_{gb} - \gamma_{SL}}{\delta RT} V_{LM}^S \right) - 1 \right] t \quad (19)$$

Here V_{SM}^S and V_{LM}^S are the atomic volume of SM in the solid matrix and dissolved in the LM, respectively, V_{LM}^L is the atomic volume of the SM. δ is the grain boundary width.

1.3.4. Others

Other descriptions

Desré [DES1997] proposed that the grain boundary diffusion of the LM atoms should induce the formation of an amorphous layer after that the concentration of LM atoms in the GB reaches a critical value. This analysis is in agreement with the theory of premelting phase transition (detailed in section 1.2).

In agreement with Desré's model, Klinger and Rabkin [KLI2010] proposed that the stress at the root of the penetration channel, in addition to the melting transition of the boundary promoting high increase of the diffusivity, should be the basis of a model of rapid penetration.

To explain GB channel thickening, Rabkin [RAB1998] supposed that the coherency strain energy in the bulk at the root of the channel after GB diffusion of LM atoms causes the preferential dissolution of the root, even if the liquid is saturated in SM atoms regarding the unstressed solid crystal. In other words, dissolution can occur at the penetration tip even if the LM was previously saturated in SM atoms. The analysis found that the width of the channel, around 100 nm, is in agreement with experimental observations.

Influence of residual stress

Several authors question the influence of internal stress (residual stress), or stress caused by the fixation of the specimen in the experimental apparatus, on penetration [LUD2004][PER2005]. This uncontrolled source of stress could be the cause of the dispersion in penetration rate and thickening of the penetration channel (elastic stress relaxation after grain decohesion).

1.3.5. Comments

Even if linear kinetics are observed and modeled by localized (atomic or nanometer scale) reaction at the groove, it is generally accepted for long penetration time and long distance (for example when channel thickness is stabilized) [GLI2003] that the kinetic will be obligatory governed by diffusion in the liquid, i.e. following a parabolic well-defined kinetic law.

Thickening of the channel may be promoted by elastic stress relaxation caused by residual stress, diffusion-induced stress or dissolution-induced residual pressure in the SM at the root. The transport in the channel is partially or totally not due to diffusion, but due to liquid flow after channel opening. This mechanism may explain the absence of the kinetic limitation by liquid diffusion. As pointed out in [LUD2004], if mechanical stresses are involved in GB penetration, the description should be made in terms of crack propagation and an appropriate atomic-scale mechanism should describe the interaction between physical/chemical and mechanical aspects. This has been named "LME" and is reviewed in the paragraph below.

1.4. LME: cracking in liquid metal environment

This paragraph focuses on cases where exterior stress is applied to the SM in contact with the LM, involving crack propagation and resulting in the embrittlement of the SM.

The last exhaustive review of LME phenomena was made in 1999 by Joseph, et al [JOS1999]. In this paper a large compilation of the most striking experimental facts is presented. It would be difficult to make a list of them and readers should refer to this paper and references therein. In this section the existing models for crack propagation are summarized and classified according to the fundamental mechanism that they involve: adsorption, dissolution, GB diffusion, and modification of the plastic properties.

1.4.1. Adsorption-based models

Rehbinder effect

The Russian researcher Rehbinder demonstrated that some active surface media can modify the mechanical strength of material. In other word, mechanical properties of materials are environment-dependant. The considerations of this paragraph are mainly reproduced from existing reviews [NIC1979][MAL2011].

When a specimen cracks, a new free surface is created. The fracture strength σ_s of a brittle material is thermodynamically related to the free surface energy γ_s of the material following the well-known Griffith criterion [GRI1921].

$$\sigma_s = C \sqrt{\frac{E\gamma_s}{l_0}} \quad (20)$$

Here C is a constant, E the Young modulus, and l_0 the length of the nucleated crack. By definition, surface active media decrease the surface energy, i.e. $\gamma_{SL} < \gamma_s$. Thus the brittle fracture strength is reduced.

Adsorption-induced reduction in strength

The adsorption-induced weakening of interatomic bond was formulated to propose an atomic scale crack propagation mechanism for the Rehbinder effect. It was named SJWK as Stoloff and Johnson [STO1963], and Westwood and Kamdar [KAM1973]. It has been recently renamed adsorption-induced reduction in strength (AIRS) in Malkin's paper [MAL2011]. AIRS refers principally to a situation where, at no force, the interface (grain boundary) is thermodynamically stable. It doesn't take into account bulk phenomena such as dissolution and the formation of bulk intermetallic phases. The adsorption results in a decrease of the surface energy $\Delta\gamma_s$.

$$\Delta\gamma_s = -\frac{1}{2S_B} (U_{AA} - U_{AB}) \quad (21)$$

Here S_B is the interface area per B atom, U_{AA} the energy of the SM atomic bond, U_{AB} the energy of the bond between SM atom and LM atom. According to the equation (20), this reduction in surface energy should induce a reduction in fracture strength. Following brittle fracture theory and the SJWK interpretation, the adsorption of LM atoms at the crack tip will reduce the maximal normal strength but not the shear strength, resulting in propagation by cleavage (brittle).

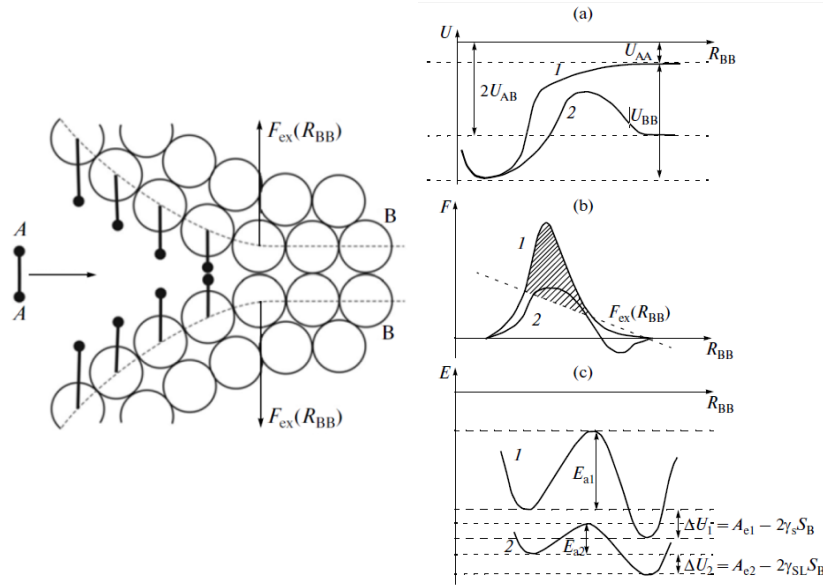


figure 13: Adsorption of LM atoms at the crack tip induces a reduction in atomic bond strength. (a) Mors function diagram for the endothermic bond rupture, (b) force between B atoms as a function of B-B bond length, and (c) energy diagram of the bond rupture under the action of external force $F_{ex}(R_{BB})$. Reproduced after [MAL2012]

1.4.2. Dissolution-based models

The first report of a dissolution based mechanism was made by Robertson [ROB1956] and then refined, for example in [IGO1994]. In the 2000's Glickman finally derived the DCM model to account for higher crack velocity and define the GALOP model [GLI2003][GLI2003bis][GLI2007][GLI2011].

Dissolution-condensation model

The Robertson's dissolution-condensation model (DCM) [ROB1956][JOS1999] considers that cracks propagate by dissolution of the SM at the crack tip in the LM under an applied stress. The stress at the crack tip increases the chemical potential of the SM and promotes dissolution. In other words, dissolution occurs even if the LM is saturated considering equilibrium conditions. Then dissolved SM atoms are removed from the crack and redeposited on the walls as shown by figure 14.

For a crack of width a , crack tip radius $a/2$, depth l , with an applied stress σ , the final crack velocity V is given by

$$V = \frac{1}{(a/2)^2} \left(\frac{l\sigma^2}{E\gamma_{SL}} - 1 \right) \frac{C_0 D_L \Omega^2 \gamma_{SL}}{kT}. \quad (22)$$

Here E is Young's modulus, γ_{SL} the solid/liquid energy, C_0 the solubility of SM atoms in the LM, D_L the diffusivity of SM atoms in the LM, and k the Boltzman constant. This model has the advantage to correlate crack velocity with stress intensity $\frac{l}{E}$ and interfacial effect at the crack tip $\frac{\gamma_{SL}}{a}$. When the stress intensity is high, and the mechanical effect predominant, i.e. $\frac{l}{E} > \frac{\gamma_{SL}}{a}$, the maximal velocity V_{max} is

$$V_{max} = \frac{1}{2k} \frac{\Omega^2 E}{\delta} \frac{C_0 D_L}{T}. \quad (23)$$

δ is close to the GB width.

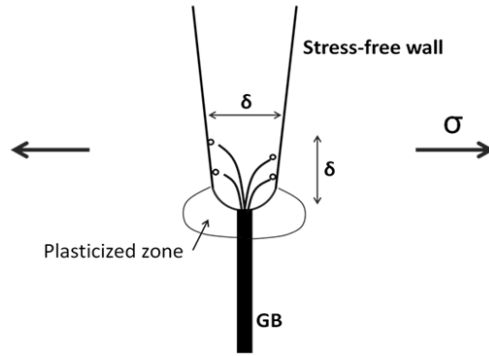


figure 14: Diffusion-condensation model of crack propagation. High chemical potential atoms at the stressed crack tip are dissolved and redeposited on the stress-free walls through high speed liquid diffusion. δ : plastic opening displacement

Refinement of the DCM: Glickman-Robertson (RG) model

According to the review [GLI2013], the refinement of the DCM called Glickman-Robertson model predicts

$$V_{max} = \exp\left(\frac{-\gamma_{SL}2\Omega^{2/3}}{kT}\right) \frac{D_L C_0 \sigma_y \Omega}{akT}. \quad (24)$$

Here σ_y is the yield strength of the SM.

Glickman's GALOP model

After contributing to the refinement of DCM, Glickman proposed a new conception to take into account the effect of plasticity. He proposed a mechanism of successive events of Mullins' GB grooving and crack tip blunting as described by figure 15.

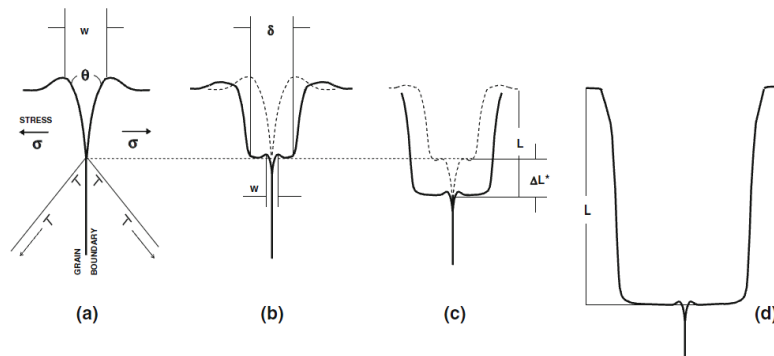


figure 15: GALOP model for crack propagation. Reprinted after [GLI2003]

According to Glickman, this model can describe the two main features of LME, i.e. threshold stress intensity and a maximal crack velocity (crack tip reaction controlling the propagation). The description of a $V - K$ curve is given in figure 16.

$$K_{TH}^2 = \varphi \Delta L \tan\left(\frac{\theta}{2}\right) \sigma_Y E \quad (25)$$

$$V_{max} = \frac{D_L C_{\infty} \gamma_{SL} \Omega}{kT} \frac{1}{\Delta L^2} \left(\tan\left(\frac{\theta}{2}\right)\right)^3 \quad (26)$$

Here φ is a numerical factor expected to be in the range $1 < \varphi < 50$. According to Glickman the GALOP model fits well the experimental GB energy dependence of the crack velocity [GLI2003]. To fit the experimental results, the ΔL value, i.e. the elementary step for crack propagation, is found to be around 1nm, which is commented by Glickman to be quite unrealistic, or at least unexplained.

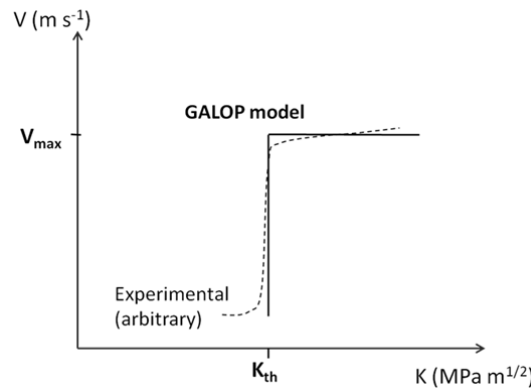


figure 16: GALOP description for crack velocity dependence to the stress intensity factor

1.4.3. Grain boundary diffusion of the embrittler

The dynamic embrittlement model of McMahon, et al. [BIK1995][PFA1999][MCM2013] considers that the GB diffusion of LM atoms, considered as embrittler species for the SM, will induce decohesion of the grain boundary ahead of the crack tip under sufficient tensile stress, as shown by the figure 17. The idea of crack propagation based on grain boundary diffusion was first schematically proposed by Gordon [GOR1978][GOR1982]. But no kinetic prediction has ever been made. “*Liquid-metal-induced cracking is thought to be a form of dynamic embrittlement, but this has not yet been demonstrated satisfactorily*” [MCM2013].

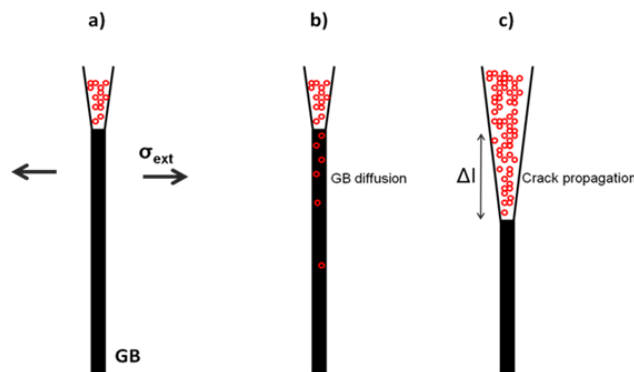


figure 17: Crack propagation inspired by the dynamic embrittlement model [MCM2013]

Recent pieces of evidence for a diffusion-based mechanism are given by molecular dynamics simulation [NAM2007][NAM2009]. In this paper, external stress or strain is assume to provide the stress field at the crack tip to enhance dislocation climbing and to accelerate grain boundary diffusion and to keep the boundary open to allow sufficient transport of LM atoms.

$$V = \frac{\Omega D g b}{kT} \frac{Eb}{(1-\nu^2)l_c^2}. \quad (27)$$

Here l_c is the dislocation core size (a few angstroms). Equation (28) for Ga in Al yields to a velocity around 0.1 m s^{-1} . This refers to the coupled elasticity-diffusion problem. According to Nam and Srolovitz, LME results of a stress-driven diffusion caused by dislocation stress field at the crack tip. External stress is just considered as a facilitator for the nucleation of a dislocation. After that, the strain (due to external stress) opens the crack and drives Ga to the root through a non-diffusionnal mechanism ($\sim$ capillarity, liquid flow).

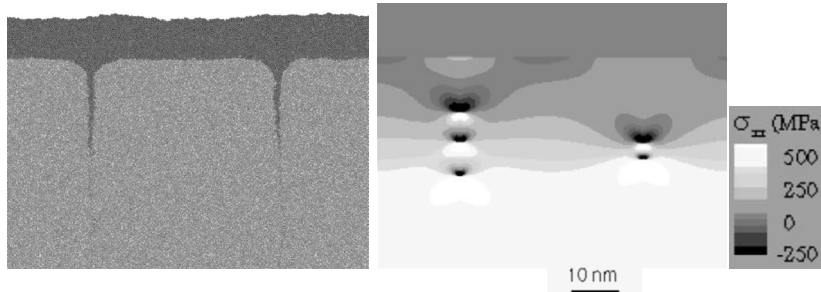


figure 18: Simulation of Ga penetration in Al GBs after 50 ns and under a 500 MPa tensile stress. Left panel: Ga atoms (dark), Al atoms (Light). Right panel: stress associated with the periodic emission of dislocation during crack propagation

1.4.4. Ductile failure models

As summarized in [JOS1999], Lynch proposed, first, that the adsorption of LMs atoms at the crack tip reduce the atomic strength between SMs, and then, facilitates the dislocation motion in the plastic zone ahead of the crack tip. Thus the plastic zone for crack propagation in LM environment is localized and the macroscopic strain for fracture is consequently reduced. Figure 19 shows the proposed mechanism for LME. This model was proposed after the observation of plasticity pieces of evidence on fracture surfaces after LME. Popovitch [JOS1999] had also proposed the idea that the adsorption of LM atoms should modify the plastic behavior of the SM at the crack tip. Nevertheless this model does not provide any kinetic description.

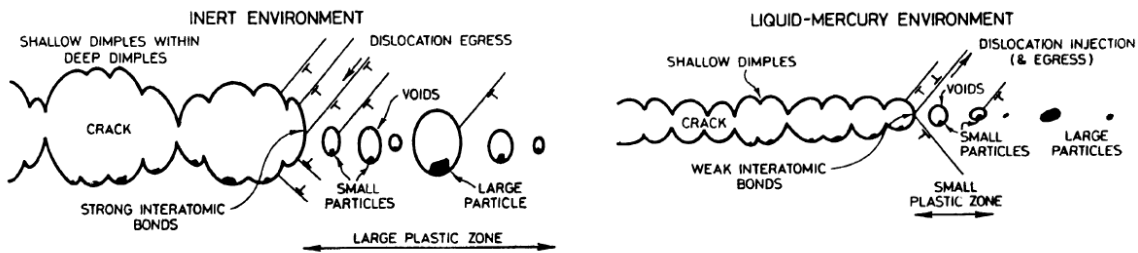


figure 19: Lynch's model

1.4.5. Comments on crack propagation models

Conceptual limitation of the brittle model

If the Griffith criterion is applied to a grain boundary crack in liquid metal environment, γ_s is replaced by $2\gamma_{SL} - \gamma_{gb}$ in the equation (20). In the study of the contact without external stress, conditions where $2\gamma_{SL} - \gamma_{gb} < 0$ (above the wetting transition) may be found. But the application of the equation (20) with $\gamma_{SL} - \gamma_{gb} < 0$ is mathematically impossible. So the Griffith criterion does not provide any description above the wetting transition.

In other words, the Griffith criterion describes the reduction of fracture stress in LM environment for $2\gamma_{SL} - \gamma_{gb} > 0$: the fracture strength tends to zero when $2\gamma_{SL} - \gamma_{gb}$ tends to zero. For $\gamma_{SL} - \gamma_{gb} < 0$ the “spontaneous” decohesion of material grains in LM environment may be interpreted from the Griffith criterion (in an analog manner than the Mullins model for GB grooving, Griffith brittle criterion is able to predict the wetting transition when $2\gamma_{SL} = \gamma_{gb}$). Consequently adsorption-induced reduction in strength following a brittle fracture (Griffith) analysis may be hardly applicable to subcritical crack growth above the wetting transition observed in several studies for LME couples, for examples in [GLI1999].

Comments on Glickman's equation parameters

Dissolution-based model (Robertson, Glickman, and others) gives a framework for the analysis of LME as an analogy with stress corrosion cracking mechanism (SCC). A correlation between reactions at the crack tip and mechanical aspects is made. Like in SCC, it describes a threshold stress intensity factor and a velocity controlled by a crack tip reaction.

But the physical concepts are quite complicated; and the equations (25) and (26) may be questioned, especially regarding parameters φ and ΔL that can be adjusted at will and have not been found to be correlated to any material parameter. About ΔL , crack kinetics matching the experimental measurement are predicted only with geometrical parameters for the channel close to the GB width (a few interatomic distances, $\Delta L < 1\text{ nm}$), while the model involves a “mesoscopic-scale” dissolution-redeposition process. For example, how to define the concept of surface curvature for a surface area in the order of the nanometer?

Comments about plasticity enhancement at the crack tip

Ductile failure model involving a modification of local plastic properties after adsorption of LM atoms appears difficult to be applied to several classical LME systems such as Al-Ga, Cu-Bi, Ni-Bi where LME is observed without any plasticity evidence, as reported by the author of the theory [LYN2008]. This may demonstrate that it cannot represent a general framework for LME study.

Furthermore this model appears not in contradiction, but really not connected with what has been described about the contact between SM and the LM polycrystal, regarding the GB behavior and GB penetration.

Comments about diffusion models

Simple GB diffusion model of the embrittler like the one of McMahon has the advantage to be based on a classical and well-known GB phenomenon, but still need to predict fast (linear) kinetics which seems in appearance in contradiction with diffusion kinetics. Taken into account the step-by-step propagation as in the

Glickman's model should avoid this apparent limitation. The equation (28) provided by Nam and Srolovitch appears not satisfactory since it is not balanced regarding the units of the different parameters. Thus it appears hardly applicable with numerical material parameters.

Concluding remarks about kinetic predictions for crack propagation

Glickman and coworkers on one's side, and Nam and coworkers on the other side, provided simplified kinetic equations involving physical and chemical parameters (diffusion coefficients, atomic diameter, solubility limit, etc.) and macroscopic mechanical parameter (bulk modulus, yield strength, stress intensity factor, etc.). Even if models are based on diffusion phenomena, the resulting kinetic for crack propagation is linear because (i) crack opening induces LM atoms supply at the crack tip by liquid flow (capillarity) and not by liquid diffusion from the surface of the material specimen, and (ii) a step-by-step propagation composed of diffusion and cracking events is modeled.

In their papers authors conclude that their models are relevant but no pieces of evidence like direct observation of the atomic scale mechanisms at the crack tip can be made. So these approaches give the framework to discuss the description of a specific experimental case, such as the order of magnitude of the crack velocity and its dependence with temperature and stress intensity. But proposed local mechanisms at the crack tip need to be considered with caution. Furthermore the predictive quality of these equations should also be questioned.

1.5. Summary of the review of LME mechanisms

The review has summarized the different aspects of the contact between LM and the SM GB. Involving GB grooving, diffusion and transitions, this contact causes GB penetration following parabolic or linear kinetics depending on surface and interfacial energies. In most cases, the order of penetration rate is lower than 1 μ m/s. It is also clear that residual (internal or external) stress enhances penetration rate.

Under external stress in the order of the yield strength of the SM, specific GB cracking mechanisms takes place involving a wide range of crack velocities depending of the SM/LM couple from 1 μ m/s to 10 cm/s. Models for the local reaction at the crack tip have been defined but do not systematically refer to the description of contact between LM and SM, and GB penetration.

As already pointed out in [LAP2005], it is striking that the conceptual correlation with basic penetration phenomena is so poor in the description of LME cracking mechanisms. Furthermore the thermodynamical equilibrium in polycrystal binary material permits complexions of GBs (premelting, prewetting, and wetting) and thus the loss of GB cohesion, or high diffusivity. This relatively recent formalism gives material for new explanations of LME and GBP that was not effectively taken into account, or just approached, in penetration and crack propagation models listed in paragraph 1.3. and paragraph 1.4.

It is also important to keep in mind that different situations are described as LME cases. This type of classification was already made in [LAP2005].

- Grain boundary penetration: without exterior stress or under very low stress in conditions, above the wetting transition temperature. The mechanical equilibrium of the material is kept.

- Grain boundary embrittlement induced by liquid metal penetration: after long time of contact and penetration, all GBs of the sample experience a complexion supposed to have negligible resistance; if an exterior stress is applied, the fracture is completely brittle.
- Liquid metal assisted cracking: stress is applied to a system in conditions such as, if no stress was applied, grain boundary penetration would occur. A local mechanism, resulting in the combination of the tendency of the GB to experience wetting transition and the action of stress, leads to fast crack propagation.

This review has not been dedicated to make a compilation of experimental results, but to give the framework for a conceptual analysis of LME-related phenomena. Parameters involved in LME such as diffusion coefficient, solubility, phase diagram, grain boundary properties will be needed for the discussion. In the next section, material data for the investigated couple (steel/Zn) are reviewed. The specificity of the steel/Zn system should also be questioned.

2. The Steel-Zn couple

2.1. Material data for steels

Steels are basically Fe-C alloys. The main physic-chemical parameters for Fe are given. Then Fe-C system is described, especially regarding microstructural aspects. After that, information about the influence of other alloying elements used in steels is given.

2.1.1. Fe: general properties

Iron is a transition metal with atomic number 26. Some of the most important data for Fe are given in the table 1, as summarized in the Wikipedia page for iron [WIK1] and references to be found therein.

table 1: Some general properties for Fe

Properties	Value
General physical	
Solid density (near room temperature)	7,874 g cm ⁻³
Liquid density (at melting point)	6,98 g cm ⁻³
Melting point	1538 °C
Heat of fusion	13.81 kJ mol ⁻¹
Atomic radius	126 pm
Miscellanea	
Currie point	760.5 °C
Thermal expansion (25 °C)	11 μm m ⁻¹ K ⁻¹
Electrical resistivity (20 °C)	96.1 nΩ.m
Thermal conductivity (20 °C)	80.4 W m ⁻¹ K ⁻¹
Young modulus	211 GPa
Shear modulus	82 GPa

2.1.2. Fe-C binary system

Steel is basically a Fe-C alloy. The Fe-C equilibrium diagram is quite complex but the only part to be used is the Fe rich part with C wt% < 7 %, as shown in the figure 20. The diagram to consider is actually the Fe-Fe₃C diagram. C is an interstitial element in solid solution with Fe, either in α-Fe (ferrite) or γ-Fe (austenite). The diagram shows that the maximal solubility of C in ferrite is 0.022 wt% at 722 °C. Maximal solubility in austenite is much larger: 2.14 wt%C at 1147 °C. The main attribute of the diagram is the eutectoid transformation found at 0.76 wt%C and 727 °C.

As described below for steels of the study (paragraph 3.2.1), the carbon content of the automotive steels is in the range 0.05 – 0.2 wt%. On the diagram, a red arrow has been positioned at 0.2 wt%. At low temperature, the equilibrium microstructure is a mix of ferrite and eutectoid microstructure (alternating layers of ferrite and Fe₃C). When increasing temperature, the material will experience a transition from low temperature microstructure to austenite. Start of ferrite-to-austenite transformation is found at the eutectoid temperature, called Ac1. End of ferrite-to-austenite transformation is found at Ac3. Theses transformation

temperatures will be characterized for the investigated steels (3.4). For 0,2 wt%C, the diagram shows $Ac1 \approx 730\text{ }^{\circ}\text{C}$ and $Ac3 \approx 840\text{ }^{\circ}\text{C}$.

The transformation kinetics is limited by the diffusion of carbon which needs to move from crystalline interstitial sites of the bcc structure to those of the fcc lattice. The same appears during cooling, is sufficiently slow. If rapid cooling (for example air or water quenching), the austenite-to-ferrite does not have sufficient time to take place and metastable hard microstructures will appear (for example bainite or martensite). In industrial steels, other elements are added into the Fe-C alloy. Some of them have the ability to improve the stability of austenite, others enhance ferrite stability. As a consequence, $Ac1$ and $Ac3$ can be controlled by alloying. In specific cases, it is possible to keep austenite at room temperature. As described below for steels of the study (3.2.2), specific alloying and thermal treatments gives metastable microstructure (base metal) for automotive steels. In the next paragraph, effects of elements typically added to steels are detailed.

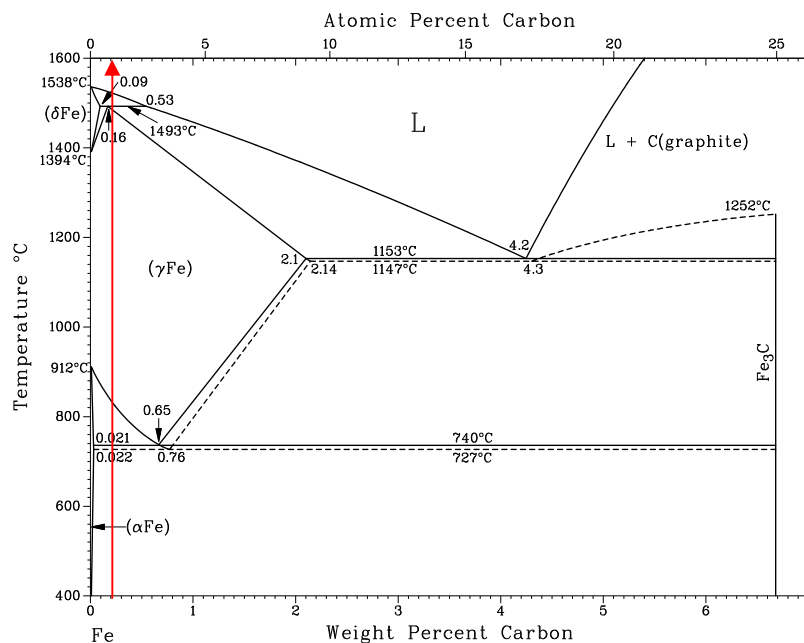


figure 20: Fe-C (solid line) and Fe-Fe₃C (dashed line) metastable diagrams

2.1.3. Influence of alloying elements in steels

Properties of steels

The main alloying elements according to their influence on the properties of steels are summarized.

- Stabilizing austenite: Manganese, Cobalt, Nickel, Copper
- Stabilizing ferrite: Silicon, Aluminum, Chromium, Molybdenum
- Carbide forming: Chromium, Tungsten, Molybdenum, Titanium, Niobium, Tantalum and Zirconium. The formation of strong metal carbides increases hardness and strength (for high speed steels and hot work tool steel)

- Decrease of eutectoid concentration: Titanium, Molybdenum, Tungsten, Silicon, Chromium and Nickel
- Increase corrosion resistance: Aluminium, Chromium, and Silicon. Surface oxide layers formation.

Main alloying elements (in automotive steels)

Manganese in concentration from 0.2wt% to several percent is a sulfur scavenger and thus increases hardness at high temperature. It also increases hardenability. Silicon is widely used as a deoxidizing agent. Final concentration is in the range 0.2 – 2.0 wt%. It improves strength and increases grain size. Aluminium also has deoxidizing properties and limit growth of austenite grain size. Chromium, in concentration in the range 0.01 – 0.5 wt% increases hardenability, strength and corrosion resistance. Molybdenum and also Titanium have slightly the same general effects than Chromium. Other microalloying elements such as Vanadium, Zirconium, Niobium, increases hardness and strength even if used in small amounts (< 0.1 wt%). Impurities such as Phosphorus or Sulfur may result in low temperature or high temperature brittleness and their amounts are carefully controlled.

2.2. Material data for Zn

Zinc is a transition metal with atomic number 30. Some of the most important data for Zn are given in the table 2, as summarized in the Wikipedia page for iron [WIK2] and references to be found therein.

table 2: Some general properties for Zn

Properties	Value
General physical	
Solid density (near room temperature)	7,14 g cm ⁻³
Liquid density (at melting point)	6,57 g cm ⁻³
Melting point	419.53 °C
Heat of fusion	7.32 kJ mol ⁻¹
Boiling point	907 °C
Heat of vaporization	123.6 kJ mol ⁻¹
Atomic radius	134 pm
Miscellanea	
Thermal expansion (25 °C)	30.2 µm m ⁻¹ K ⁻¹
Electrical resistivity (20 °C)	59.0 nΩ.m
Thermal conductivity (20 °C)	116 W m ⁻¹ K ⁻¹
Young modulus	108 GPa
Shear modulus	43 GPa

2.3. Metallurgical basis for the steel-Zn couple

2.3.1. Equilibrium phase diagram

Description of the diagram

The Fe-Zn phase diagram is reproduced from [RAG2003]. A large α zone exists with high solubility of Zn, about 40 wt% at the peritectic temperature 782 °C. On the other side, the solubility Fe in liquid Zn

increases from 0 at 419.5 °C, to approx. 22 wt% at 1100 °C. Several intermetallic phases exist in the Zn-rich part of the diagram. These phases can be observed after immersing a steel plate in a molten Zn bath, as shown in the figure 22.

Remarks regarding LME literature

The existence of intermetallic phases and large mutual solubility is in contradiction with the empirical rule, sometimes named “specificity of LME” saying that LME is preferentially observed for SM/LM couple with low mutual solubility and without intermetallics [KAM1972][FER1996].

Is LME more difficult to observe in this type of SM/LM system since the bulk reactivity may avoid or conceal the penetration or cracking phenomenon?

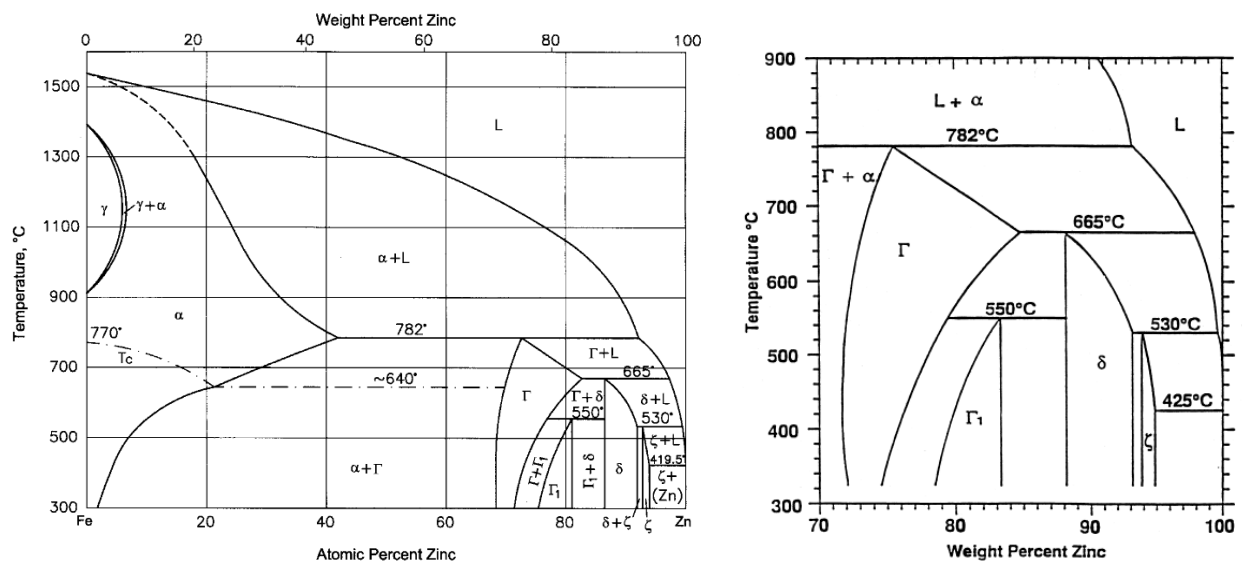


figure 21 : Fe-Zn phase diagram (left panel) and enlarged view of the Zn-rich corner (right panel). Reprinted after [RAG 2003]

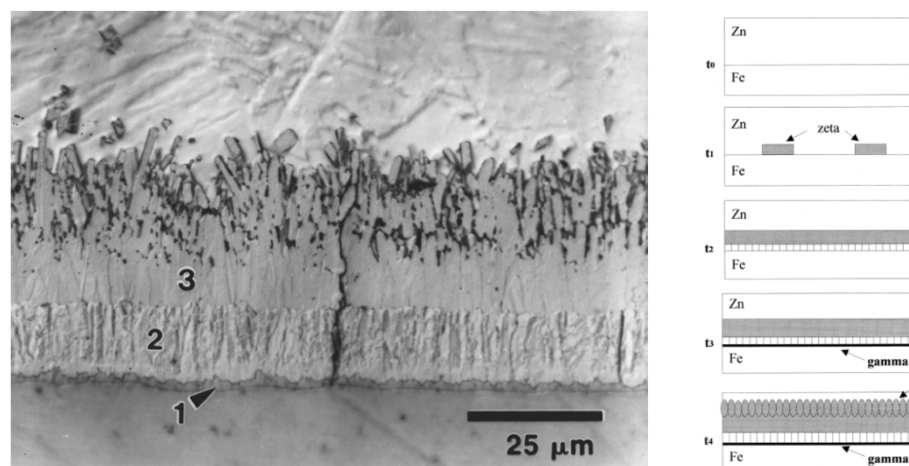


figure 22: Fe-Zn intermetallics at 450 °C (left panel). 1: gamma (Γ); 2: delta (δ); 3: zeta (ζ). Chronology of Zn phase formation (right panel). $t_0 < t_1 < t_2 < t_3 < t_4$. Reprinted after [MAR2000]

2.3.2. Reaction kinetics

The reaction between steel and zinc has been extensively studied (for numerous steels) at galvanizing temperature, i.e. mostly in the range 450°C – 550°C. Figure 22 describes the phase formation chronology. Figure 23 shows the intermetallic phases growth rate. The full layer growth rate is approximately $10 \mu\text{m s}^{-1}$ for $t = 10 \text{ s}$ to $0.4 \mu\text{m s}^{-1}$ for $t = 300 \text{ s}$. At all investigated temperatures the total layer growth rate has parabolic kinetics [MAR2000], i.e. $\propto t^n$ with $n \leq 0.5$.

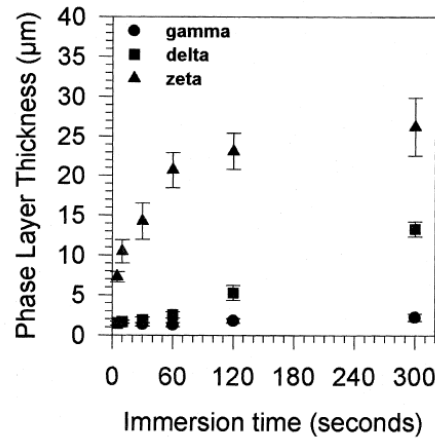


figure 23: Intermetallic layers growth rate after contact between Fe and Zn at 450°C

2.3.3. Diffusivity data

Bulk diffusion

The volume interdiffusion data of Zn in Fe can be compared according to the compilation of results made in [RAB1991] and summarized in table 3. The diffusion for Zn is close to the interdiffusion for Fe. The dependence of bulk diffusivity ($\text{m}^2 \text{s}^{-1}$) with the temperature is shown in the figure 24.

table 3: Bulk diffusivity for Zn in Fe and elements of comparison. Data from [RAB1991]

Matrix	Diffusant	E (kJ mol ⁻¹)	$10^4 \times D_0$ (m ² s ⁻¹)	Temperature (°C)	Reference
α-Fe	⁵⁹ Fe	257	1.7	800-900	cited in [RAB1991]
α-Fe	⁵⁹ Fe	266	10	1000-1050	cited in [RAB1991]
α-(Fe-7.64% Si)	⁵⁹ Fe	228	1.4	900-1100	cited in [RAB1991]
α-(Fe-11% Si)	⁵⁹ Fe	212	0.63	900-1100	cited in [RAB1991]
α-Fe	Zn	264	60	800-910	cited in [RAB1991]
α-(Fe-5% Si)	Zn (0%)	227	5	750-908	[RAB1991]
α-(Fe-5% Si)	Zn (5%)	243	32	750-908	[RAB1991]
α-Fe	¹¹³ Sn	222	2.4	800-910	cited in [RAB1991]
α-(Fe-5% Si)	Sn	210	0.9	750-908	[RAB1991]

Grain boundary diffusion

The GB diffusion for Zn in Fe has been studied in several studies [RAB1991][DOH2007]. Table 4 gathers these results. The dependence of GB diffusivity ($\text{m}^2 \text{s}^{-1}$) with temperature is shown in the figure 24. For the processing of literature results and the comparison with bulk diffusivity, the grain boundary width and the segregation factor have been set up to:

$$\delta = 5 \cdot 10^{-10} \text{ m},$$

$$s = 1.$$

table 4: GB diffusivity for Zn in Fe and elements of comparison

Matrix	Diffusant	$E_{gb} \text{ (kJ mol}^{-1}\text{)}$	$10^4 \times D_{gb0} \text{ (m}^2 \text{s}^{-1}\text{)}$	Temperature ($^{\circ}\text{C}$)	Reference
$\alpha\text{-(Fe-5\% Si)}$	Zn	192	24	750-908	[RAB1991]
$\alpha\text{-Fe}$	Zn	162	34	400-725	[DOH2007]

Diffusion in liquid Zn

Data for diffusion in liquid Zn are summarized in table 5. The literature for liquid diffusion of Fe in Zn mainly focuses on hot dip galvanizing temperature, i.e. $T < 550^{\circ}\text{C}$. Figure 24 gives graphical representation of the orders of magnitude that separate the different types of diffusion regimes.

table 5: Diffusivity in liquid Zn

Liquid	Diffusant	$E \text{ (kJ mol}^{-1}\text{)}$	$10^4 \times D_0$	$10^{10} \times D_L \text{ (m}^2 \text{s}^{-1}\text{)}$	Temperature ($^{\circ}\text{C}$)	Reference
Zn	Fe	33,6	0.002	-	600-900	Cited in [GIO2004]
Zn	Fe	-	-	9.8	465	[GIO2004]

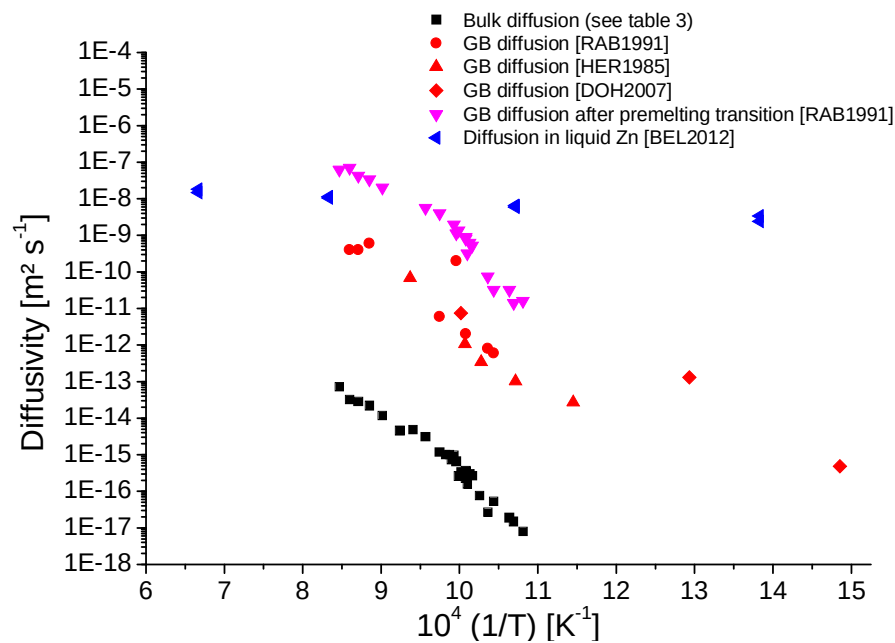


figure 24: Diffusion data for the steel/Zn couple

2.4. Examples of LME of steels by Zn

2.4.1. GB transitions and penetration

The contact between Fe-3at.%Si bicrystals and liquid Zn was studied in [RAB1991]. Non-Mullins penetration channel were observed at different temperatures. Fine investigations near the penetration channel front were made to characterize the GB concentration c_{gb} of Zn ahead of the micrometric penetration root. The concentration limit for a grain boundary transition has been evidenced at the discontinuity in the slope of the $c_{gb}(y)$ curve as shown in figure 25. The GB experienced a complexion transition from solid to nanometer liquid channel when the concentration reaches a threshold concentration c_{gbt} in the GB by GB diffusion, i.e. when

$$c_{gb} > c_{gbt}.$$

Rabkin, et al. determined the evolution of c_{gbt} with the temperature shown in the figure 26 and added the GB phase transition line to the bulk equilibrium diagram for the Fe-5wt%Si alloy. The influence of Si on the bulk diagram is also clear: the solubility limit of Zn in Fe is reduced.

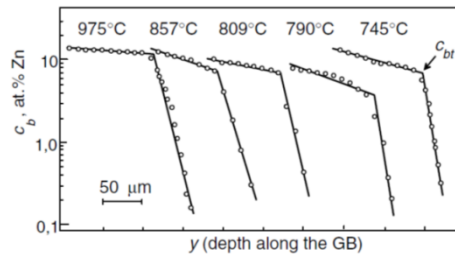


figure 25: Penetration profile of Zn in Fe-5at.%Si bicrystals. High diffusivity part and low diffusivity part are visible

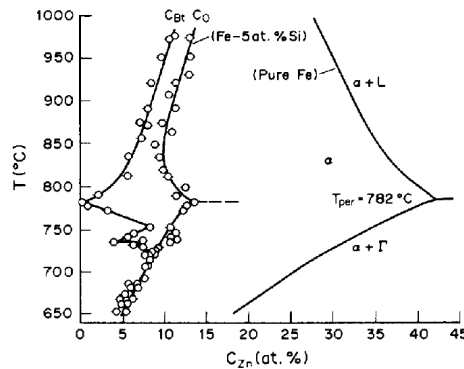


figure 26: GB premelting transition added to the bulk phase diagram for Fe-5at.%Si. Reprinted after [RAB1991]

After grain boundary transition, the diffusivity increases by a 10^2 factor. This factor is in agreement with data reported for GB complexion. These data have been added to the figure 24. But, in the figure 24, a constant GB width of 0.5 nm was considered for the calculation of the diffusivity (easier for comparison),

whereas Rabkin, et al. supposed that the diffusion coefficient is constant and that the increase in diffusivity comes from the increase of the width, i.e. the formation of a nanometer-thick GB channels.

2.4.2. Embrittlement and cracking

Low and intermediate temperature

Liquid zinc cracking of welded or deep drawn parts during galvanization ($T \approx 450^\circ\text{C}$) has been reported [CAR2008][CAR2010][KIN2004], as shown in figure 27. High stress concentrations are involved in this type of embrittlement. For information the residual stress can be in the order of the yield strength at room temperature, i.e. 800 - 1200 MPa for quenched microstructure (martensite) expected for example in the heat-affected zone of welds.

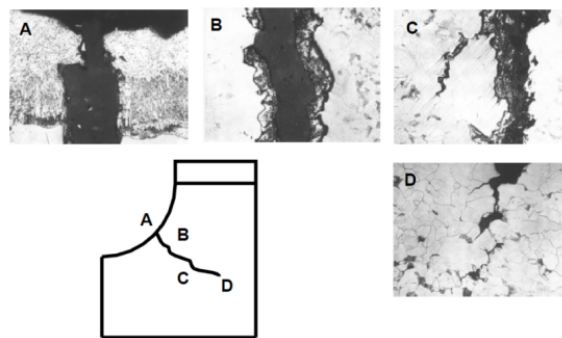


figure 27: Liquid zinc crack in structural beams after hot dip galvanizing. Reprinted after [KIN2004]

During tensile testing, liquid zinc embrittlement at low temperature ($400^\circ\text{C} - 500^\circ\text{C}$) was identified by Japanese research teams (reports in Japanese language) [IKO1984][KIK1980][KIK1981][KIK1982][NAK1984][NAK1985][NAK1988][NAK1998][NIS2005], and in [KIN2004]. Figure 28 shows the reduction of the elongation from 20 % to 5 % as the consequence of the presence of liquid zinc at 450°C . For information, the yield strength is around 380 MPa at this temperature.

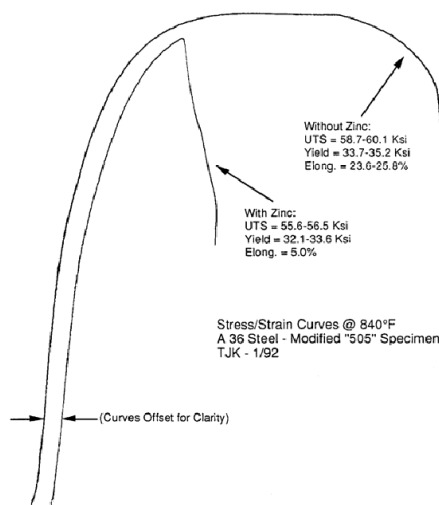


figure 28: Stress-strain curves for a structural steel with and without Zinc at 450°C

High temperature

Recently, liquid zinc cracking was identified during high temperature stamping processes of galvanized steels [LEE2012]. In this study it has been found that steel experiences surface cracks when strained at 850 °C but keep safe at 700 °C. It is concluded that embrittlement appears only for temperature higher than the peritectic temperature (780°C, fusion of the gamma phase) of the Fe-Zn diagram. For lower temperature, the reaction between Fe and Zn before straining allows the formation of a gamma layer inhibiting the contact between steel GBs and liquid Zn.

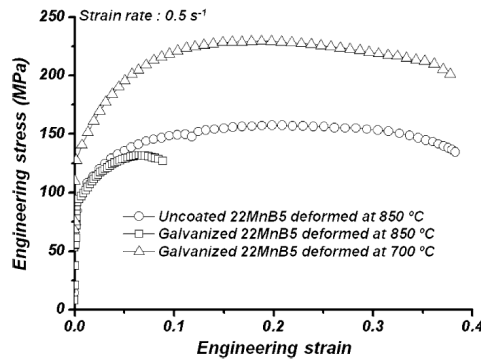


figure 29: engineering stress-strain curves of the bare and Zn-coated steel for different temperatures. Zinc weakens steel at 850°C but not at 700°C. Reprinted after [LEE2012]

The temperature dependence of the ductility of Zn-coated steels was also investigated by Beal, et al. [BEA2011][BE2012]. Figure 30 illustrates the drastic loss of ductility in an intermediate temperature range between 700°C and 1000°C. It has to be noticed that the beginning of the “ductility trough” is different for the three grades and significantly below 780 °C what seems *a priori* in contradiction with the results of Lee, et al. In Beal’s study, the ductility recovery between 950 °C and 1000°C is attributed to the evaporation of the Zn thin coating. DP and TRIP grades behavior (figure 30) must be compared with the results of the present work. Both cited studies [BEA2011][LEE2012] demonstrated that sufficiently long high temperature holding before straining avoids cracking, as the result of Zn-Fe alloying and intermetallic formation (no more liquid Zn). Both studies used similar experimental methods.

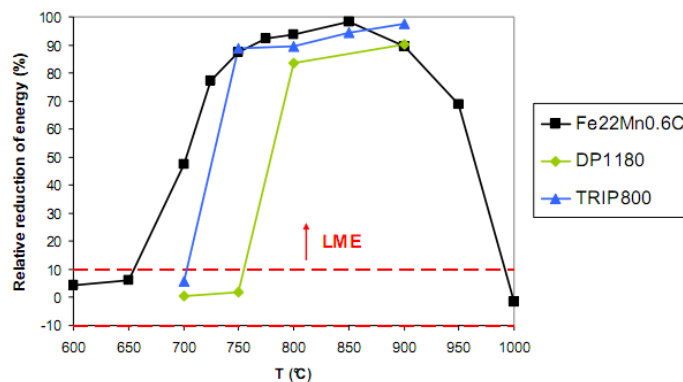


figure 30: Embrittlement of high strength steels by Zn in tensile tests at $1.3 \cdot 10^{-1} \text{ s}^{-1}$. The relative reduction of energy is proportional to the area under the stress-strain tensile curve. Reprinted after [BEA2012]

3. Materials

As described in the introduction, the study is focused on the behavior of automotive advanced high strength steels (AHSS) of first generation. That refers in particular to two steel families: DP and TRIP steels.

3.1. Galvanized steel sheet processing

3.1.1. Steel processing

Investigated steel sheets have been processed following the industrial schedule as follows: continuous casting, hot rolling, coiling, stripping and cold rolling, final heat treatment and galvanizing. Details about these processes can be found in general references [BIRMACOMBE1998][ROBERTS1983], and in particular for DP and TRIP steels [KUZIYAK2008][LIS2006][ROCHA2005].

For cold rolled products, the final heat treatment is the key point to achieve the expected microstructure, as shown in the figure 31. As it detailed below for steels of the study (paragraph 3.2.2), DP steel microstructure is composed of ferrite (α) and martensite (α'), while TRIP microstructure is composed of ferrite, bainite (α_B) and retained austenite (γ_R).

Precise knowledge of transformation diagram (ferrite, pearlite, bainite transformation, martensite start temperature M_s) of steel to be produced and good control of thermal processing are needed.

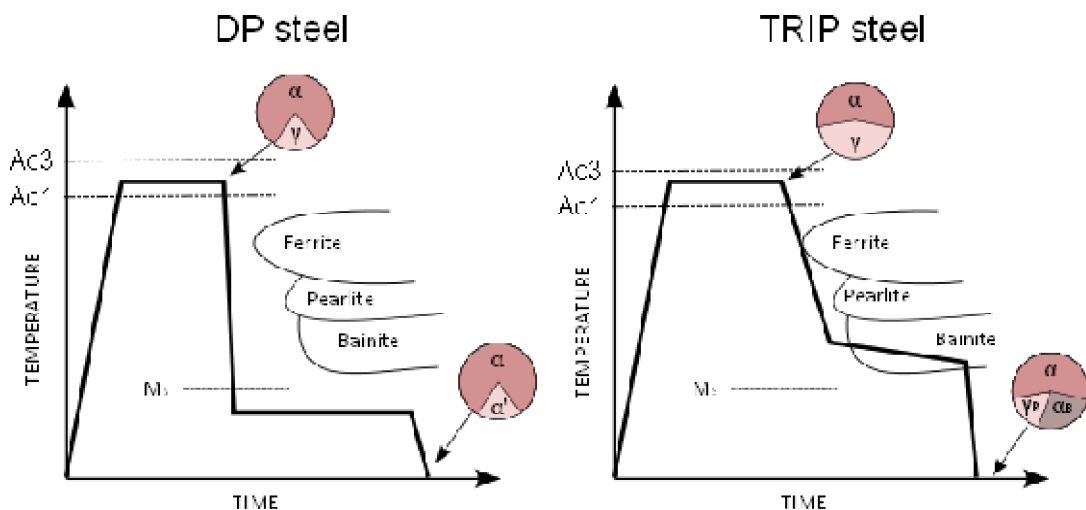


figure 31: Thermal treatment for DP and TRIP steels

3.1.2. Electro-galvanizing

Investigated steel sheet have been electrogalvanized after thermal treatment. Electro-galvanizing (EG) is one of the two industrial galvanizing methods. The other is hot dip galvanizing and consists in immersing the sheet in a molten zinc bath ($T \approx 450^\circ\text{C}$).

After immersing the steel sheet in a Zn^{2+} containing bath (Zn ion concentration is maintained thanks to fusible Zn cathode), EG coating is electrodeposited by polarizing the steel sheet as the anode.

3.2. Base metal characterization for steels of the study

3.2.1. Chemical composition

The chemical composition of the investigated steels is given in table 6. Steels contain Mn, Si and Al as main alloying elements. Cr and Mo are also important elements but with lower fraction than main alloying elements. As a general observation, steel contains also other microalloying elements such as Ni, Cu, and Ti, N or Nb and unavoidable impurities such P, S, Sn or As. Main differences between steel grades are as follows.

- C content is about two times higher in TRIP than in DP
- Mn content is high for the three grades, but higher for the DP steel than for the TRIP steels.
- Si content is low for the DP, medium for the TRIP AlSi and high for the TRIP Si
- Al content is very low for DP and TRIP AlSi steels, but high for the TRIP AlSi steel. It has been demonstrated in TRIP steels that Al can be an alternative to Si. The (Si+Al) value can be seen as a constant in TRIP steels.

table 6: Chemical composition of the three investigated steel grades ($\times 10^{-3}$ wt%)

Grade	C	Mn	Si	Al	Cr	Mo
DP	0.08	1.93	0.15	0.03	0.11	0.05
TRIP Si	0.20	1.65	1.63	0.06	0.03	0.00
TRIP AlSi	0.20	1.64	0.80	0.68	0.04	0.00

3.2.2. Microstructure

Sample for microstructural observation are prepared according to the method described in Appendix 1. Microstructures of the three investigated steel grades characterized by SEM after nital etching are shown in figure 32. The microstructure of the DP steel is composed of ferrite grains surrounded by martensite islands. The mean ferrite grain size is in the range to be 3 – 4 μm , and the martensite volume fraction to be in the range 20 – 30 %. The microstructures of the TRIP steels are composed of ferrite grains surrounded by retained austenite and ferrite-bainite grain islands. For TRIP Si, the mean ferrite grain size is 3 – 4 μm and the retained austenite fraction is 20 - 30 %. For the TRIP AlSi, the mean grain size is 6 μm and the retained austenite fraction is about 10 %. Grain size distribution and statistical characterization of phase volume fraction have not been made.

For both steels it can be assumed that ferrite/ferrite GB represents only a small amount of GB total surface area. Most of the boundaries are interphase boundaries: ferrite/martensite for DP steel and ferrite/retained austenite for TRIP steels.

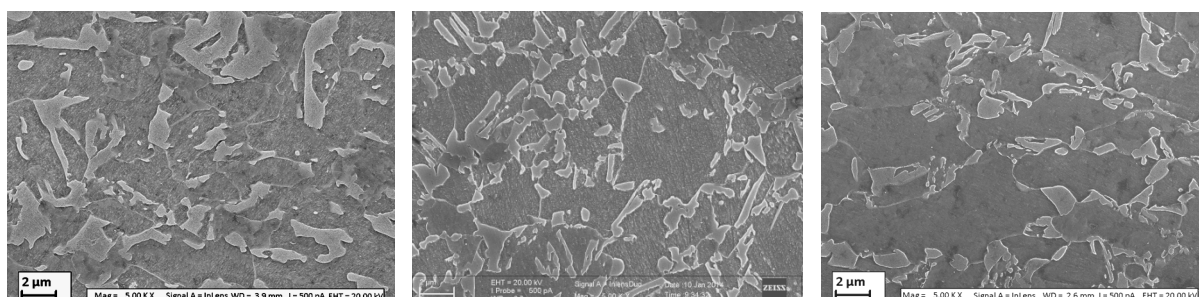


figure 32: Microstructure of the three investigated products observed on nital etched cross section. Left: DP, center: TRIP Si, right: TRIP AISi.

3.3. Initial state of the steel/Zn interface

The contact between steel and Zn at high temperature occurs first at the steel/coating interface. The figure 33 shows the initial state of this interface. There is a quasi-pure Zn coating with thickness about 7.5 µm. The depth of the transition between the EZ coating (100% Zn) and the steel substrate (0% Zn) is negligible.

On the DP steel, intergranular defects can be observed along GBs just under the coating, on a depth of 4 – 5 µm corresponding to the grain size. This defect is typical of the intergranular oxidation that can potentially occur during the processing of steel (hot rolling, coiling). These defects have been characterized by SEM-EDX analyses as shown by the figure 34. SEM-EDX method is detailed in Appendix 1. Enrichment in several alloying elements and of Zn from the coating has been found.

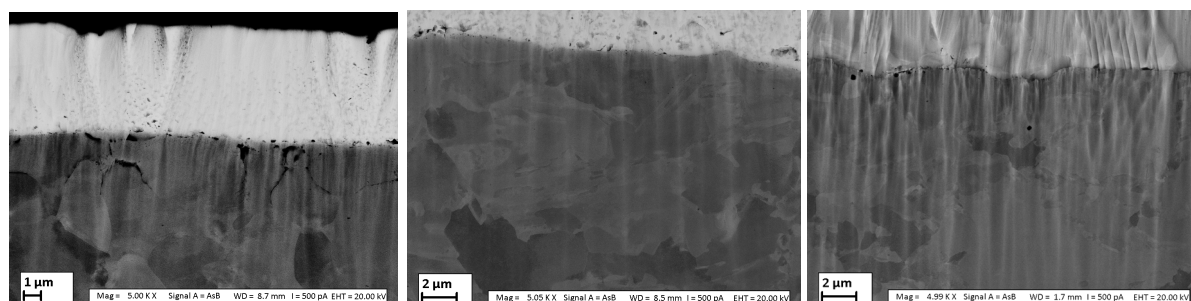


figure 33: Steel/coating interface. Left: DP, centre: TRIP Si, right: TRIP AISi

In the experimental study (section 4 of this chapter) the behavior of steel without the presence of Zn, i.e. the steel without coating, is investigated. For that the material is immersed in a 10% nitric acid-EtOH solution until the coating is removed. The steel surface after dissolution of the coating is shown in figure 35. No particular defect can be evidenced thus the (electro-galvanized + acid-etched) surface is supposed to be representative of the initial surface of steel before electro-galvanizing.

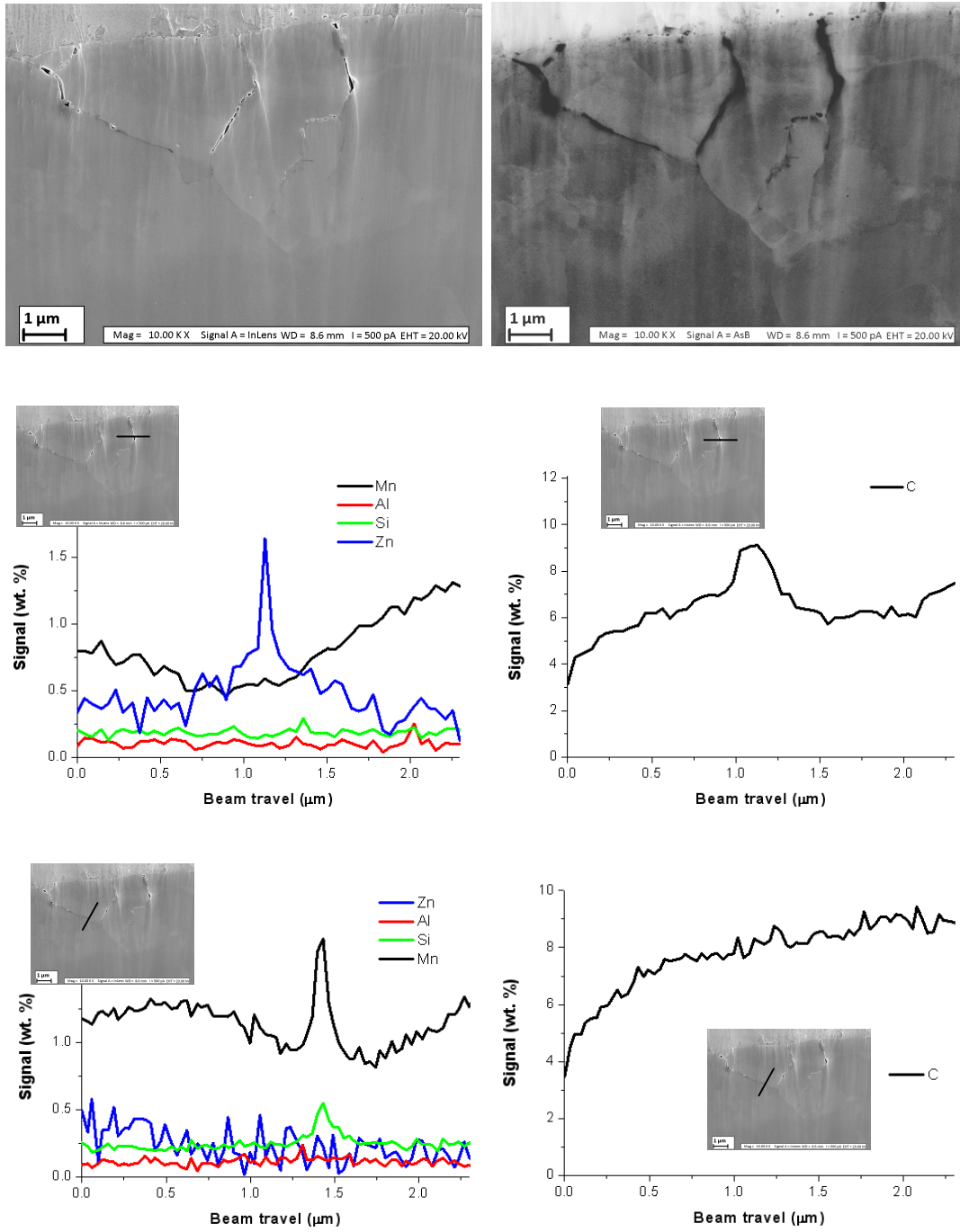


figure 34: SEM-EDX characterization just under the initial steel/coating interface for the DP steel. Up: se electron (right) and backscattered electron (left) maps; middle: EDX profile across a precipitated GB with enrichment of Zn and C; down: EDX profile across a GB with enrichment of Mn and Si

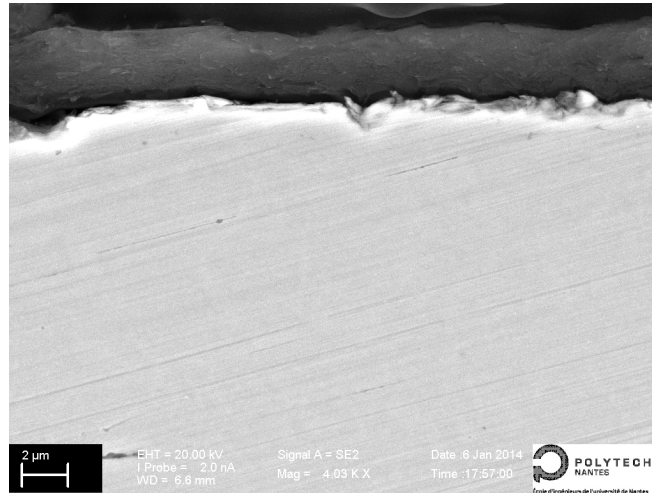


figure 35: Bare steel surface after removing the coating with nitric solution

3.4. Steel phase transitions during heating

Because the three steels have different base metal microstructures and chemical compositions, it is difficult to rigorously describe crystallographic phases, chemical heterogeneities and microstructures expected to be observed. Nevertheless, if sufficiently high heating rate can be considered to neglect the decomposition of metastable phase (martensite and retained austenite), the microstructure for the three steels can be simply described as follows.

- Base metal (mainly ferrite), for $T < A_{c1}$
- Base metal (mainly ferrite) + Austenite, for $A_{c1} > T > A_{c3}$
- Austenite, for $T > A_{c3}$
- Liquid, for $T > T_{\text{melting}}$

A_{c1} and A_{c3} are different for the three steels and can be estimated as a function of their chemical composition. The influence of the different alloying elements can be measured by the coefficient of empirical formula such as the one obtained by Kasatkin and Vinokur (K&V) which take into account the influence of the main alloying elements in the investigated steels [KAS1984]. A_{c1} and A_{c3} phase transition temperatures have also been characterized by dilatometry measurements at the heating rate of $100\text{ }^{\circ}\text{C min}^{-1}$ as shown in the figure 36. The results for A_{c1} and A_{c3} temperatures are summarized in table 7 and compared to the K&V formula.

table 7: Transition temperatures of the investigated steels ($^{\circ}\text{C}$). K&V model [KAS1984]. Heating rate for dilato: $100\text{ }^{\circ}\text{C min}^{-1}$.

Grade	A_{c1} (K&V)	A_{c1} (dilato)	A_{c3} (K&V)	A_{c3} (dilato)
TRIP Si	710	760 ± 5	854	920 ± 10
TRIP AISi	730	748 ± 5	861	965 ± 20
DP	733	720 ± 5	889	840 ± 10

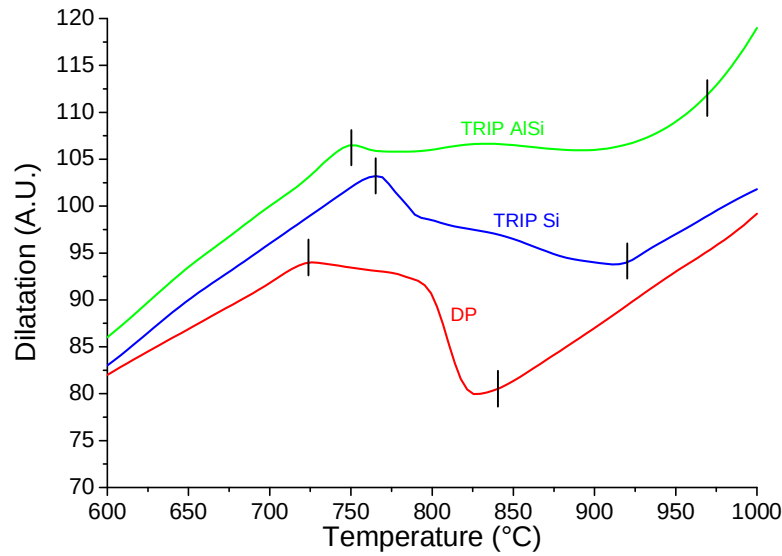


figure 36: Thermal dilation of steel samples used for the determination of phase transitions temperature A_{c1} and A_{c3}

3.5. Mechanical properties

Room temperature mechanical properties

Figure 37 gives the tensile curves for the three investigated products at room temperature. The three steels have similar UTS, around 800 MPa. The maximal elongation of TRIP steels is higher than for DP steel. The difference for the hardening behavior between TRIP and DP steels can be observed. The mechanical properties are summarized in the table 8.

table 8: Mechanical properties of the investigated steels at room temperature

Grade	Yield strength (MPa)	UTS (MPa)	Maximal elongation (%)
TRIP Si	525	820	29
TRIP AISi	440	800	29
DP	560	820	20

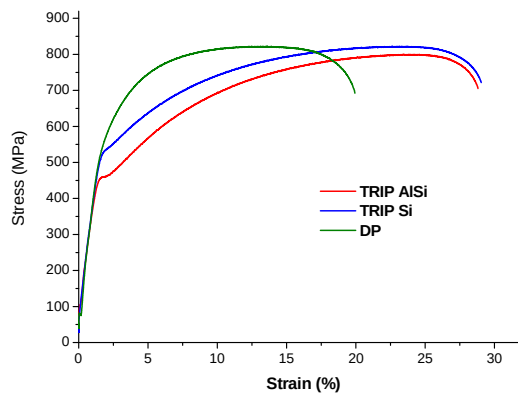


figure 37: Engineering stress vs. engineering strain at 22°C. Strain rate = $1.4 \cdot 10^{-1} \text{ s}^{-1}$

4. Mechanical characterization of the embrittlement

4.1. Method

Tensile specimens ($L_0 = 35$ mm, $w_0 = 8$ mm, $e_0 = 1$ mm) are tested into a thermo-mechanical analyzer Gleeble 3500 shown in the figure 38. After high temperature holding (during straining) the specimen is water quenched. Investigated temperatures are in the range 400 - 1100 °C. Temperature control is made using a K-type thermocouple welded near the center of the specimen. The force F , the stroke d , and the temperature T are recorded during the test, as shown in figure 39. The specimen is first heated (Joule heating) during 1 s up to the test temperature and immediately strained at a constant strain rate. Immediately after the test, the specimen is water quenched.

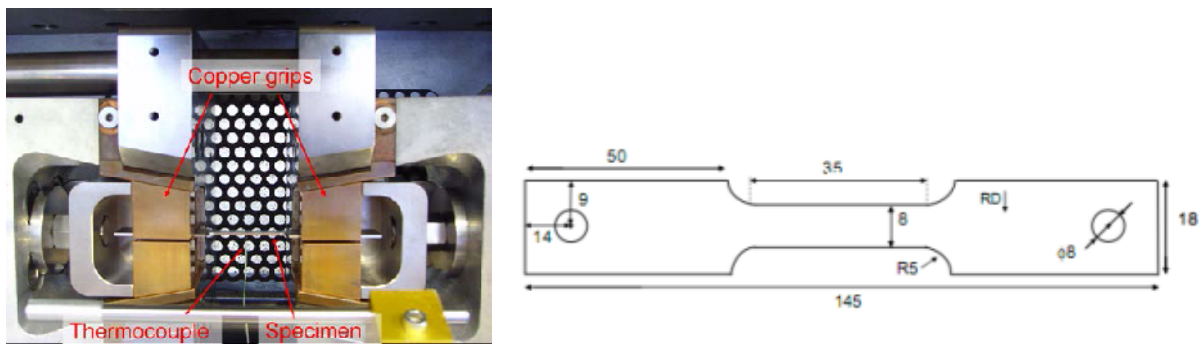


figure 38: Gleeble 3500 for high temperature tensile tests (left) and specimen geometry. Reprinted after [BEA2012]

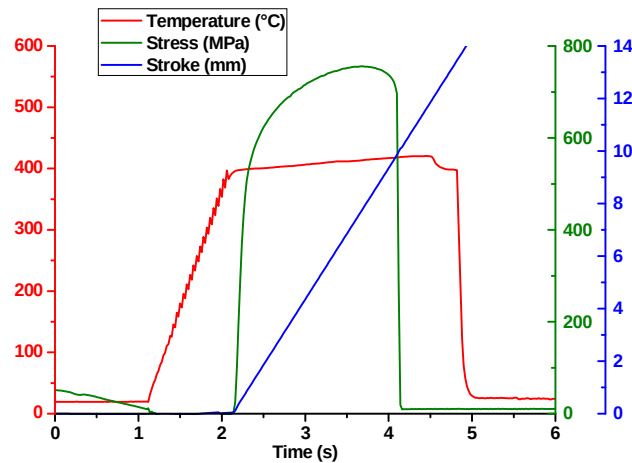


figure 39: Typical temperature-time diagram during the tensile test

The engineering stress σ (MPa) and engineering strain ε (%) are calculated respectively from the measured force F and stroke L . Stroke is not measured locally but on the driving chuck.

$$\sigma = \frac{F}{e_0 w_0}$$

$$\varepsilon = \frac{L - L_0}{L_0} \cdot 100$$

Strain to failure ε_{max} , *i.e.* maximal elongation, corresponds to the elongation for which the stress falls to zero. Ultimate tensile strength (UTS) is the maximal stress recorded during the tensile test.

4.2. Characterization of the ductility

4.2.1. Loss of ductility for TRIP Si

Figure 40 shows the tensile curves obtained at 855 °C for TRIP Si with and without coating. The bare steel has a maximal elongation around 50 % whereas it is only 5% for the coated product.

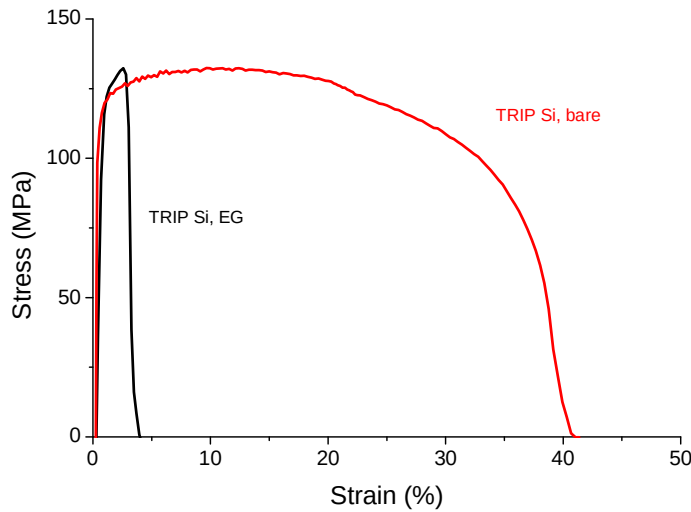


figure 40: Tensile curves for the TRIP Si with and without coating at 855°C. Strain rate = 0.14 s^{-1}

The figure 41 shows temperature dependence of the maximal tensile elongation for both bare and coated TRIP Si steels. For bare steel the maximal elongation increases approximately linearly as temperature increases, from 25 % at 300 °C to 40 % at 1100 °C. Due to the dispersion of the results, an absolute uncertainty of 5 % needs to be considered for maximal elongation values. As explained in the appendix 1, an absolute uncertainty of 20 °C should be considered for the temperature values.

For coated steel, the maximal elongation increases in the same manner than for the bare steel but drops down when temperature reaches 700 °C. The elongation drops down to about 5 % at 730 °C and then remains constant up to 920 – 930 °C. It increases abruptly at 950 °C. The maximal elongation recovers the same level than that of the bare steel for temperature above 950 °C.

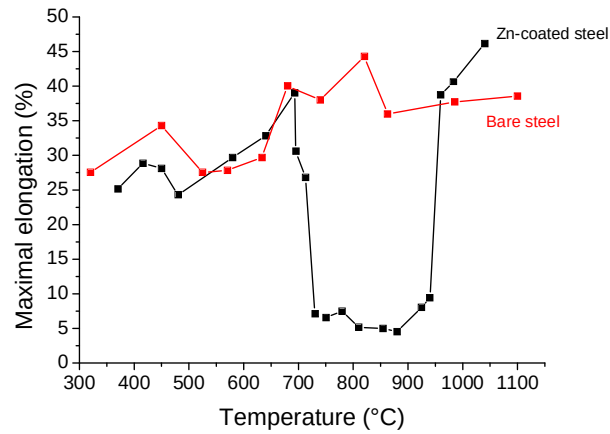


figure 41: Temperature dependence of the maximal elongation for the TRIP Si, with and without Zn coating. Strain rate = 0.14 s^{-1}

4.2.2. Comparison between TRIP Si, TRIP AlSi and DP

For comparison between steels, temperature dependence of the maximal elongation for the three investigated steels is given in figure 42. Several differences can be noted, particularly between the two TRIP steels on one side, and DP steel on the other.

First the maximal elongation out of the ductility trough (where the maximal elongation is supposed to be close to that of the bare steel) seems higher for medium strain rate than for others. This observation could probably be discussed by studying the literature about creep for this type of alloy but the discussion is not conducted here.

The width of the ductility trough from an arbitrary strain = 20 % gives a numerical value to characterize the loss of ductility extend. It is 174 °C, 228 °C and 231°C, respectively for DP, TRIP Si and TRIP AlSi.

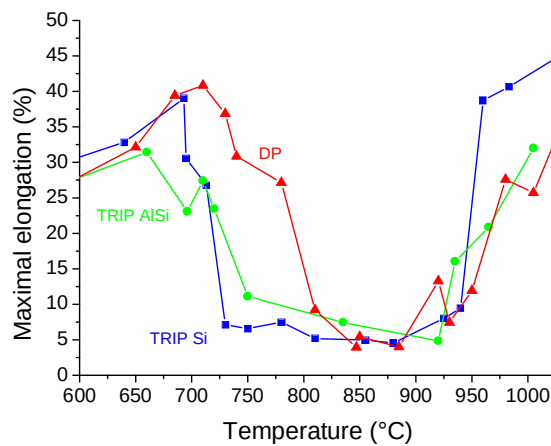


figure 42: Temperature dependence of the maximal elongation for the three grades with Zn coating. Strain rate = 0.14 s^{-1}

4.3. Effect on UTS

Figure 43 shows the temperature dependence of UTS for the TRIP Si steel. There is no significant difference between maximal stresses measured for EG steel and bare steel. It means that cracking occurs at the UTS or above. Thus “brittle” cracking is achieved during general plastic flow. Figure 44 shows the temperature dependence of UTS for the three steels. Like for TRIP Si, no drop of UTS is observed in the temperature range of the ductility trough. The mechanical properties of the three investigated products are nearly the same, at least for UTS of the coated steels.

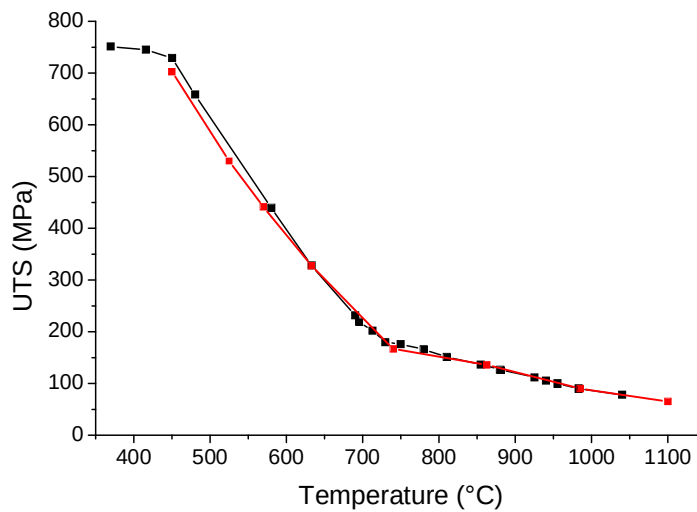


figure 43: UTS vs. temperature for the TRIP Si steel. Strain rate = 0.14 s^{-1} . Black: coated steel. Red: bare steel

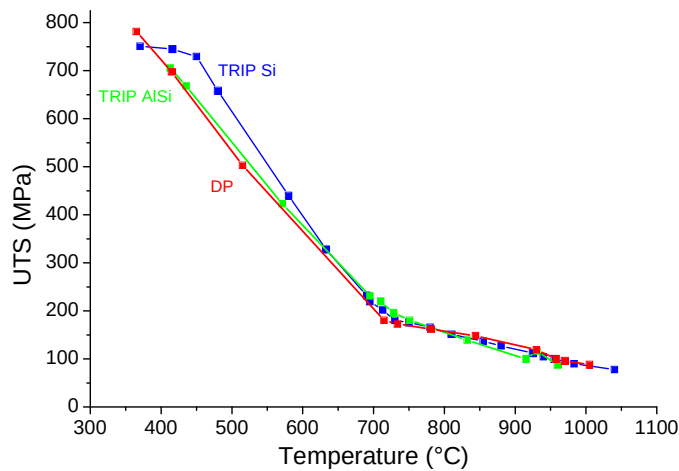


figure 44: UTS vs. temperature for three steels with Zn coating. Strain rate = 0.14 s^{-1}

4.4. Influence of strain rate

Figure 45 gives the maximal elongation for TRIP Si at different strain rates. A ductility trough is observed for all investigated strain rates. Some differences can be noted, but some are unclear.

First the maximal elongation out of the ductility trough (where the maximal elongation is supposed to be close to that of the bare steel) depends on strain rate and is maximal for medium strain rate. This observation could be probably discussed by studying the literature about creep for this type of alloy but the discussion is not conducted here.

Then T_{start} seems to decrease as strain rate increases. T_{end} seems to be shifted to higher temperature for the highest strain rate, but unchanged for the others. The residual ductility is nearly the same for $1.4 \cdot 10^{-2} \text{ s}^{-1}$ and $1.4 \cdot 10^{-1} \text{ s}^{-1}$, but is higher for 1.4 s^{-1} .

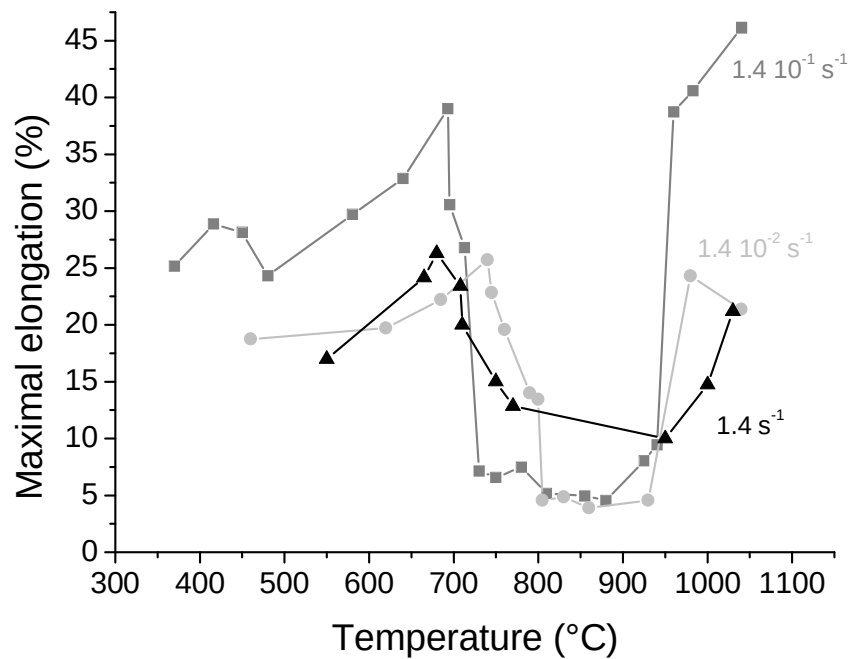


figure 45: Effect of the strain rate on the ductility trough for the TRIP Si grade with Zn coating

Figure 46 gives UTS for TRIP Si at different strain rates. The strength of the material increases with strain rate. It has already been pointed out that UTS for the coated steel is the same than for the bare for $1.4 \cdot 10^{-1} \text{ s}^{-1}$. As the curve shape is the same for 10^{-1} s^{-1} , it is supposed that there is also no difference for low strain rate. For 1.4 s^{-1} a drop of UTS is observed. The dashed curve has been plotted by linking the two points out of the ductility trough (figure 45).

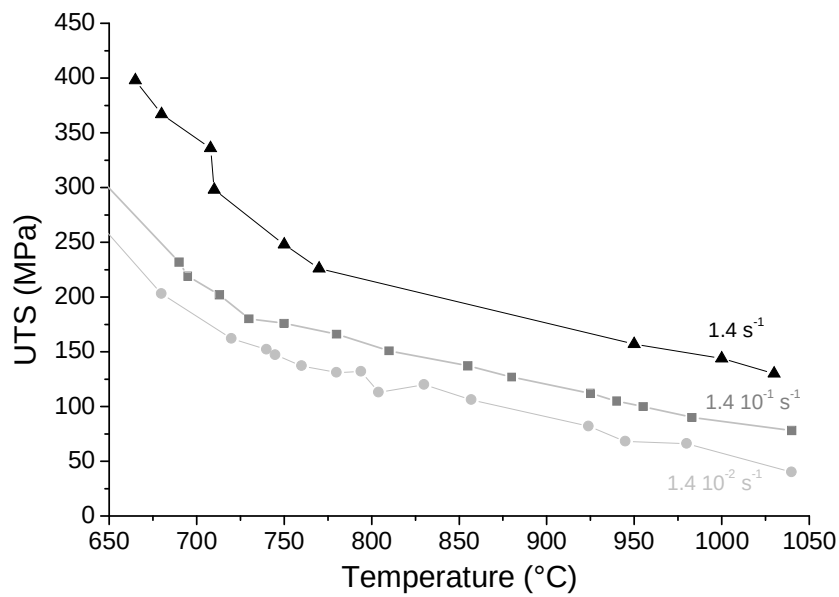


figure 46: Effect of the strain rate on the tensile strength for the TRIP Si grade

4.5. Imposed stress conditions at 850°C

While previous paragraph shows results of tensile tests with imposed strain rate conditions, imposed stress conditions have also been investigated. These tests have been performed at 850 °C. An example of tensile curve with 105 MPa imposed stress is given in figure 47. After increasing the stress up to the target value, the stress level is maintained upon failure of the specimen. Four tests have been performed at different stress levels: 65 MPa, 77 MPa, 95 MPa, and 103 MPa. For comparison the UTS was 108 MPa, 138 MPa and 198 MPa, respectively at $1.4 \cdot 10^{-2} \text{ s}^{-1}$, $1.4 \cdot 10^{-1} \text{ s}^{-1}$ and 1.4 s^{-1} .

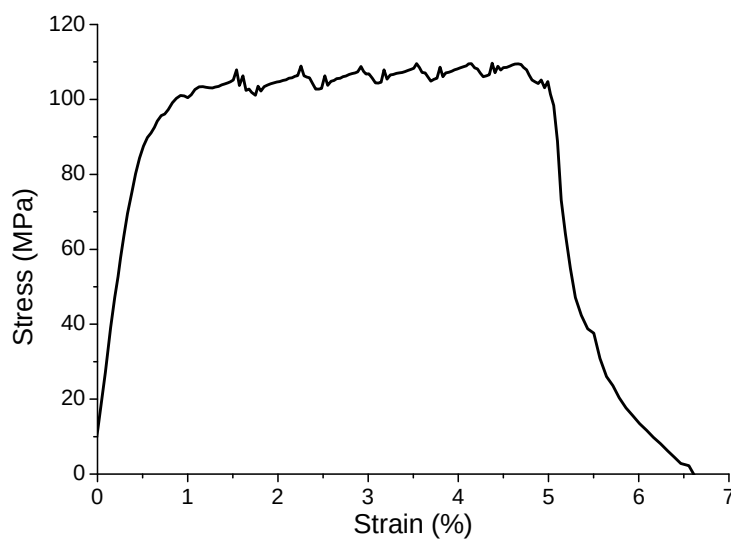


figure 47: Stress-strain curve with imposed stress conditions at 850°C. Constant stress about 105 MPa is maintained until failure

The time-to-failure is given in figure 48. The time-to-failure decreases as imposed stress increases. It is about 130 s at 65 MPa and less than 10 s for 95 and 103 MPa. The maximal elongation is given in figure 49. The maximal elongation is around 25 % for 65 MPa and 77 MPa, and around 8 % for 95 MPa and 103 MPa. There are two distinct behaviors that have not been noticed on the graph for time-to-failure (figure 48): high maximal elongation for stress lower than 80 MPa, low maximal elongation for stress higher than 90 MPa. These maximal elongations can be compared with what was found with imposed strain rate conditions. Indeed for stress lower than 80 MPa, the maximal elongation of 25 % can be compared to the elongation of the bare steel at $1.4 \cdot 10^{-1} \text{ s}^{-1}$ at 850 °C, i.e. around 35 % (figure 41). For stress higher than 90 MPa, the maximal elongation of 8 % is close to the residual elongation in the ductility trough, i.e. around 5% (figure 41).

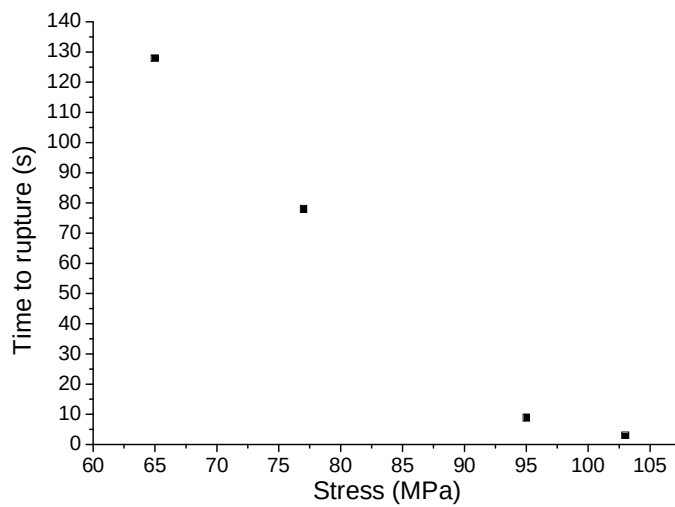


figure 48: Influence of imposed stress on time-to-failure for coated TRIP Si

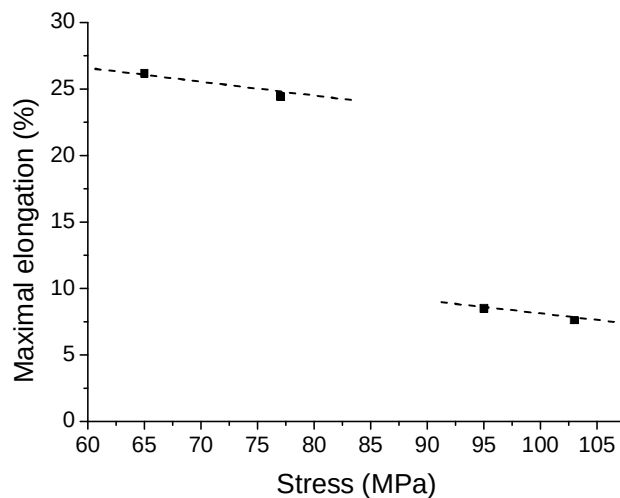


figure 49: Influence of imposed stress on the maximal elongation for coated TRIP Si

4.6. Comments on mechanical characterization

The results clearly show that strong embrittlement occurs for the three investigated Zn-coated products. For example, the ductility trough for TRIP Si, found by comparison between coated steel and bare steel maximal elongations, is an explicit result. Thus the steel/Zn couple has been evidenced as a susceptible couple regarding LME.

Uncertainties for temperature, stress and strain measurements are not negligible. Nevertheless this drastic embrittlement (starting around 700 °C) does not correspond to the melting point of Zn (around 420 °C). For this reason, characterization of GB wetting and penetration around 700 °C will be made in section 6 as a tentative to explain the abrupt modification of the material ductility at this temperature.

On the other hand, and according to the literature review, LME is associated with the propagation of intergranular cracks. At this point of the experimental characterization, cracks morphology inside tensile specimens is investigated in the next section.

5. Characterization of cracks

5.1. Fracture surface observation for TRIP Si

The observation of fracture surface is a common way to identify cracking path and brittleness character of fracture. In this subsection, fracture surfaces for bare steels and coated steels are compared, both inside and out of the temperature range of the ductility trough.

5.1.1. Fracture surface of bare steel

The fracture surfaces of the bare steel at 550°C and 850 °C are shown in figure 50. Both specimens show very ductile failure by void growth. The final fracture surface width is around 30 μm indicating that important striction occurs before failure (local decrease of the thickness from 1 mm to 30 μm before failure). It is in agreement with the maximal elongation between 30 % and 40 % measured for bare TRIP Si (figure 41).

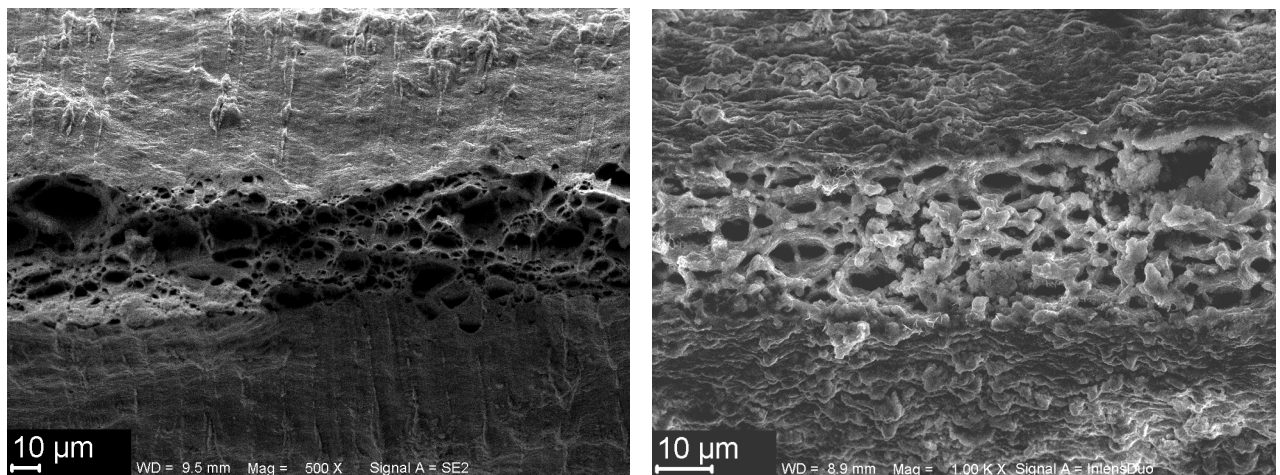


figure 50: Fracture surface for bare TRIP Si at 550 °C (left, SE2) and 850°C (right, SE2 in lens). Striction and ductile fracture surfaces are evidenced

5.1.2. Fracture surface of coated steel

Fracture surface are covered by zinc

Figure 51 shows the fracture surface of coated steel at 940 °C (in the ductility trough). It does not exhibit striction, contrary to bare steel specimens. Two crack zones can be roughly seen indicating that cracks nucleate on both faces of the sheet. Figure 52 shows the same specimen (figure 51) at higher magnification. The fracture surface is covered with zinc.

The intergranular character of the rupture can be nevertheless identified. Indeed the apparent “grain” structure has an elemental size around 5 μm what is close to the grain size of the base metal. The characterization after dissolving the Zn layer is made in the next paragraph.

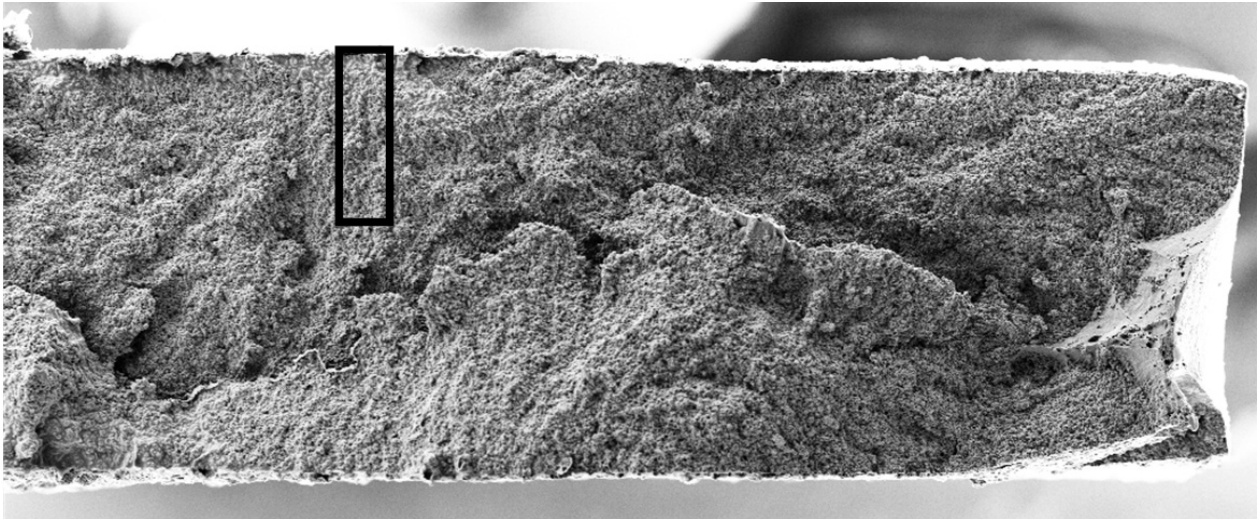


figure 51: Fracture surface for the sample strained at 940°C. Cracks nucleate on both faces since two cracking zones are visible. The black rectangle shows the area displayed by the figure 52

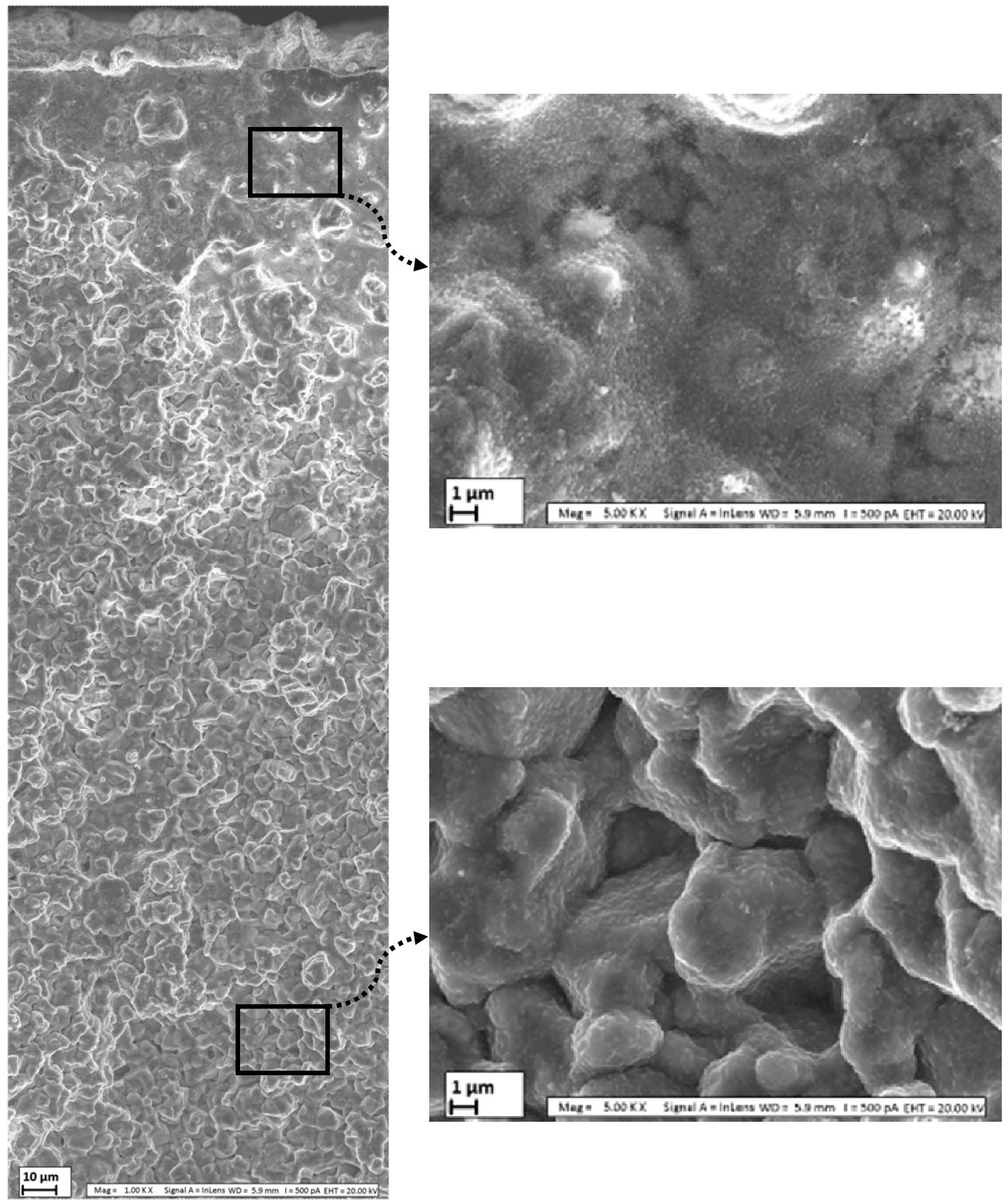


figure 52: Fracture surface for a sample strained at 940°C covered by Zn layer. The layer thickness decreases with the depth.

Fracture surface after Zn dissolution

The fracture surfaces of the coated steel, with observation of the whole sheet thickness, are shown in figure 53. At 550 °C (temperature out of the ductility trough) striction and ductile surface with voids are observed, like for bare steel (figure 50). For the other specimens, temperature is between 690 °C and 920 °C. No significant striction can be observed. At 690 °C - the observed specimen is the first to experience a decrease of the maximal elongation, i.e. the first in the ductility trough – two different fracture modes are observed, as shown at higher magnification in figure 54. On a depth about 200 µm on both sides of the sheet, intergranular aspect is observed, while the core keeps ductile (voids). Figure 55 shows the fracture surfaces at 720 °C and 820 °C, i.e. for temperature in the temperature range of the ductility trough. Fracture is intergranular. The austenite/ferrite microstructure is observed with ferrite grains in dark grey and austenite in light grey or white color.

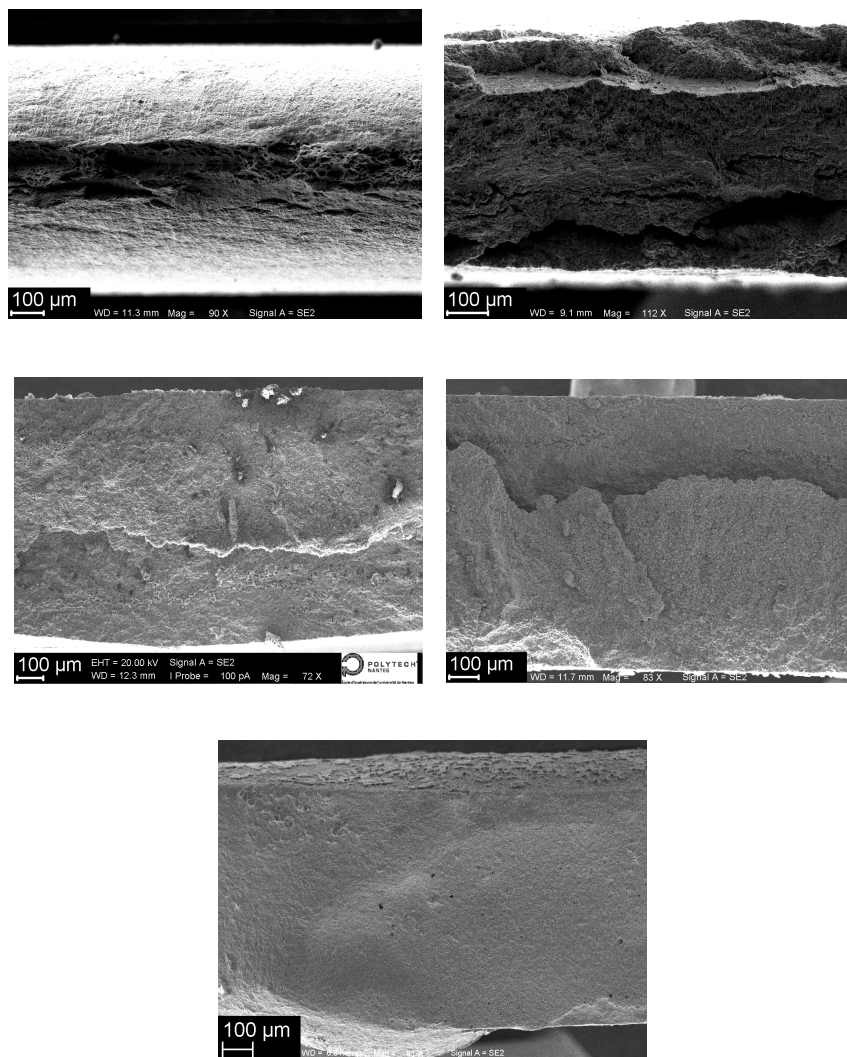


figure 53: Fracture surface of the coated TRIP Si after dissolution of the Zn layer. Top-right: 550 °C; top-left: 690 °C; middle-left: 720 °C; middle-right: 820 °C; bottom: 920 °C

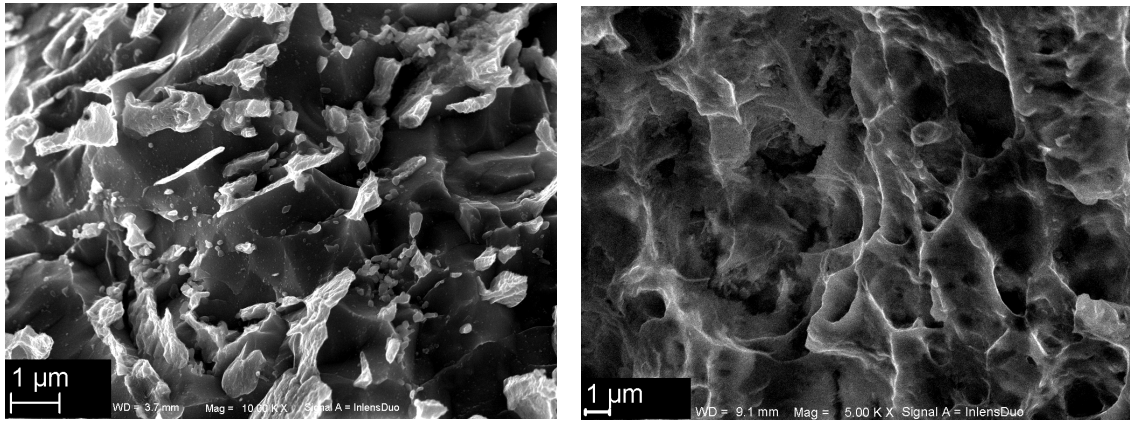


figure 54: For the specimen strained at 690°C, fracture is intergranular for a depth about 200 µm (left), the core is ductile (right)

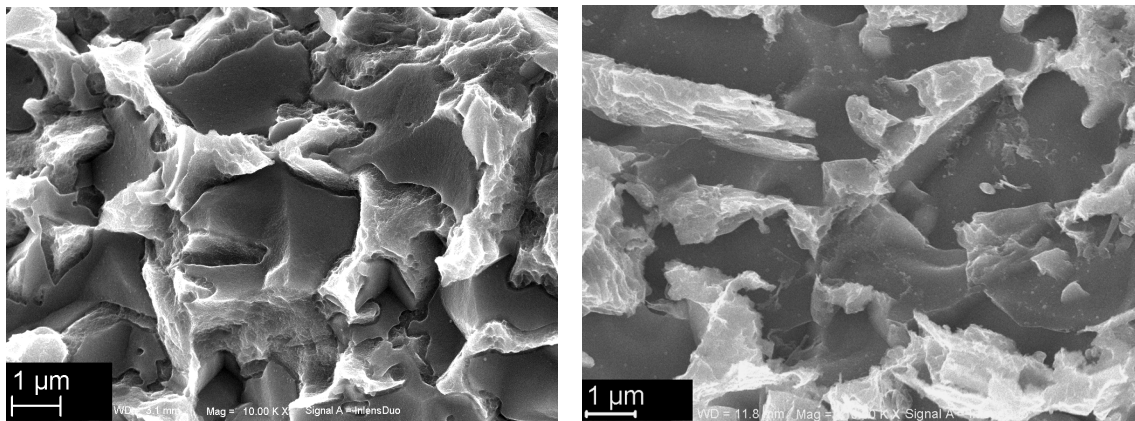


figure 55: Fracture surface at 720 °C (left) and 820 °C (right). Ferrite: dark grey, austenite: light grey/white. At the bottom of the ductility trough fracture is intergranular along ferrite/austenite interphase boundaries

5.2. Cross section observations of cracks for TRIP Si

Observations are conducted on post mortem specimens. Central cross sections show the failing crack and several other deep cracks as schematically shown in figure 56.

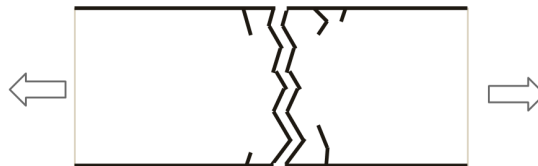


figure 56: Scheme of a typical cross section of a specimen, main failing crack are surrounded by several deep cracks

5.2.1. Cross section observation at $T \approx A_{c3}$ (full austenite microstructure)

Figure 57 is one of the most impressive cases that occurred at 940 °C. The failing crack is on the left side; one other full thickness crack is present; several other deep cracks are observed on both sides of the specimen; material grains decohesion is dramatic since several “islands” can be seen.

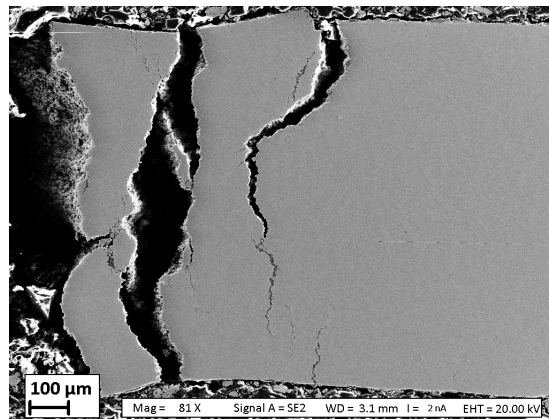


figure 57: Cross-section of the TRIP Si strained at 940°C

Figure 58 shows the cracking path on a polished cross section thanks to chemical contrast in the SEM. Indeed Zn channel, or opened crack-filled with Zn, is observed. The very fine grains microstructure makes the identification of the cracking path very difficult. One can expect that cracking occurs along γ/γ (prior austenite grain boundaries) for $T > A_{c3}$.

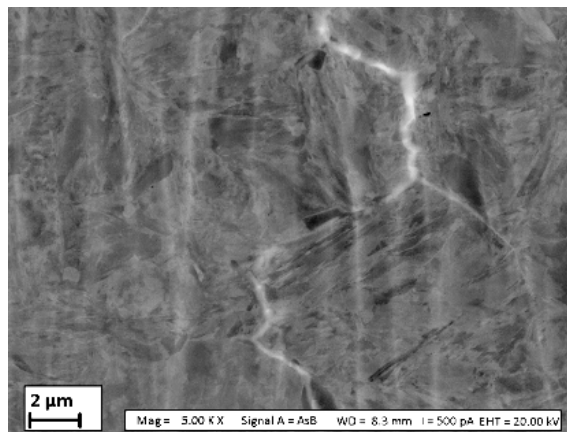


figure 58: At 940°C the crack propagates in the γ microstructure (BSE)

Figure 59 shows that Zn channel thickness in the range of 30 - 50 nm can be imaged by SEM as indicated by the black arrows. In a single GB path, this thickness can be observed on a depth of a few microns. Furthermore this fine investigation shows that the cracking path is not smooth, or well-defined, as indicated

by the red arrows. Indeed it seems that lateral penetration occurs in subgrain microstructure, with a typical GB wetting shape (as described in section 6). It can also be supposed that an out-of-equilibrium (rich Fe)-Zn microstructure appears after bulk lateral diffusion of Zn in Fe and quenching. Analog morphology is observed just under steel/coating interface after high temperature holding (see section 6 of this chapter). It is not clear if this observation is important or only secondary.

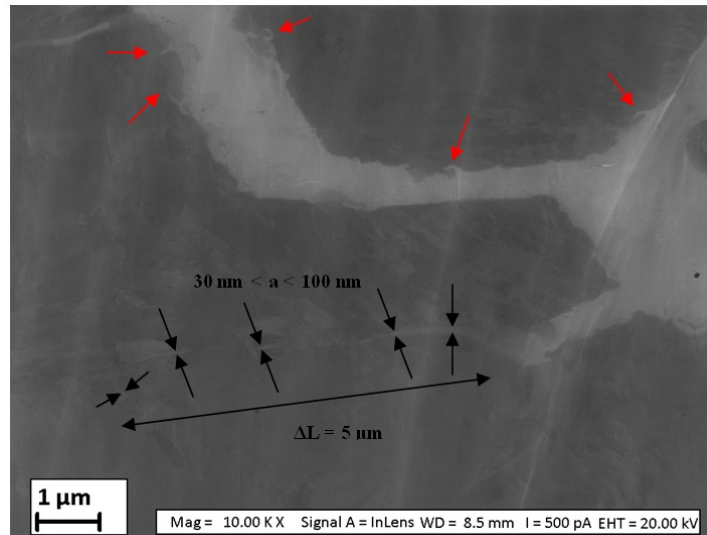


figure 59: Zn channel with thickness less than 50 nm, probably in a prior austenite GB (SE)

5.2.2. Cross section observation at $T < A_{c3}$ (dual-phase microstructure)

Figure 60 shows the cross section of coated TRIP Si specimen strained at 800 °C. The failing crack is on the left side. A secondary crack is also observed. By comparison with the behavior at $T \approx A_{c3}$ (figure 57), cracking extent is smaller since there is only one very deep crack, and secondary cracks are less and shorter.

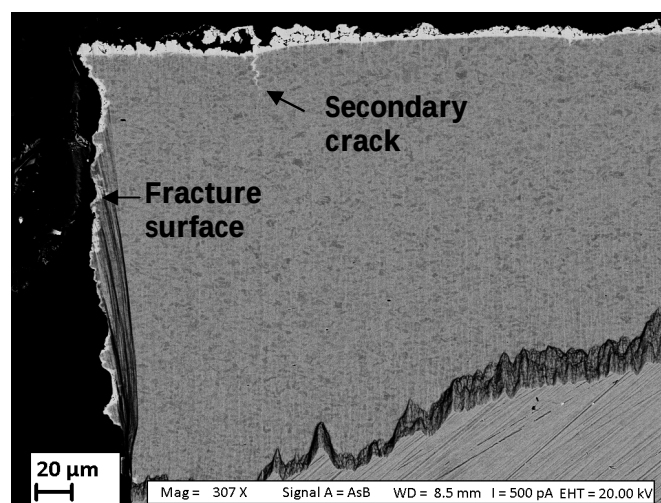


figure 60: Cross-section of the sample strained at 800°C

Figure 61 shows cracks having propagated in the ferrite/austenite microstructure at 800 °C. As already observed on fracture surfaces (figure 55), cracks propagate along ferrite/austenite interphase boundaries. At 800 °C the austenite fraction is observed to be higher than in the base metal (see base metal characterization in section 3.2). This is in agreement with $A_{c1} = 750^{\circ}\text{C}$. So the austenite is “new” austenite coming from the ferrite-to-austenite transition.

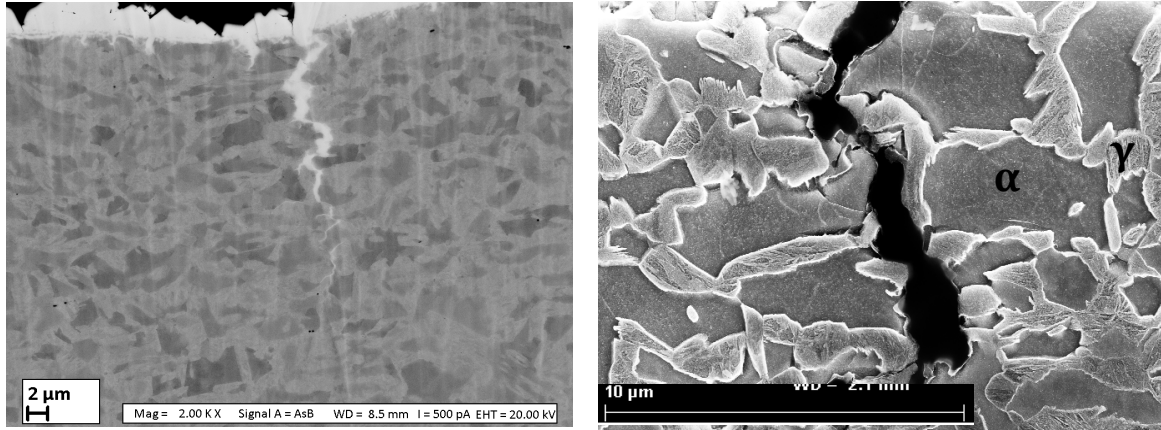


figure 61: At 800 °C the crack propagates in the α/γ microstructure. Ion beam polishing (right) and nital etching (right)

Figure 62 shows high magnification image of thin Zn channel at the crack tip in the ferrite/austenite microstructure. Zn channel thickness less than 50 nm is characterized by SEM, as previously observed for a maximal temperature around A_{c3} (figure 59).

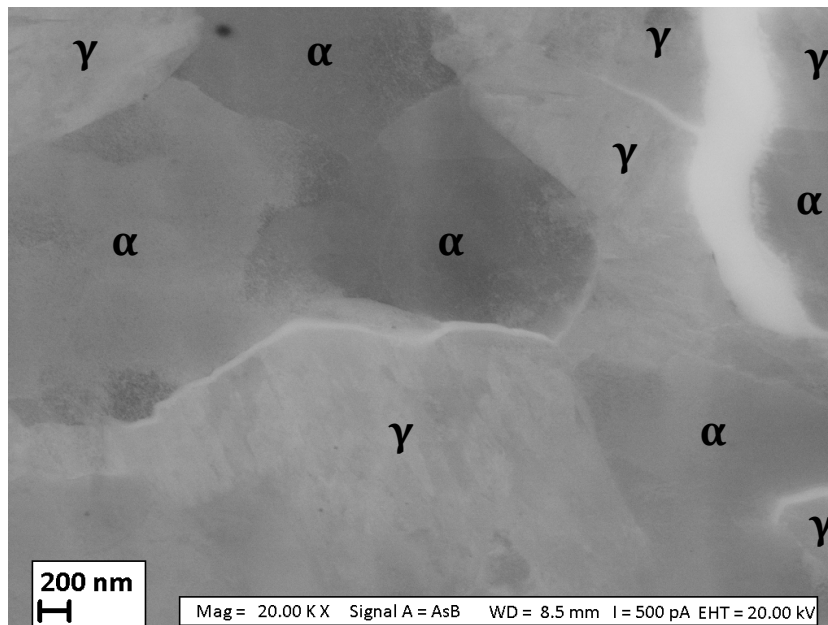


figure 62: Zn channel with thickness less than 50 nm in an α/γ boundary and a γ/γ boundary. Specimen strained at 800 °C

5.3. X-ray analyses on cross section for TRIP Si

5.3.1. EDX mapping

Energy-dispersive X-ray spectroscopy (EDX) mapping has been used to characterize Zn channels. Figure 63 shows SEM and EDX images made near the crack tip. It gives an interesting representation of crack branching, micrometer-thick and nanometer-thick Zn channels. Thin (< 100 nm) channels are present at the crack tip (bottom of the images). Then crack opening and thick channel (1 μm) are observed. It is interesting to note that thin channels also propagate laterally.

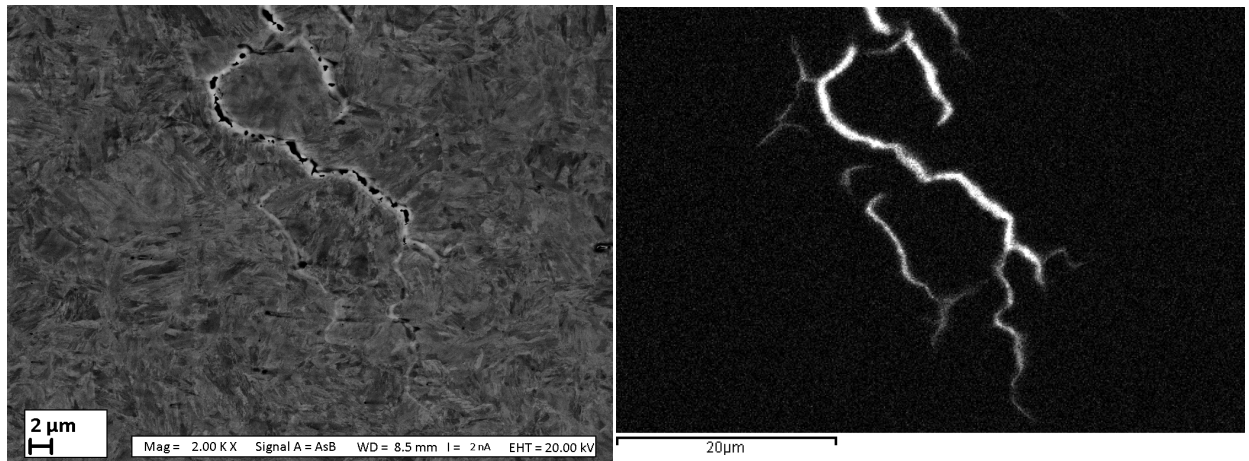


figure 63: BSE map of the sample strained at 940 °C (left) and corresponding EDX elemental map of Zn (right)

5.3.2. WDX profiling for thickness measurement

Wavelength dispersive X-ray spectroscopy (WDX) has a higher atomic resolution than EDX and can be used for detection of small Zn amount (Zn concentration in the analyzed volume less than 10^{-3} wt%). Following the method developed by Christien and coworkers [CHR2008][CHR2012][NOW2011][FER2012][ALL2013], the amount of Zn along the GB can be quantified. The method which has been referred to a “non conventional X-ray technique”, detailed in Appendix 1. It consists in making a profile across the GB with the electron beam and to measure Zn concentration vs. beam travel. If Zn is present along the GB, the curve will show a peak with its maximum at the position of the GB (supposed to be perpendicular to the polished surface). The width of the peak corresponds to two times the lateral size of the interaction volume, i.e. around 2 microns. Making the hypothesis that a pure Zn layer is present along the GB and that Zn concentration in the bulk is zero, Zn thickness t_{Zn} can be calculated from the measurement of the area under the peak A_{peak} [%. m]:

$$t_{\text{Zn}} = \frac{\rho_{\text{Fe}} A_{\text{peak}}}{\rho_{\text{Zn}} 100}.$$

This method is applied to characterize the crack tip shown in figure 64.

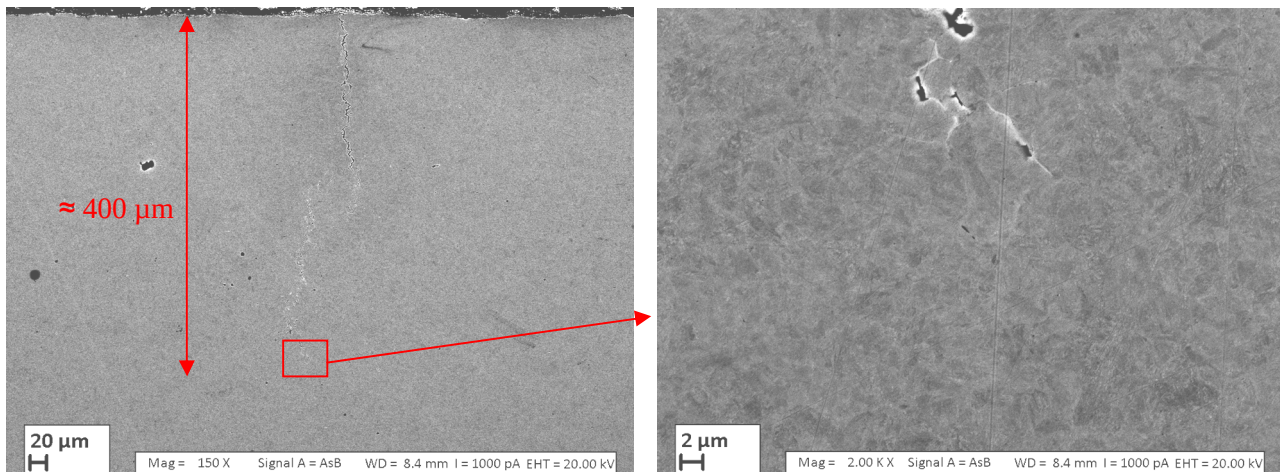


figure 64: 400 μm deep arrested crack in the specimen strained at 940 $^{\circ}\text{C}$ investigated through WDX analyses

Figure 65 shows the results of the WDX analyses made at the tip of a crack. It shows that very-thin Zn channels, under the imaging resolution of the SEM, can be detected by making WDX profile across GBs. The measurement of the peak area and the calculated thickness is given in table 9.

table 9: Thickness measured with WDX profiles

Profile	Area of the peak (wt% μm)	Zn thickness (nm)
1a	Not measured	-
1b	0.25	2
2	0.48	5
4	0.60	6
5	0	-
6	0	-
7	Not measured	-
8	3	3

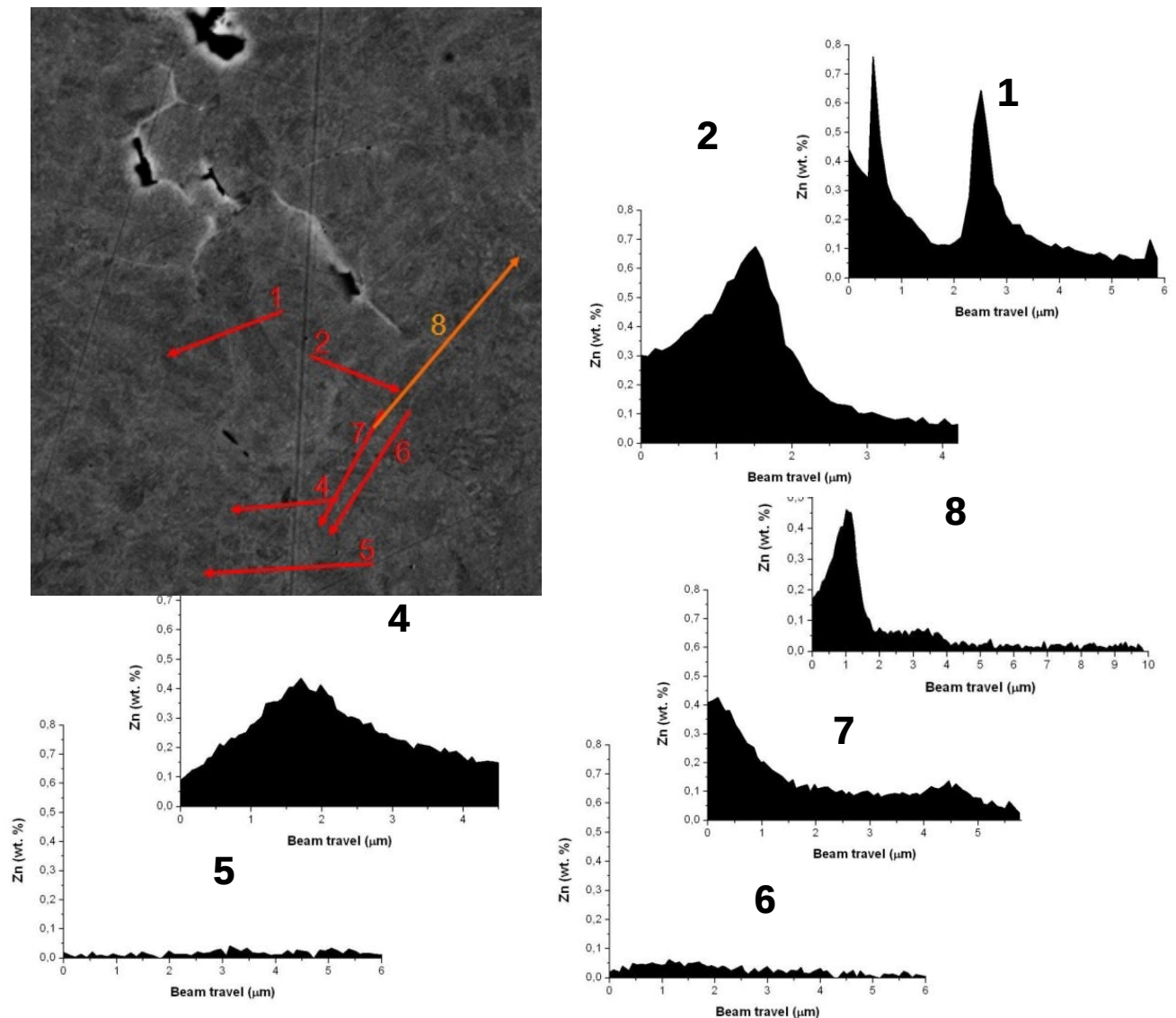


figure 65: WDX profiles at the crack tip. A Zn peak indicates the presence of a Zn channel along the analyzed grain boundary

5.3.3. Comments on the description of cracks

Cross section observation of TRIP Si shows that several cracks are present on one failed specimen. Obviously final failure of the specimen is due to a single crack, the one which has a depth (let us considering only one dimension) equal to the sheet thickness. But this observation indicates that several cracks propagate simultaneously. Furthermore nucleation of cracks on both faces of the specimens is observed.

These observations are pieces of evidence indicating that cracking is relatively slow. At the opposite in brittle material, only one crack would be observed on a fracture specimen, the first to nucleate: brittle cracking is nucleation-controlled. This is not the case in our study.

The intergranular character of cracking has been evidenced both in full austenite microstructure and in dual-phase ferrite/austenite microstructure. Furthermore, retained «metastable» austenite of the base metal or «stable» austenite created above A_{c1} seems of equal sensitivity, since cracks are present in both microstructures. Actually it seems that «new» austenite is created by growth from the retained austenite grains, meaning that difference between the two «types» of austenite is minor, at least regarding crack propagation.

SEM, EDX and WDX have demonstrated the presence of nanometer-thick channels of Zn at the crack tip. This observation can be the basis for the description of a localized process zone at the crack tip for crack propagation. What observed is: uncracked boundary (supposed to be clean, i.e. with no Zn), nanometer-thick film from the nanometer to 50 nm on a depth of 1 to 5 μm , then micrometer-thick channels (from a few hundreds of nanometer to a few micrometers. For long crack, opening displacement of several microns to tens of microns is observed. The experimental characterization techniques do not allow us to investigate the transition between a clean boundary to a nanometer-thick channel.

The implication of these results will be discussed in the final sections of this chapter. Before that the last experimental sections of the chapter describe observations at the steel/coating interface in order to precise wetting behavior of the SM/LM couple under investigation, already characterized to be susceptible to liquid zinc intergranular cracking.

6. Characterization of GB wetting and penetration

6.1. GB penetration under the steel/coating interface

6.1.1. First observation of GB wetting

In order to identify if a GB wetting behavior of GBs can be observed in contact with liquid Zn (as described in the literature review in paragraph 1.1.2), local observations at the steel/coating interface have been made. As an element of comparison, the initial steel/coating interface in the base metal was characterized as a sharp interface (figure 33).

Figure 66 shows examples of observations made at the TRIP Si steel/coating interface after high temperature holding during 0.5 s at 680 °C and 940 °C without exterior stress. The interface is not sharp, but all observed GBs are wetted by Zn. Penetration depth may vary from one GB to another. At 780 °C, a penetration depth about 1 μm is observed for one GB while others are only penetrated on 200 – 400 nm. At 800 °C all GBs are penetrated over a depth about 1.5 μm and a deeper penetration channel, about 2.5 μm , is observed in the center of the image.

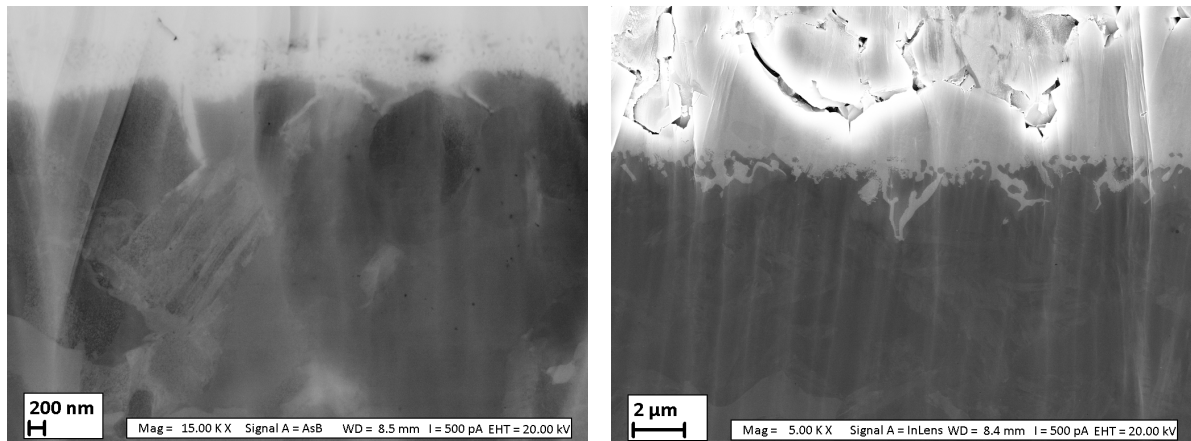


figure 66: Examples of GB wetting morphologies after 0.5 s holding at 680 °C (left) and 800 °C (right)

To compare quantitatively the different samples, an apparent wetting depth is measured according to the description in figure 67.

Measurements are conducted on tensile specimens: holding time at high temperature was 5 s and external stress was applied. Stress applied to tensile specimens can be evaluated by the UTS described previously in figure 43. Nevertheless stress is only applied up to the specimen's failure which occurs before the end of the high temperature holding. The influence of stress on GB wetting is not characterized on tensile specimens since there is only one specimen per temperature. On tensile specimens, observations are made out of the cracking areas. Indeed, even if several cracks can propagate in a tensile sample, they are also wide areas and numerous GBs observed to be free of cracks. For some specimens (figure 66), all GBs in those areas seem to experience GB penetration by Zn.

Others specimens have been tested with high temperature holding during 0.5 s. Stress-free tests have been performed but various exterior stress levels have also been applied during the holding time. Comparisons are made in the following paragraphs.

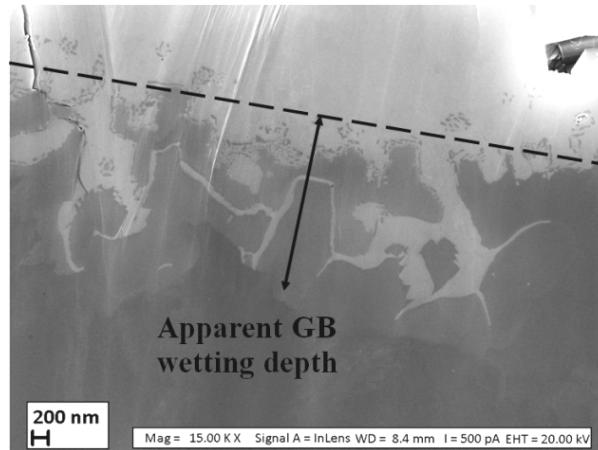


figure 67: Measurement of the wetting depth just under the apparent steel/coating interface after 0.5 s at 800 °C

6.1.2. On tensile specimens

Figure 68 shows the observation of the GB penetration just under the steel/coating interface for TRIP Si tensile specimens. At 690 °C the apparent GB penetration depth is very low. A significant penetration depth along GBs is observed at 740 °C, 800 °C and 930°C. For 930 °C and 980 °C, no more GB penetration can be seen but the coating chemical composition seems to be very different. It would be investigated later by EDX chemical analyses (section 6.2). Even if the apparent wetting depth is very low at 690 °C, the higher magnification observation in figure 69 shows that GBs are nevertheless wetted by Zn. The temperature dependence of the apparent penetration depth is given in figure 72.

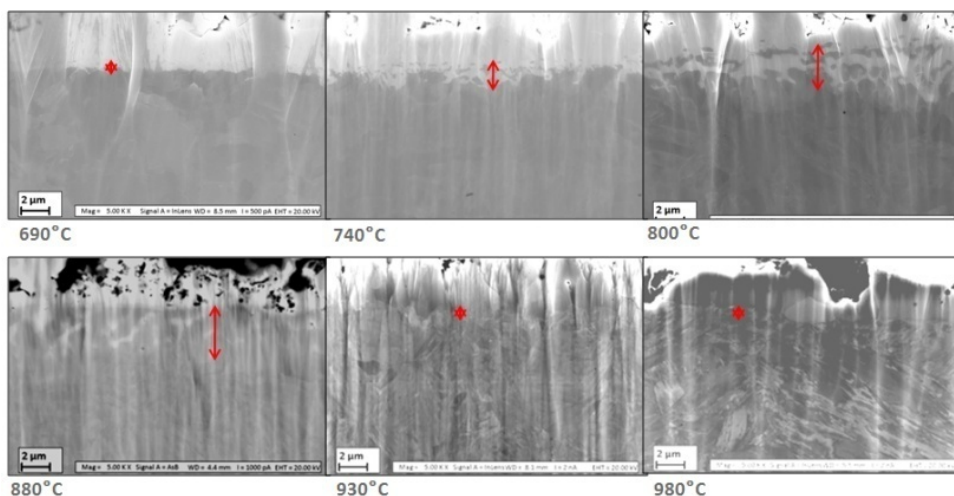


figure 68: Observation of the GB penetration under the steel/coating interface for TRIP Si made on tensile specimens ($t = 5$ s). Ion beam cross section polishing is of bad quality for some images resulting in vertical lines in SEM images.

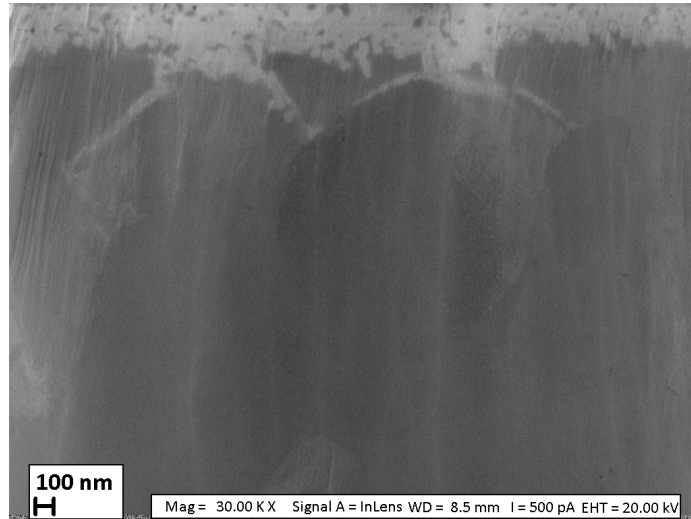


figure 69: At 690 °C, GB wetting is observed even if the penetration depth is very low, around 200 nm.

6.1.3. On 0.5 s holding specimens

The observation of GB wetting and penetration was performed on specimens sensitized by holding at high temperature during 0.5 s. Figure 70 gives the example for three temperatures without external stress. GB penetration extent is higher at 980 °C.

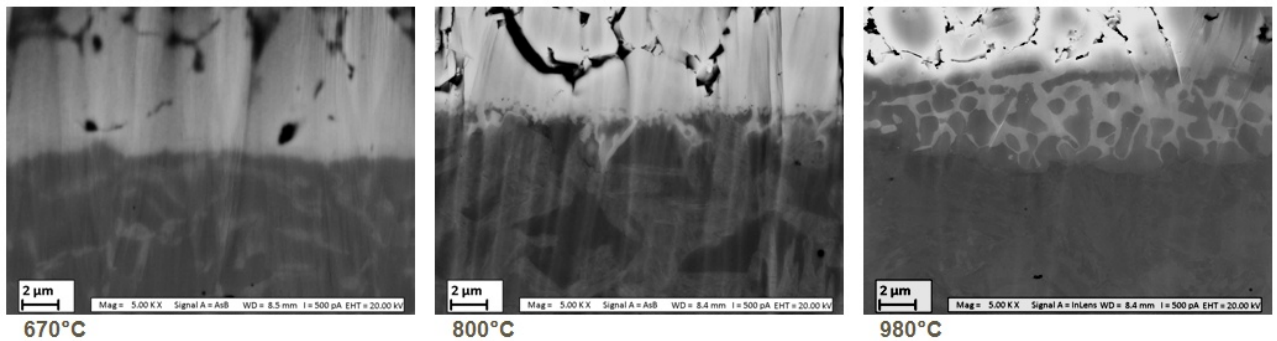


figure 70: Observation of the GB penetration under the steel/coating interface for TRIP Si ($t = 0.5$ s)

As told before, some specimens have been stressed during the 0.5 s long holding. Some specimens failed as for tensile specimens and the stress considered is the highest measured during the measurement (similar to the UTS). Figure 71 shows the influence of stress on the apparent penetration depth. No clear tendency is observed. Furthermore an absolute uncertainty of 1 μm should be considered. Thus stress lower than 300 MPa has not any significant influence compared to the influence of the temperature. The results for the temperature dependence of the penetration depth are plotted in figure 72 and comparison with tensile specimens is made hereafter.

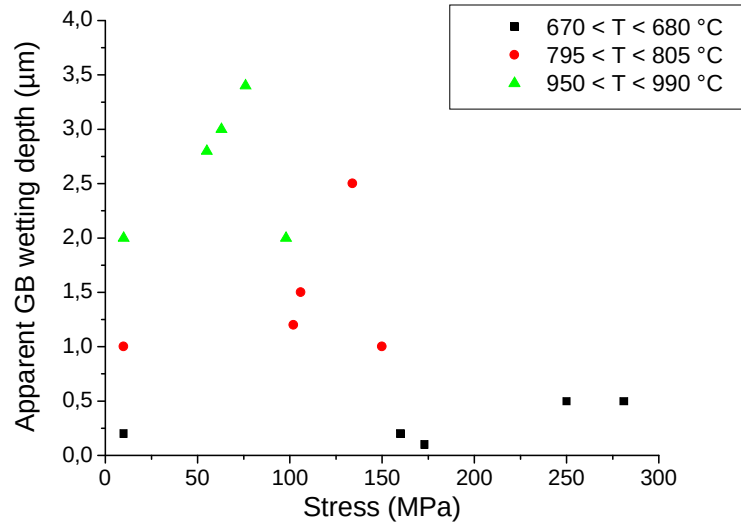


figure 71: Penetration depth vs. applied stress diagram for TRIP Si specimens after 0.5 s at high temperature. No significant influence of stress is observed.

6.1.4. Comparison of the penetration depth

As displayed in figure 72, no significant penetration is found for temperature below 650-700 °C. Above, penetration depth increases as temperature increases. At very high temperature, apparent penetration is zero. The high temperature limit is around 900°C for $t = 5$ s, and around 1000 °C for $t = 0.5$ s.

The results tend to indicate a slight influence of the holding time on penetration depth since the penetration depth is found most of the time lower for 0.5 s than for 5 s. Kinetic comparison is made in paragraph .

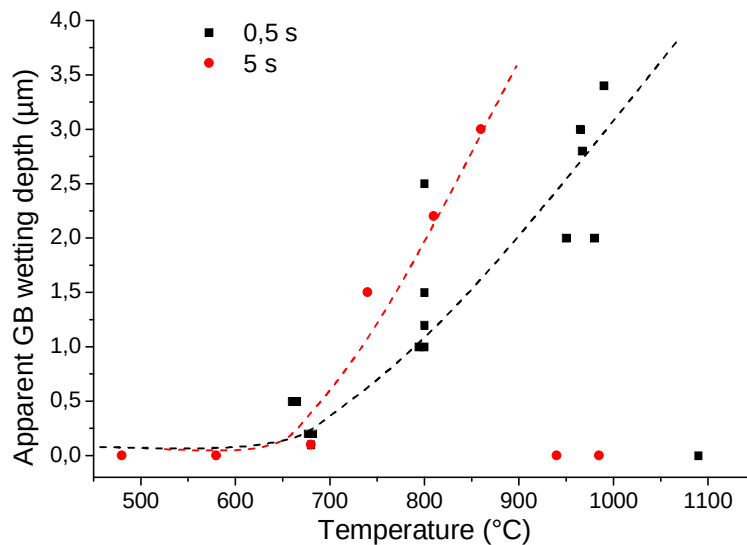


figure 72: Wetting depth vs. temperature

6.2. Characterization of the coating on tensile specimens

Figure 73 shows EDX chemical maps of the coating for tensile specimens. At low temperature, i.e. under the boiling point of Zn ($T < T_b = 907\text{ }^{\circ}\text{C}$), a significant layer of Zn is observed. Indeed the EDX maps show large areas with average Zn concentration higher than 70-80 % (in red).

At very high temperature the Zn quantity detected in the coating is significantly smaller. At $930\text{ }^{\circ}\text{C}$ and $980\text{ }^{\circ}\text{C}$, Zn concentration in the coating is considerably lower than for other temperatures. The coating thickness is also smaller. It seems that the integrated quantity of Zn would be significantly smaller at very high temperature, indicating probably the evaporation of Zn.

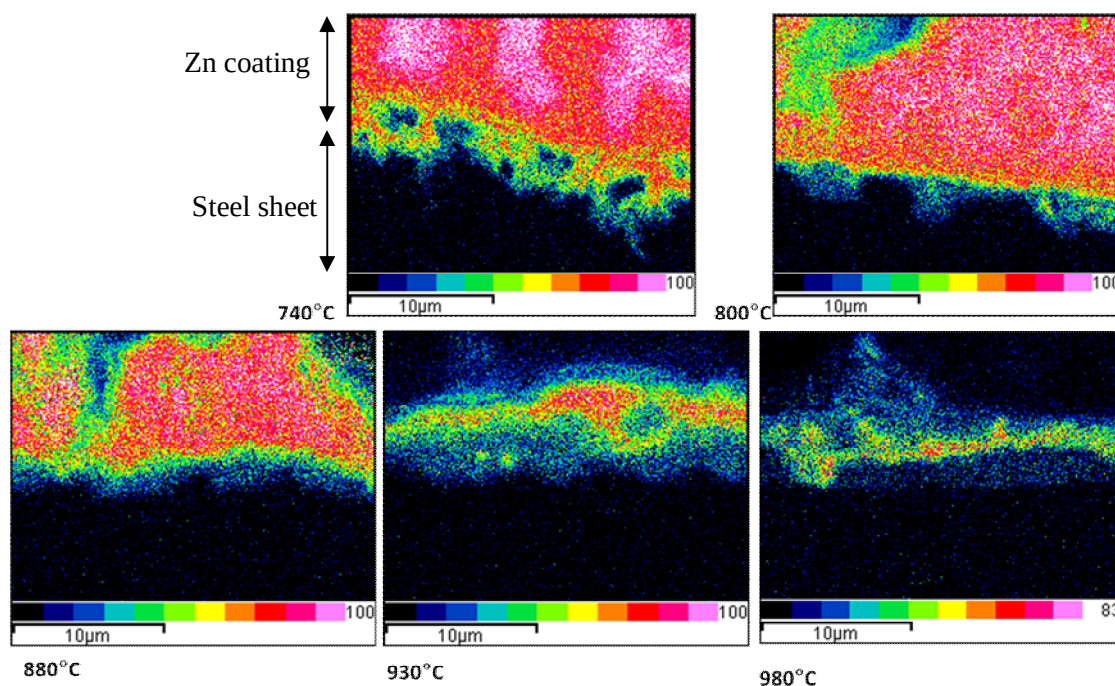


figure 73: EDX maps of the coating on the tensile specimens (high temperature holding during 5 s). Color scale differs for the image at $T = 980\text{ }^{\circ}\text{C}$

6.3. Additional characterization: long time contact between steel and Zn in steel quartz tube

6.3.1. Method

Zn-coated steel sheets are inserted in contact with large amount of Zn in a sealed quartz tube for the study of long time reaction. Both GB penetration and bulk diffusion/dissolution are expected. The tube is placed into a furnace at temperature T for 30 min. At the end of the treatment the tube is quenched in water. After cutting and polishing, the cross section of the steel plate covered by a significant Zn amount is observed. The hypothesis is made that the high quantity of Zn would consume any residual oxygen in the early stage of the high temperature holding. The Zn partial pressure in the quartz tube during the test has been estimated to be

negligible (using the ideal gas equation and assuming that the pressure at room temperature is one atmosphere, i.e. 10^5 Pa, 5 MPa in the tube at 1000 °C is found).

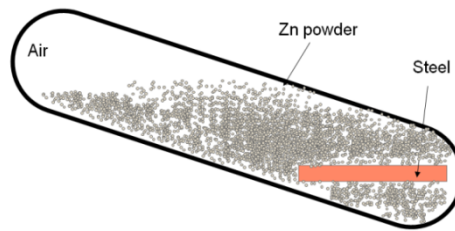


figure 74: Sealed quartz tube experimental set up. Schematic

6.3.2. Steel sheet thickness loss

Figure 75 shows steel sheets cross section after holding at various temperatures. The residual steel sheet thickness can be observed in dark grey or black. Zn and Zn-rich compounds appear in lighter grey.

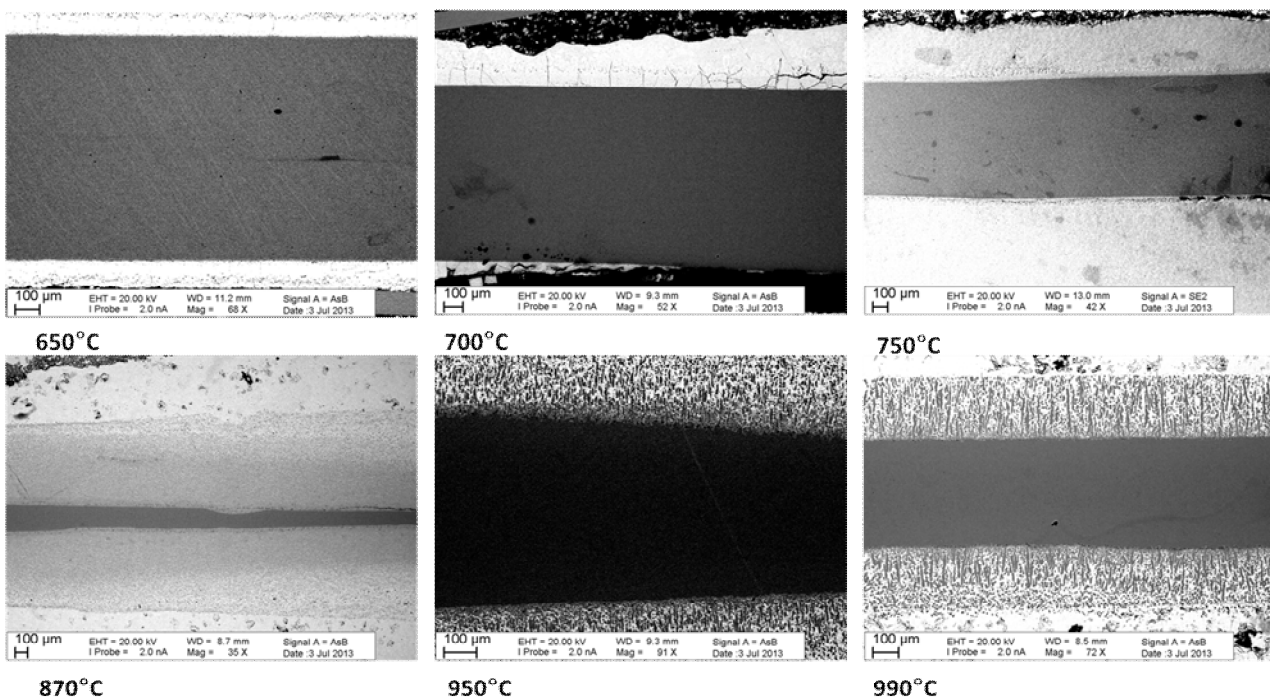


figure 75: SEM (BSE) images of the steel sheets after contact with Zn in sealed quartz tube during 30 min.

The temperature dependence of the final thickness of the steel sheet is shown in figure 76. The residual thickness is close to the initial for $T < 650^\circ\text{C}$. Thickness reduction begins to be significantly higher for $T > 650^\circ\text{C}$ and become really high for experiments at $T > 800^\circ\text{C}$.

The evolution of the thickness at high temperature is questioned. First hypothesis would be that the final thickness decreases as temperature increases and that the scatter on measurement is high. A second

hypothesis would be that the final thickness decreases as temperature increases up to 900 – 950 °C. Then a drop in reduction is observed before the thickness restart to decrease. It is not clear if this kind of hypothesis is reasonable. The boiling point of Zn at pressure of tens of atmosphere should shift to higher temperature (at 53 atmospheres pressure the boiling point is 1510 °C). Does the transition temperature Ac_3 , characterized at 930 °C for TRIP Si have an influence? According to an influence of the microstructure, the results would say that the existence of a ferrite/austenite would be more sensitive to Zn than the full austenite microstructure. The question is not answered in this study.

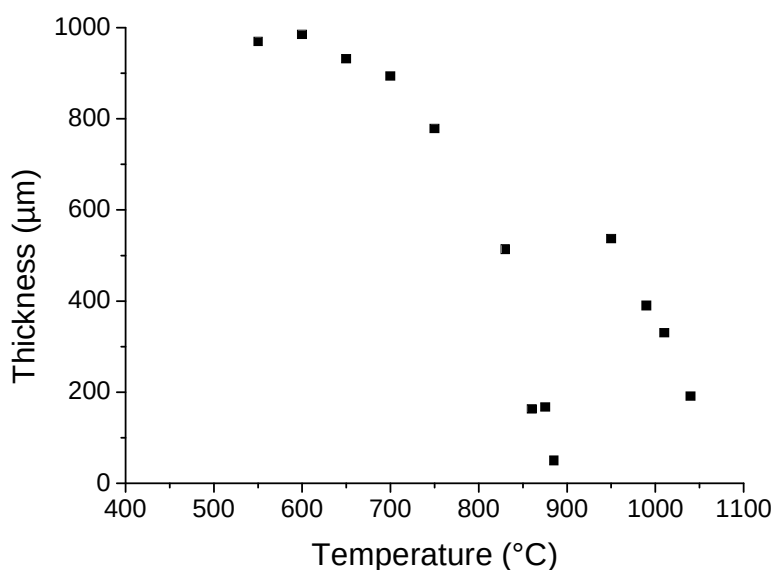


figure 76: Thickness of the steel sheet ($c_{Zn} = 0$) after thermal treatment in contact with Zn during 30 min

6.3.3. Characterization at the steel/Zn interface

Figure 77 shows steel/zinc interfaces at temperatures below 650 °C. No sign of GB penetration by Zn such as what was identified in paragraphs above can be seen. GB decorated with some dark appearance compound under the steel/coating interface is assumed to be GB oxidation (as what was identified for the initial surface of DP steel sheet, see paragraph 3.3) caused by the residual oxygen content in the sealed tube.

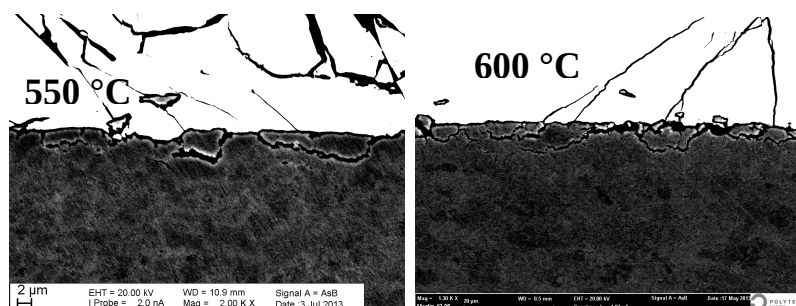


figure 77: "Penetration" front for $T < 650$ °C. Various magnifications (bse)

The micrograph shows a cross-section of a metal with a dark, granular surface layer and a lighter, more uniform interior. Red boxes and arrows highlight specific features: a small square box in the upper left, a larger square box in the middle left, a rectangular box in the lower left, and a rectangular box in the lower right. The phase diagram on the right shows the Fe-Zn system with temperature on the y-axis (300 to 1500 °C) and weight percent zinc on the x-axis (0 to 100). Key features include the liquid phase (L), the gamma-iron phase (γ-Fe), the delta-iron phase (δ-Fe), the epsilon-iron phase (ε-Fe), the zinc phase (Zn), and the intermetallic phases FeZn, Fe₂Zn, Fe₃Zn, Fe₅Zn₂₁, and Fe₂₁Zn₈. The diagram also shows the magnetic transformation line and the eutectic point at 419.58 °C.

70

microstructure is still present at a depth d , while Zn melt has already reached laterally a superior depth of penetration.

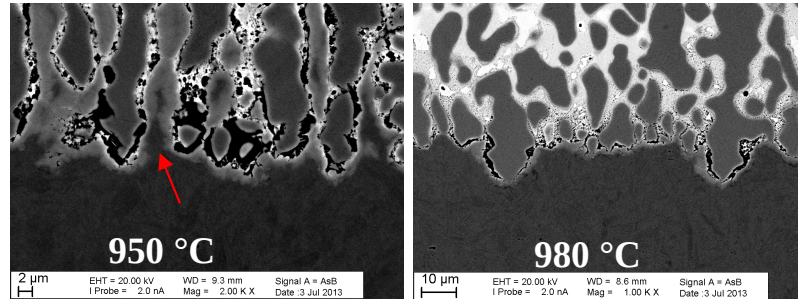


figure 80: "Penetration" front for $T \geq 800$ °C. Pieces of evidence for GB penetration-driven phenomena? Various magnifications (bse)

6.4. Comments on GB penetration and wetting characterization

First wetting of grain boundaries under the steel/coating interface is observed for temperature above $(780 \pm 30)^\circ\text{C}$ for low holding time (0.5 s and 5 s).

For the discussion about penetration kinetics, three point are available at 0.5 s, 5 s and 1800 s (30 min), for example at 850°C . The penetration depth as a function of time is shown in figure 81. Results of fits of the curves are given in table 10. The *a priori* best fit is $n^{\circ}3$ since it is free and carried out on the all three points. It seems to indicate a quasi-linear penetration. Nevertheless this is in contradiction with the fit made only on the two first points. It is very difficult to explain the apparent linear kinetic in this long time range contact in an unstressed sample. But, by comparison of forced parabolic fits, the diffusivity found is much higher when fitted with the long time point. This is also difficult to explain since the rate of the phenomenon is expected to be higher for low time value.

So the results for the penetration kinetic are unclear. It is possible that the measurement of the apparent penetration depth by wetting for low time is false. Indeed the displacement of the coating interface by bulk diffusion/reaction is not taken into account.

A parabolic law can be reasonably assumed for the long time diffusion test. Furthermore the uncertainty on this point may be much lower. The apparent diffusivity found is in the range $10^{-10} \text{ m}^2 \text{ s}^{-1}$ what correspond to high GB diffusivity or liquid-type diffusivity for the iron-zinc system (figure 24, $850^\circ\text{C} \leftrightarrow 8.9 \cdot 10^{-4} \text{ K}^{-1}$)

table 10: results for penetration kinetics and fit with $y = At^n$ or $y = (D_{app}t)^{0.5}$

Fit type	A ($\mu\text{m s}^{-1}$)	n	D_{eff} ($\text{m}^2 \text{ s}^{-1}$)
1/ Fit for $t < 5$ s, n free	1.86	0.30	-
2/ Fit for $t < 5$ s, n forced at 0.5	1.87	0.50	$3.5 \cdot 10^{-12}$
3/ Fit for the high value of t, n free	0.72	0.91	-
4/ Fit for the high value of t, n forced at 0.5	18.9	0.50	$3.6 \cdot 10^{-10}$

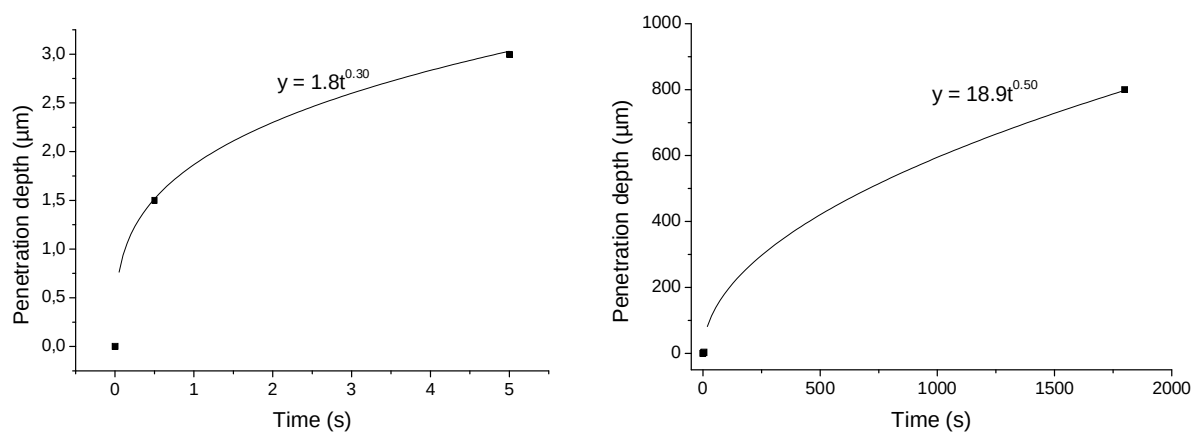


figure 81: Representation of the apparent penetration kinetics at $850\text{ }^{\circ}\text{C}$ for low time with the free fitted curve (left) and with the long time value with a fit imposed with $n = 0.5$ (right)

7. Interpretation: effective occurrence of crack propagation

7.1. Low temperature limit for crack propagation

7.1.1. Evidence for a wetting transition

Failing hypotheses for the low temperature limit

On one's hand the loss of ductility of steel strained in contact with liquid zinc has been clearly demonstrated above 690 - 700 °C for TRIP Si. As soon as 720 °C the bottom of the trough is reached with a residual ductility of about 5 % for the tensile specimen. The ductility drops from 40 % to 5 %. In other words the material loses 90 % of its ability to be strained. It has already been noticed that such an abrupt transition is often associated with the melting of the embrittler, it is not the case since Zn melting point is around 420 °C.

In paragraph 2.4.2, the melting point of the Fe-Zn intermetallic Γ was hypothesized as the low temperature boundary for the embrittlement in a specific study [LEE2012]. The melting point of Γ is 782 °C for the Fe-Zn system. This temperature is only slightly modified by alloying addition in Fe: it is 775 – 780 °C for the alloy Fe-5wt%Si (figure 26). Furthermore the difference between 700 °C (beginning of the ductility trough) and 780 °C is superior to the experimental uncertainty. So the embrittlement takes place for TRIP Si below the melting point of Γ .

The transition temperature A_{c1} has been found at 760 °C for TRIP Si. This temperature can be slightly influenced by the heating rate. Nevertheless it is known that transition temperatures should increase as heating rate increases. Whatever the extent of the influence of the heating rate, the difference between 690 – 700 °C and 760 °C is significant. So embrittlement takes place for TRIP Si below the ferrite-to-austenite transition temperature A_{c1} . Considering the low temperature limit, the embrittlement behavior of TRIP AISi is found to be the same and the discussion above is also relevant for this steel grade.

For DP steel the ductility trough is found at higher temperature. The ductility reached the bottom of the ductility trough at 800°C but it is not clear if ductility starts to decrease at 720 - 730 °C or at 760 – 780 °C. If the last observation is true, it would be difficult to say if A_{c1} or the melting point Γ may play a role, and least of all to discriminate their respective influence. Tentative explanations of the difference between steel grades will be conducted in Chapter III.

At this point of the study the abrupt transition is not explained by any known materials parameters for TRIP steels. The next paragraph shows that the characterization of GB wetting and penetration has given evidences to explain this materials behavior.

Interpretation: a wetting transition

A GB wetting morphology has been evidenced for TRIP Si. Micrometric and submicrometric liquid Zn channels wet steel GBs under the steel/coating interface, for example at 800 °C and 900 °C. At lower temperature, for example 600 °C, a sharp interface is observed as observed in the initial state (before high temperature holding). The temperature dependence of GB wetting has been graphically observed with the

measurement of an apparent penetration depth under the coating. These results represent strong evidence for the existence of a wetting transition between 650 °C and 700 °C

The study in sealed quartz tube has not permit to directly observe GB penetration. Indeed even for a bulk penetration of say 500 μm , the penetration front in GBs is just a few micrometers. Then bulk reaction lead to the formation of phases found in the different domains of the equilibrium diagram. It is supposed that the high bulk reactivity of the Fe-Zn system might hide the initial GB character of the penetration. In other words, the difference between GB diffusivity and bulk diffusivity is too small to rightly observe GB penetration, as it was made for SM/LM systems at low temperature, for example Al/Ga, or for systems with very low solubility even at high temperature, for examples Cu/Bi and Ni/Bi. Whatever the extent of bulk diffusion, penetration is found to be significant only for temperature above 650 °C. It is admitted here that this is the consequence of an abrupt transition, meaning the GB wetting transition, and not to a thermally activated phenomenon like bulk dissolution. Following this analysis the thickness loss for Fe in Zn at high temperature (say typically above 650 °C) is assumed to be driven by (or associated to) GB penetration. So GB penetration is expected to occur simultaneously with bulk reaction as schematically described in figure 82. The action of stress may have a negligible effect on bulk reactions while it may enhance GB penetration. That is why bulk reactions will be neglected in the rest of the study. It is nevertheless clear that additional work is needed to rigorously say if the presence of intermetallics can avoid or delay penetration and cracking in specific conditions of embrittlement.

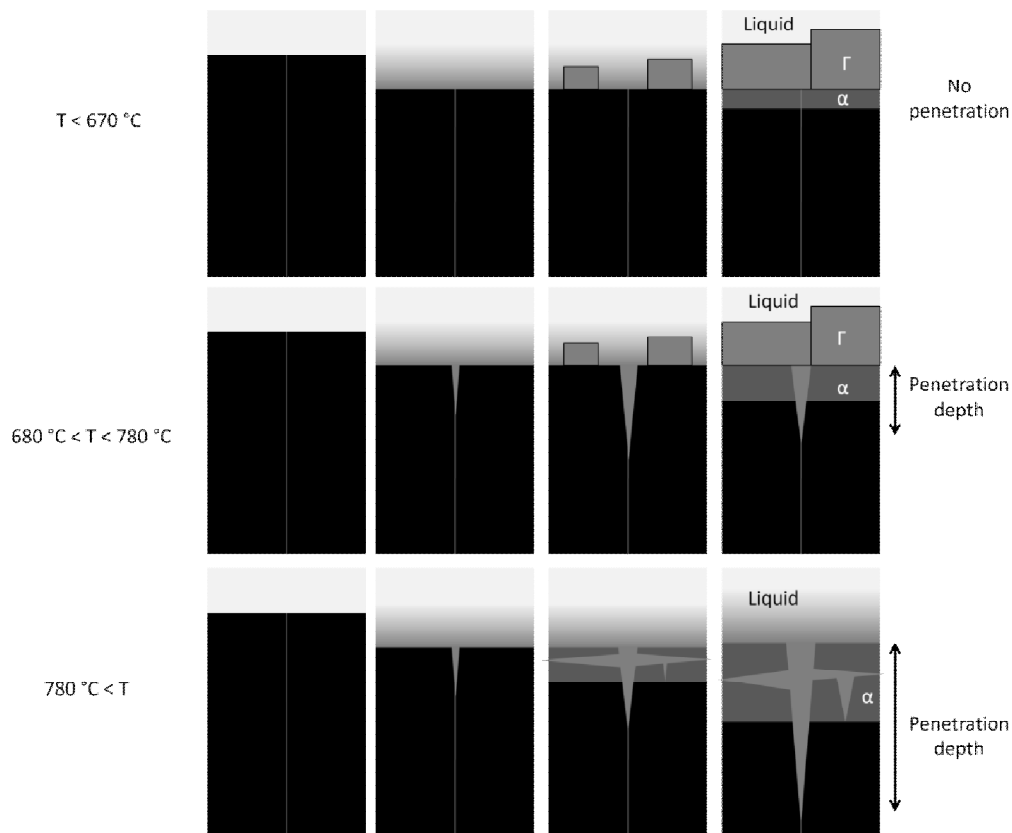


figure 82: Schematic representation of GB penetration occurring simultaneously to bulk reactions

So a GB wetting transition has been characterized for TRIP Si at the temperature, say

$$T_{wet} = (680 \pm 30) ^\circ\text{C}.$$

The definition of GB wetting transition described in the literature review to the TRIP Si microstructure at T_{wet} is applied, and cracks propagate in the ferrite/austenite boundary. So above T_{wet} , the interfacial energies are according to equation (14):

$$\gamma_{ferrite/austenite} > \gamma_{ferrite/Zn} + \gamma_{austenite/Zn}.$$

$\gamma_{ferrite/austenite}$ is the energy of the ferrite/austenite interphase boundary, $\gamma_{ferrite/Zn}$ and $\gamma_{austenite/Zn}$ are the interfacial energies of liquid Zn, respectively with the ferrite grain and the austenite grain.

One should now conduct an estimation of these interfacial energies. Data for the order of magnitude for GB energies have been found in modeling study of phase transformation [BOT1998][LOG2004][TON2004][THI2006][CHO2013]. Numerical values for $\gamma_{ferrite/austenite}$ are found between 0.2 J m^{-2} and 1 J m^{-2} . GB energies should decrease as temperature increases.

Concerning liquid Zn/solid iron or steel interfacial energies, no data have been found in the temperature range of interest. Data at lower temperature are only for intermetallic phases, or energies of « work of adhesion » used for galvanizing studies [SON2011]. The system under consideration, steel in contact with liquid Zn, is far from the macroscopic thermodynamical equilibrium. According to the Fe-Zn equilibrium diagram, the surface energy of a ferrite saturated with Zn and a liquid Zn saturated with Fe should be estimated from thermodynamical parameters. But, for examples, contact between austenite and liquid Zn, like between Zn-free ferrite and liquid Zn, is not described. The consequence of this discussion is that $\gamma_{ferrite/Zn}$ and $\gamma_{austenite/Zn}$ should be only investigated in a transient manner, i.e. with sufficiently low time to neglect bulk reaction.

Because no satisfactory data can be found, the hypothesis of a wetting transition cannot be validated with numerical values of interfacial energies. Direct measurements of surface energies at high temperature have been envisaged by liquid Zn droplet characterization on steel surfaces. But the experimental difficulties would not have allowed this investigation in this thesis study.

7.2. High temperature limit for crack propagation: Zn disappearing

The high temperature limit for the ductility trough has been found around 950°C , and almost constant for the three investigated steels and strain rates. It corresponds also to the temperature where apparent wetting depth drops to zero on tensile specimens. This has been attributed to Zn disappearing from the sheet surface. That is why an intrinsic ductility recovery due to the decrease of the mechanical strength of steel at high temperature does not seem to be the right explanation for the end of the ductility trough. Consequently Zn disappears from the surface at high temperature due to (i) the evaporation of Zn, (ii) the surface oxidation of Zn or Fe, or (iii) the predominance of the bulk reaction between Zn and steel (bulk dissolution of Zn in Fe). The EDX analyses show that the Zn total quantity detected at the steel surface is smaller and smaller when temperature increases. This is piece of evidence to show that the evaporation of Zn is the most probable hypothesis for Zn disappearing and the ductility recovery observed during tensile tests.

For $\Delta t = 0.5$ s, GB wetting is observed at higher temperature because Zn is still present at the surface. These results tend to show a kinetic dependence for Zn evaporation in the temperature range 900 - 1000 °C. Thus for extreme heating rate and strain rate, the high temperature limit of the ductility trough should be expected to be higher.

The following question remains. If a concentrated Zn environment could be maintained during tensile tests, would any high temperature limit for the ductility trough be observed? Designing a closed and tight compound to be adapted to the tensile specimen might be difficult, but possible. Nevertheless these experiments have not been conducted during the thesis study.

7.3. Understanding LME as time-dependent cracking

The presence of liquid Zn and GB wetting has been demonstrated to be the prerequisite for LME cracking. At this point of the study, these conditions define only the temperature range for LME. In this temperature range, LME cracking occurs during tensile tests for the experimental strain/stress conditions tested in the experimental section. The right criterion for the effective occurrence of LME cracking is discussed in this subsection. The following description is only valid for temperature in the ductility trough, i.e. in conditions of GB wetting.

7.3.1. A nucleation time

A critical stress for cracking?

Trying to find a criterion for LME cracking, the classical attempt is to investigate the existence of a critical stress, as it was made for example in [BEA2011]. A critical stress criterion is actually consistent if LME is analyzed in the frame of the brittle fracture theory. But several pieces of evidence show that LME cracking is not exactly brittle.

Figure 83 shows a compilation of tensile curves to compare material behavior at 850 °C. There are the three tests at different strain rates and also the two tests with imposed stress conditions. The curve for the highest strain rate was made at 780 °C. But the curve at 950 °C at this strain rate is practically the same. That is why the comparison from this curve at 780 °C and the other made at 850 °C is possible. In all these tests, specimens cracked abruptly and fracture surface are brittle. Consequently, failure of TRIP Si by LME is described by these five curves.

First, strain hardening is very low for low stress level (95 MPa, 103 MPa, 10^{-2} s⁻¹). Cracking occurs arbitrary after some time at a constant stress level. This is not consistent with a critical stress criterion.

Then, by comparison of the different curves, no apparent critical stress exists for cracking occurrence. Indeed if LME cracking appears at 95 MPa and if cracking is described by a critical stress, it should appear in the elastic domain for the higher stress conditions. This is not observed.

To finish, the dependence of the maximal elongation with stress is not monotonous as shown in figure 84. For very low stress (< 70 MPa) no LME cracking is observed. Above 80 MPa, maximal elongation first decreases as (flow) stress increases. But it becomes higher for very high stress (for the highest strain rate), indicating probably that ductility should be recovered for extremely high strain rate. In other words,

embrittlement characterized by the maximal elongation of the specimen is not more important at high stress level. Consequently, cracking occurrence and maximal elongation of tensile specimens are not satisfactory described by a critical stress criterion.

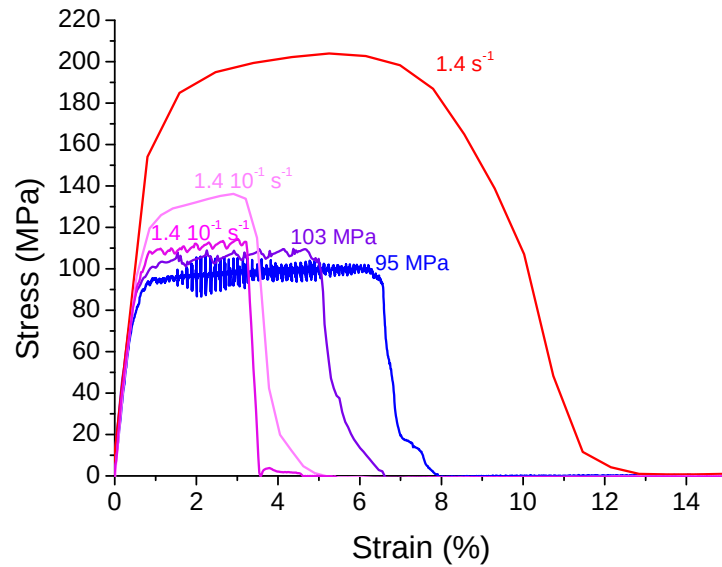


figure 83: Stress-strain curve at 850°C for coated TRIP Si with different straining conditions

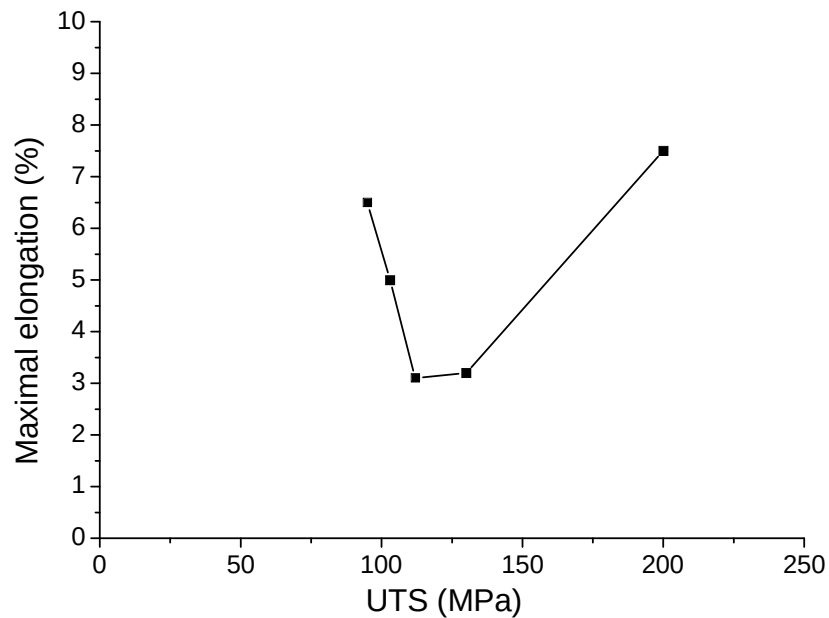


figure 84: Maximal elongation vs. UTS for TRIP Si at 850 °C. Embrittlement is not more important at high stress level experienced for very high strain rate

Stress dependence of the nucleation time

Figure 85 shows stress-time curve of the tensile experiments at 850 °C. The time to cracking decreases as stress level experienced during the tensile test increases. The monotonous stress dependence of this nucleation time is shown in figure 86.

It seems that the rigorous way to describe the apparent arbitrary cracking occurrence during plastic flow is to consider the stress-dependence of the nucleation time. This framework for the description of tensile test results was already synthesized in Glickman's paper "Mechanism of liquid metal embrittlement by simple experiments: from atomistic to life-time" [GLI2000].

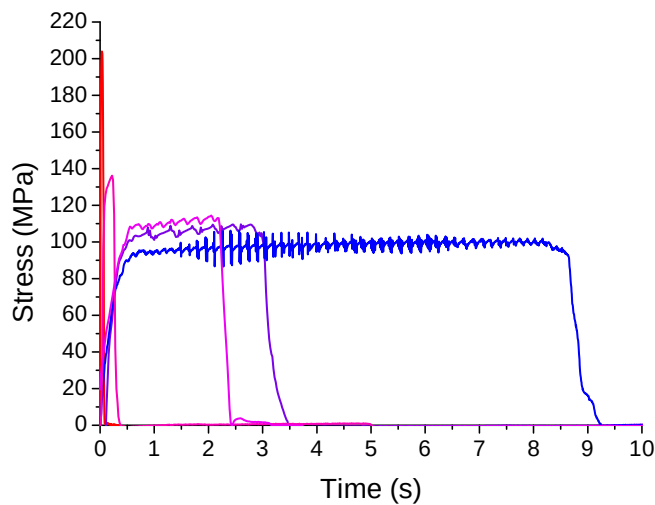


figure 85: Stress-time curve for Zn-coated TRIP Si at 850 °C showing a monotonous dependence of the time-to-failure with stress

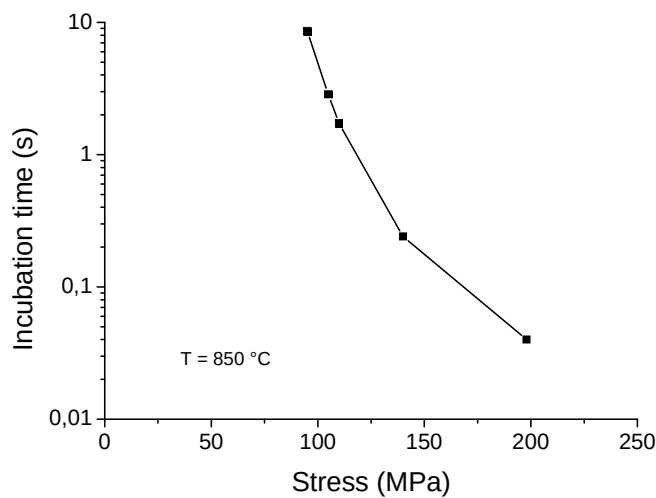


figure 86: Stress dependence of the time-to-failure by LME cracking for Zn-coated TRIP Si at 850 °C

Subcritical crack growth

Following several authors [GLI2000][LYN2008], an analogy between LME and other environmentally assisted cracking mechanisms can be drawn, in particular with stress corrosion cracking (SCC). In this framework the nucleation time involves subcritical crack growth. In the case of liquid metal cracking, it means that small cracks will grow during the incubation at several points from the steel sheet surface. This is in agreement with the observation of several secondary cracks on cross sections of tensile specimens. When one of them reaches a critical depth, fast LME cracking occurs. This description is drawn in figure 87.

The nucleation time has been characterized to be adequately described according to the stress level experience by steel during the experiment (figure 86). Further description of subcritical crack growth will be made in paragraph 7.4.2. Once the characterization of the nucleation time has been made (at 850 °C for TRIP Si steel), the cracking part of the tensile test is described in the paragraph below.

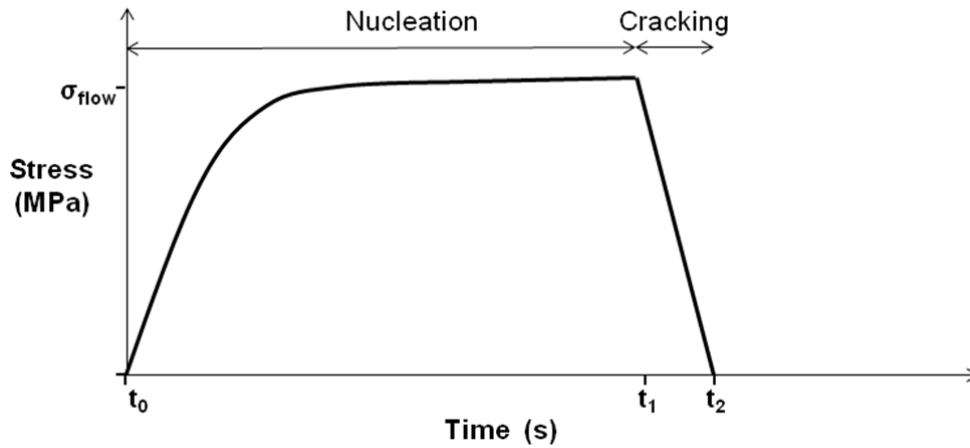


figure 87: Schematic description of the tensile test with LME cracking. Fast and dramatic cracking of the specimen occurs after a nucleation time

7.3.2. Crack velocity

The cracking path has been experimentally described by microscopic observations in section 5. Main result for TRIP Si is that crack propagates in austenite/ferrite interphase boundaries and in austenite/austenite grain boundaries. The characterization shows also that nanometer-thick Zn channels are present at the crack tip. The discussion on the very local, probably atomic-scale, mechanism of crack propagation is carried out later in the section 8.

Here a macroscopic estimation of crack velocity involved for liquid Zn cracking of TRIP Si is carried out. The failing crack surface at the end of the tensile test is $S = e_0 w_0$, if the reduction of section is neglected during plastic deformation. By neglecting subcritical crack growth, cracks is considered to entirely extent between t_1 and t_2 (figure 87). The crack velocity can be approached according to equation (28).

$$D_{crack} [m^2 s^{-1}] = \frac{e_0 w_0}{(t_2 - t_1)}$$

Table 11 gives the results at different temperatures for specimens tested in the ductility trough. The average velocity is about $2 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$, $5 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$ and $1.5 \cdot 10^{-4} \text{ m}^2 \text{ s}^{-1}$, respectively at $1.4 \cdot 10^{-2} \text{ s}^{-1}$, $1.4 \cdot 10^{-1} \text{ s}^{-1}$ and 1.4 s^{-1} strain rates. The D_{crack} value has the dimension D^2T^{-1} and can be considered as the “crack diffusivity”. This result can be compared, for examples, to the bulk, GB or liquid diffusion coefficients found for the Fe-Zn system (paragraph 2.3.3). It is several orders of magnitude higher than GB diffusion coefficient or diffusion coefficient in liquid Zn, which are both lower than $10^{-7} \text{ m}^2 \text{ s}^{-1}$ in the temperature range of interest.

Since tensile test is not dedicated to crack velocity measurement, and because of the high uncertainty, these results does not provide any direct information on the influence of the temperature on crack velocity. But differences between investigated strain rates are significant.

table 11: Crack velocity for the TRIP Si measured for temperature in the ductility trough for the three.
Uncertainty: $\Delta D_{crack}/D_{crack} = 50 \%$

Temperature (°C)	Strain rate (s ⁻¹)	10 ⁵ x D_{crack} (m ² s ⁻¹)
750	0.14	5.0
780	0.14	5.0
815	0.14	5.0
850	0.14	4.4
855	0.14	5.7
880	0.14	4.0
925	0.14	2.4
945	0.14	2.5
810	0.014	1.0
825	0.014	2.6
870	0.014	3.2
750	14	10
760	14	16
940	14	20

To find a one spatial dimension-crack velocity, D_{crack} need to be multiplied by one of the dimensions of the tensile specimen's section ($e_0 = 1 \text{ mm}$, $w_0 = 8 \text{ mm}$). The simplest is to choose the thickness of the steel sheet. The crack velocity is $2 \cdot 10^{-2} \text{ m s}^{-1}$, $5 \cdot 10^{-2} \text{ m s}^{-1}$ and $1.5 \cdot 10^{-3} \text{ m s}^{-1}$ respectively at $1.4 \cdot 10^{-2} \text{ s}^{-1}$, $1.4 \cdot 10^{-1} \text{ s}^{-1}$ and 1.4 s^{-1} .

The same measurements have been made for the two points with imposed stress conditions. Results are given in table 12 with comparison with imposed strain rate conditions. The stress (flow stress or UTS) dependence of crack velocity is plotted in figure 88. The crack velocity increases as imposed stress increases. Crack velocity is approximately one order of magnitude higher for 200 MPa than for 100 MPa.

table 12: Summary of crack velocity measurements

Imposed stress	Strain rate (s ⁻¹)	UTS or flow stress (MPa)	10 ⁵ x D_{crack} (m ² s ⁻¹)	10 ³ x V (m s ⁻¹)
-	0.014	110	2.0	20
-	0.14	140	5.0	50
-	1.4	198	15	150
95	-	95	0.80	8
103	-	103	1.6	16

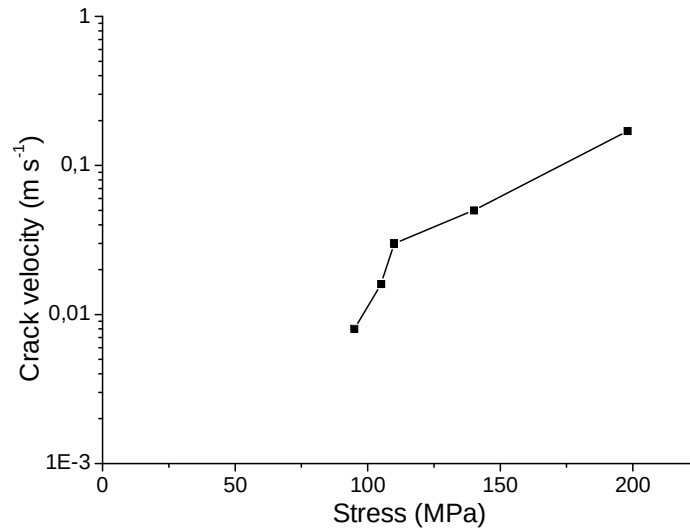


figure 88: Stress dependence of the crack velocity

In this paragraph, the crack velocity has been estimated from tensile curves. As carried out for the incubation time (figure 86), the crack velocity has been described as a function of stress level during straining. Our interpretation of mechanical characterization has given the framework for a rigorous description of tensile curves and a quantitative analysis of the incubation time at 850 °C and of average crack velocities experienced during liquid zinc cracking of steel.

In the next section these results are discussed further to link subcritical crack growth supposed to occur during the incubation time and crack velocity observed during failure of steel. A fracture mechanics analysis will be conducted even if uniaxial tensile test as performed in this study are not dedicated to this type of analysis.

7.4. Crack growth rate vs. stress intensity

When dealing with crack growth rate (subcritical crack growth during incubation time or fast crack propagation), one needs to characterize the stress intensity experienced by the material at the crack tip. It is well known in fracture mechanics that the stress intensity factor K_I is a relevant parameter to describe crack propagation as pointed out for example in [AND2005]. For brittle and quasi-brittle fracture, the tenacity K_{Ic} is assumed to be the relevant material properties to take into account, instead of the yield strength or the ultimate tensile strength. In this subsection the evaluation of the stress intensity factor K_I experienced at the crack tip is given. Then experiments at 850 °C will be further discussed to investigate if a threshold stress intensity factor $K_{I,th}$ describing LME cracking occurrence can be found.

7.4.1. Estimation of stress intensity factor involved in crack propagation

Some analytical model exists to calculate the stress intensity factor. Even if they are dedicated to brittle or quasi-brittle fracture, they can give an approximation in our study. In fracture mechanics handbook, like

Mukarami's example [MUK1987], the analytical solution for a single-edge notch tension panel, like in figure 89, is given:

$$K_I = \left[1.12 - 0.23 \left(\frac{d}{e} \right) + 10.56 \left(\frac{d}{e} \right)^2 - 21.74 \left(\frac{d}{e} \right)^3 + 30.42 \left(\frac{d}{e} \right)^4 \right] \sigma \sqrt{\pi d} . \quad (29)$$

Here d is the depth of the crack and $e = e_0 = 1 \text{ mm}$ is the thickness of the sheet.

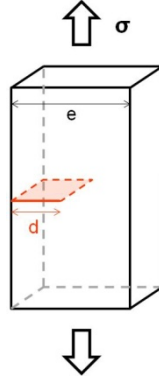


figure 89: Steel sheet of with crack analyzed as a single-edge notch tension panel

Figure 90 gives calculated values for K_I for different stresses using equation (29). The external stress σ is assumed to be representative of the flow stress of steels observed during tensile tests. Calculations have been made for stresses between 50 MPa and 250 MPa, which are in the range of stresses measured during tensile tests. The equation (29) describes imposed-stress conditions on a brittle material. In the present case plasticity is generalized and apparent stress decreases during crack propagation. That is why this equation is probably not relevant for high crack depth values.

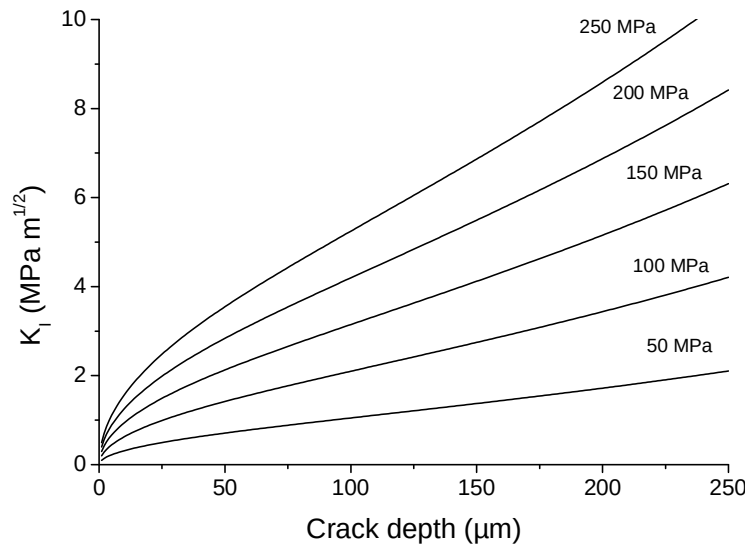


figure 90: Effect of crack depth on K_I using brittle fracture theory for different flow stress

As an element of comparison, a finite element (FE) model designed with the Comsol software is used to evaluate the plastic J-integral and the stress intensity factor. Details about this FE model and references for the software are given in Appendix 2. In this model a deformation is applied to the specimen containing a crack of depth d . 5 % has been chosen since it is roughly the strain to rupture found at 850 °C for TRIP Si (maximal elongation found between 3 % and 7 % at 850 °C). In this model the 5% deformation is held during cracking, while stroke increases during tensile tests. The difference between strain at t_1 (time where stress begins to fall) and t_2 (time where stress is zero) is assumed to be small enough to be neglected.

Figure 91 gives an example of results for K_I calculations. It has been obtained by modeling a perfectly plastic material with a flow stress of 160 MPa. K_I increases and stabilizes at a constant value when the crack depth reaches a value around 40 μm . Using this model K_I for the crack propagation through the steel sheet thickness is found around 2.3 MPa $\text{m}^{1/2}$ for 160 MPa flow stress. Several material behaviors with different hardening models were tested. In all cases, the stress intensity factor is in the range 1.8 and 2.4 MPa $\text{m}^{1/2}$ for a 160 MPa stress at 5 % strain.

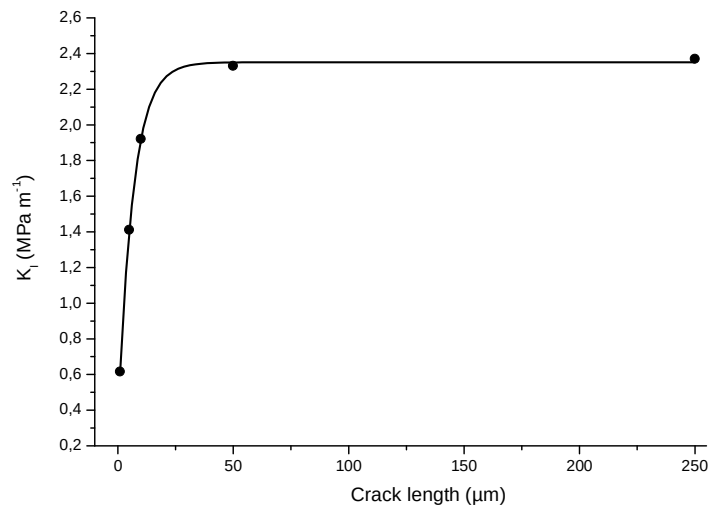


figure 91: Effect of crack depth on K_I with the static FE model. 5% strain and 160 MPa flow stress. Comparison with the analytical solution

Even if the absolute value of K_I should be questioned, this model is assumed to give a reasonable estimation for high crack depth. Because the analytical solution is easier to manipulate than the FE model, equation (29) is used to evaluate K_I for d comprised between 0 μm and 40 μm and K_I is assumed to keep constant for $d > 40 \mu\text{m}$. Using this method, critical value of K_I for LME cracking occurrence is quantified by analyzing the results obtained at 850 °C.

7.4.2. Building the V-K_I diagram at 850 °C

Threshold stress intensity factor

In this paragraph the existence of a threshold stress intensity factor $K_{I,th}$ at the crack tip is assumed. Below $K_{I,th}$ “slow” crack growth occurs. Above it, fast LME cracks propagates. Further interpretation of experiments made at 850 °C will be carried out to make an estimation of this threshold parameter.

Imposed stress conditions experiments at 850 °C have shown that LME cracking occurs for 95 MPa and at higher stresses but not for 77 MPa and lower stresses. The evolution of K_I at the crack tip for the experiments made at 850 °C has been drawn in figure 92 for crack depth up to 50 μm .

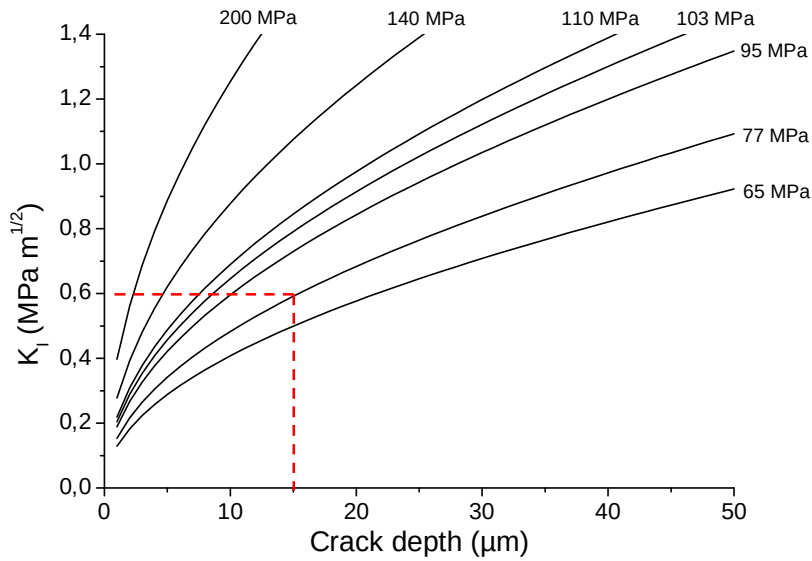


figure 92: K_I vs. crack depth for the experiments carried out at 850 °C

First, the stress intensity factor calculated at 95 MPa is enough for LME cracking occurrence since LME has been experimentally observed in this case. So $K_{I,th} < 1.3 \text{ MPa m}^{1/2}$ is characterized since it is the maximal value of K_I calculated for this experiment. Then, cross section observation of the specimens strained at 77 MPa has revealed several subcritical cracks. The maximal depth observed for these subcritical cracks is 15 μm , as shown in figure 93. The corresponding value for K_I on the curve calculated at 77 MPa is $0.6 \text{ MPa m}^{1/2}$. The threshold stress intensity factor is:

$$0.6 < K_{I,th} < 1.3 \text{ MPa m}^{1/2}.$$

Based on the hypothesis that a threshold stress intensity factor exists, the analysis of the mechanical results coupled with the estimation of the stress intensity factor as a function of crack depth leads to a reasonable estimation of $K_{I,th}$ for TRIP Si steel at 850 °C. In the next paragraph $K_{I,th} = 1 \text{ MPa m}^{1/2}$ is considered.

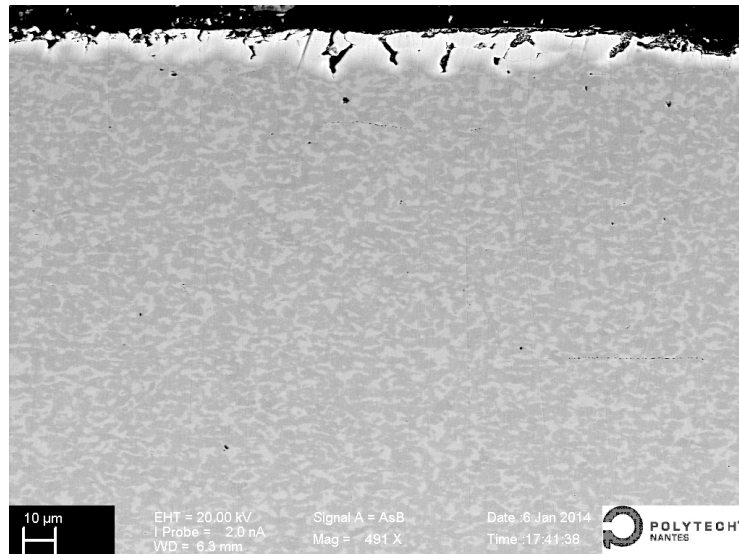


figure 93: Shallow surface cracks with depth < 15 µm. 850 °C, imposed stress = 77 MPa

Subcritical crack growth rate

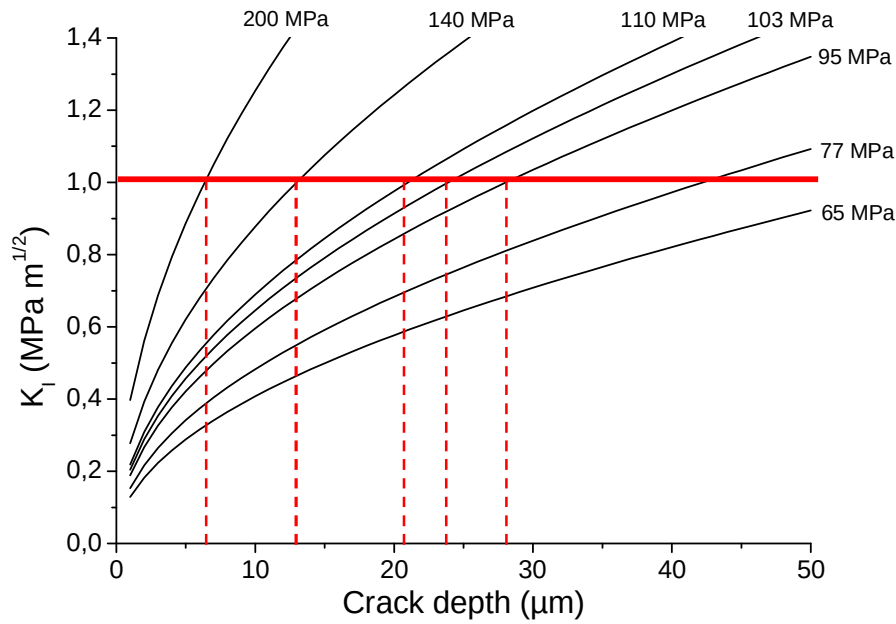
Knowing $K_{I,th}$ it is possible to determine a critical crack depth as a function of the imposed stress. $K_{I,th}$ is reached at the threshold depth d_c , as described in figure 94. The incubation time t_c to reach this critical depth has already been characterized (figure 86). Assuming that the subcritical crack growth rate is constant during the incubation time (this hypothesis is not true since the literature review has shown that GB penetration is extremely sensitive to imposed stress), the average subcritical crack growth rate V_I can be found:

$$V_I = \frac{d_c}{t_c}.$$

The numerical results are given in table 13. The results shows that subcritical crack grow rate increases as stress increases.

table 13: Calculations of the subcritical crack growth parameters for TRIP Si at 850 °C

Stress (MPa)	Critical depth d_c (µm)	Incubation time t_1 (s)	Subcritical crack growth rate (m s ⁻¹)
95	28	8.5	$3.3 \cdot 10^{-6}$
103	24	2.9	$8.3 \cdot 10^{-6}$
110	21	1.7	$1.2 \cdot 10^{-5}$
140	13	0.24	$5.4 \cdot 10^{-5}$
198	7	0.040	$1.8 \cdot 10^{-4}$


 figure 94: Critical depth determination for $K_{I,th} = 1 \text{ MPa m}^{1/2}$

Building the V-K_I diagram

In this paragraph a graphical representation of these results on a V-K_I diagram is given, as sometimes made in the literature for LME and SCC studies [GLI2003][LYN2008]. At 850 °C, for TRIP Si strained in contact with liquid Zn, the following information has been measured or calculated.

- The crack velocity, named here V_{II} , during fast LME crack propagation measured at five different apparent stresses. For one experiment at a given stress level, V_{II} is assumed to be constant when crack propagates through the steel sheet thickness.
- The subcritical crack growth rate, named here V_I , during the incubation time evaluated at five apparent stresses. For one experiment at a given stress level, V_I is assumed to be constant during the incubation time.
- The evolution of K_I as a function of crack depth and apparent stress

For V_{II} values, corresponding K_I values can be estimated by K_I values obtained for a crack depth of 50 μm. This is shown in figure 95. Indeed K_I is supposed to remain constant for crack depth higher than 50 μm. This parameter should be representative for the propagation of deep crack through the steel sheet thickness. The numerical values are given in table 14.

 table 14: V_{II} - K_I couples for the five experiments carried out for TRIP Si at 850 °C

Stress (MPa)	V_{II} (m s ⁻¹)	K_I (MPa m ^{1/2})
95	$8.0 \cdot 10^{-3}$	1.3
103	$1.6 \cdot 10^{-2}$	1.4
110	$2.0 \cdot 10^{-2}$	1.6
140	$5.0 \cdot 10^{-2}$	2.0
198	$1.5 \cdot 10^{-1}$	2.8

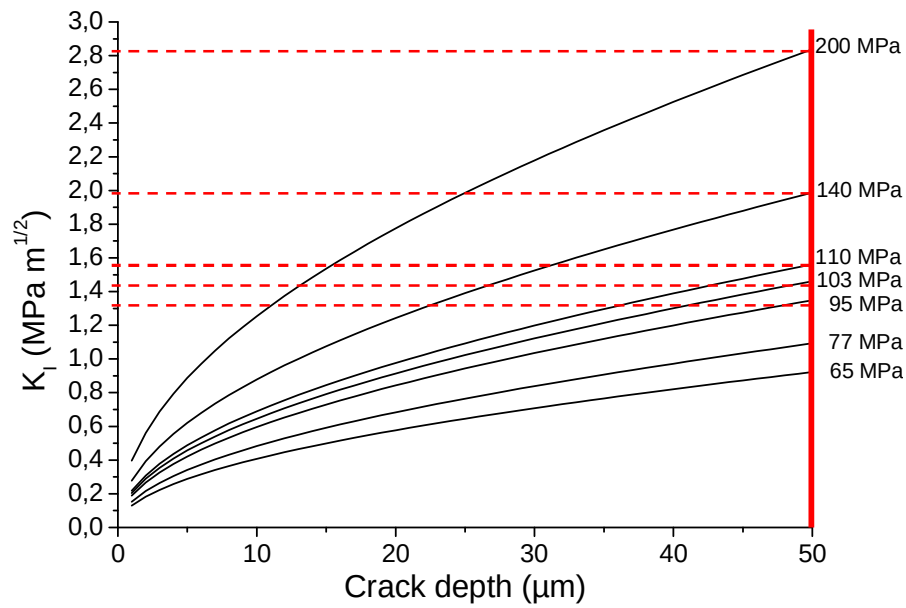


figure 95: Graphical determination of K_I associated with deep crack propagation, carried out at $d = 50 \mu\text{m}$

V_I is an average rate during the incubation time. A single equivalent K_I value characteristic of the incubation time needs to be considered (even if the growth rate should increase continuously as K_I increases). The K_I value at $5 \mu\text{m}$ is chosen to be representative. Indeed this depth inferior to the critical depth ($7 \mu\text{m}$) found for the higher stress level (200 MPa). Furthermore GB wetting depth ($< 3 \mu\text{m}$) has been found to be not influenced by stress (figure 71). That is why a value between $3 \mu\text{m}$ and $7 \mu\text{m}$ has been chosen. The K_I values corresponding to the incubation time for the different applied stresses are determined in figure 96 and summarized in table 15.

table 15: V_I - K_I couples for the five experiments carried out for TRIP Si at 850°C

Stress (MPa)	V_I (m s^{-1})	K_I ($\text{MPa m}^{1/2}$)
95	$3.3 \cdot 10^{-6}$	0.42
103	$8.3 \cdot 10^{-6}$	0.45
110	$1.2 \cdot 10^{-5}$	0.49
140	$5.4 \cdot 10^{-5}$	0.63
198	$1.8 \cdot 10^{-4}$	0.89

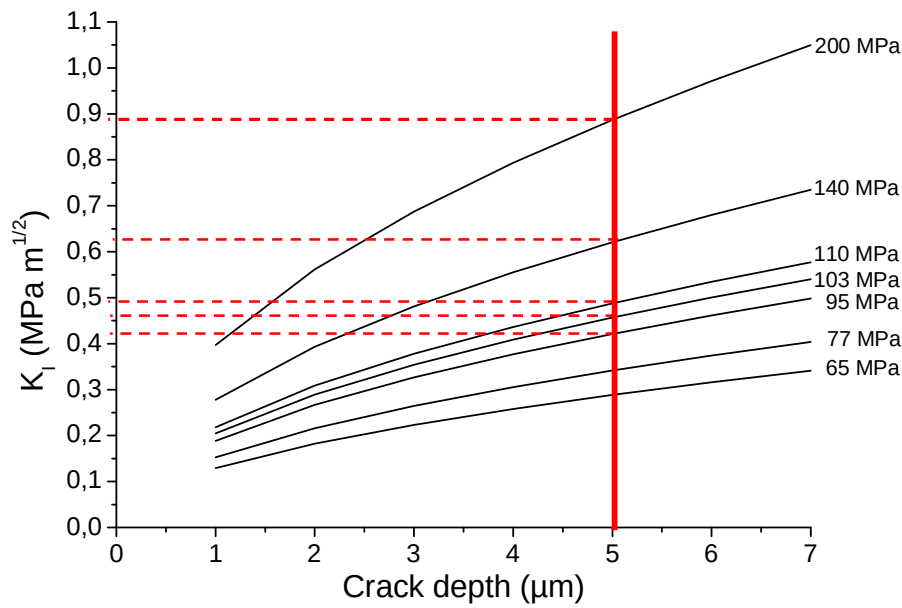


figure 96: Graphical determination of K_I associated with the incubation time, carried out at $d = 5 \mu\text{m}$

According to values summarized in table 14 and table 15, it is possible to draw a V-K diagram describing liquid zinc-assisted cracking of TRIP Si at 850 °C. The V-K diagram is shown in figure 97. One can see that this is consistent with reports for other SM/LM couples summarized in the Glickman's compilation of experimental results shown in figure 97. This diagram is also in reasonable agreement for $K_I = 0$ since GB penetration rate for holding at 850 °C of between $3 \mu\text{m s}^{-1}$ (for holding time of 0.5), and $0.4 \mu\text{m s}^{-1}$ (for holding time of 1800 s).

A threshold stress intensity factor has been considered to allow calculations. Below and above $K_{I,th}$, two different power laws (appearing linear on the log scale) have been plot. It seems that there is not such an abrupt modification of crack velocity. The experimental V- K_I diagram rather shows a continuous increase from $0 \text{ MPa m}^{1/2}$.

The rigorous way to describe LME cracking is the description of crack velocity as a function of stress intensity at the crack tip. This analysis permits to explain delayed fracture during tensile tests. The approximation of K_I made in this paragraph is very rough. As already pointed out, K_I parameter is usually used for brittle or brittle fracture. Furthermore modification of empirical expression of K_I can be found in fracture mechanics theory for very shallow cracks. This modification is supposed to be negligible since the FE model gives equivalent results to the analytical solution. The most important fact being neglected is as follows. Several cracks grow in the same time. The stress intensity is distributed on several cracks and K_I for each of these cracks should be lower than for a single crack in the specimen.

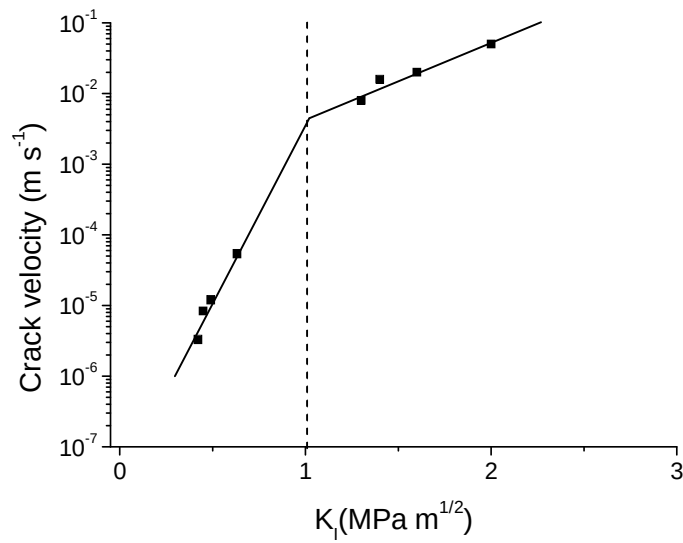


figure 97: Estimated $V-K_I$ diagram for the TRIP Si in contact with Zn at 850 °C

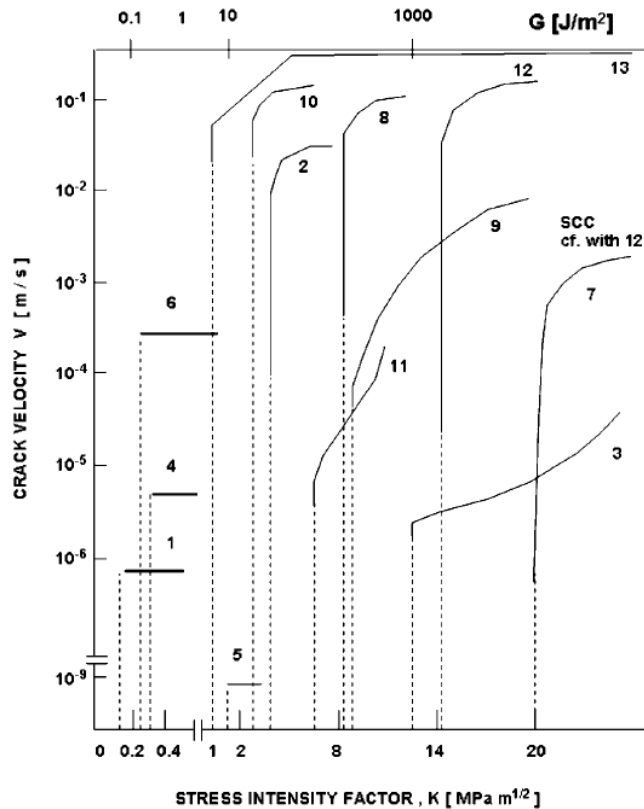


figure 98: V vs. K diagram for several SM/LM couple. Reprinted after [GLI2003]

Solid metals: 1-Cu 99.999; 2-5- α -brass; 6-Zn, single crystal; 7-Ti alloy 8Al-1Mo-1V; 8-Al alloy 1100-0; 9-Al alloy 6061-T651; 10-Al alloy 7075-T651; 11-Al, bicrystals; 12-Ti alloy 8Al-1Mo-1V, tested in 10 M HCl water solution, cf. with 7; 13-Al alloy 7075; 14-Al alloy 7075-T651. Liquid metals: 1: Bi; 2-10,13: Hg; 11:Hg +2%Ga. The driving force for crack extension G is estimated as $G \approx K^2/2E$ with E being the elastic modulus

8. Crack velocity explained by diffusion and wetting transition

After the literature review, the experimental characterization and the discussion of crack propagation kinetics, a tentative fundamental description of LME is described in this section. Indeed calculations detailed in Appendix 3 show that none kinetic model for crack propagation gives a correct estimation of velocities. Furthermore comments on the bibliographic information have demonstrated the several models are not satisfactory due to conceptual limitations.

Both penetration and cracking is supposed to occur only if GB wetting conditions are present. Furthermore a continuous evolution of crack growth rate with stress intensity has been found. As a consequence a strong link exists between what happens without stress, *i.e.* penetration, and with the application of external stresses, *i.e.* cracking. In other words, both penetration and cracking should be based on the same local mechanisms.

Even if the system under study is not a model one and if several approximations have already been made, a tentative coherent framework for the analysis of the occurrence of LME is built based on the following attempts.

- Description of GB wetting transitions for the steel-Zn system
- Assessment of GB penetration kinetics
- Discussion on the effect of stress

The complete framework and the rigorous vocabulary for description of wetting and wetting transition are addressed in recent reviews [CAN2013][KAP2013]. The wetting transition is assumed to describe the transition (no distinction between first order and critical transition) between a solid GB (fraction of an atomic monolayer of Zn segregated in the GB) to a disordered liquid-like complexion with negligible mechanical toughness. In other words no interest is taken into the equilibrium thickness of the liquid-like complexion. Indeed in the case of dynamic mechanism of crack propagation, the thickness of the GB channel after the complexion transition is not directed by equilibrium parameters, but by the mechanical crack tip opening.

8.1. Occurrence of LME: GB wetting transition

8.1.1. Influence of temperature and composition

According to the framework described in [CAN2013] and [KAP2013], figure 99 shows the metastable equilibrium diagram of the steel-liquid Zn system. Indeed, in the discussion above, bulk reactions and intermetallics formation have been neglected. The transient situation to be considered has been defined to be the contact between steel and a liquid Zn solution saturated (“equilibrated”) in Fe.

The GB wetting transition line has been added according the experimental result $T_w \approx 700$ °C. The bulk solubility of Zn in steel, which is supposed to be lower than in pure Fe, is indicated by solid black lines. In the solid part of the diagram, the red line (wetting transition locus) defines the GB solubility with a minimum

at the peritectic temperature as described for the Fe 5wt%Si – Zn system studied in [RAB1991] and already shown in the literature review (figure 26).

Figure 100 shows the GB adsorption (or segregation, or covering ratio, or GB thickness) as a function of the bulk chemical composition. Below T_w , the segregation is kept as a fraction of atomic monolayer. Above T_w , an abrupt change in GB thickness occurs for the blue curve (above T_w) and results in the formation of a disordered liquid-like GB complex. Its thickness diverges when approaching the bulk solubility (in the S+L part of the diagram above T_w , all solid grains are separated by a bulk liquid phase).

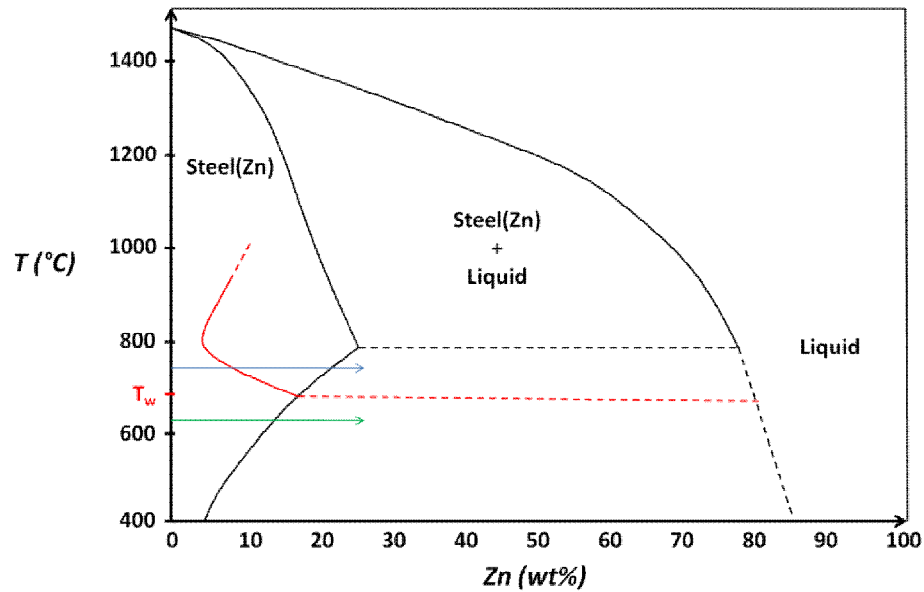


figure 99: Schematic representation of the metastable contact between steel and liquid Zn. The red line designates the locus of GB wetting transition. Two paths of approach to the bulk solubility are designated by arrows

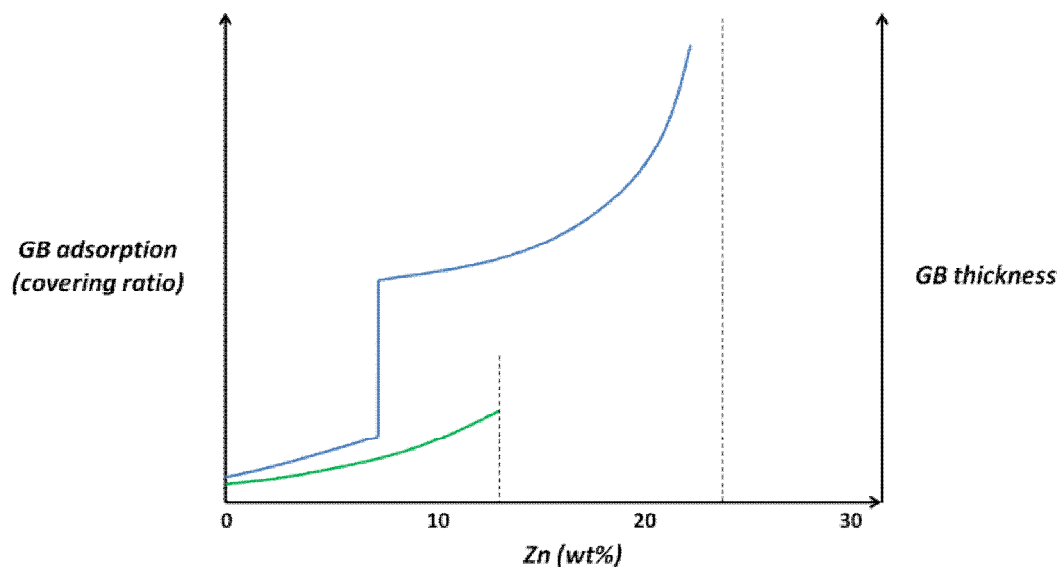


figure 100: GB adsorption behavior and corresponding thickness along the two paths identified in figure 99

8.1.2. About the influence of stress

The wetting transition can be described by analyzing the excess free energy of the GB as a function of thermodynamic parameters and functions (see references already cited). Since pressure is a basic thermodynamic parameter, it is reasonable to consider that it may have an influence on the wetting transition temperature. Experimental evidences of that can be found in [STR1996] where the influence of pressure on wetting transition in Fe-6wt%Si and Fe-12wt%Si bicrystals in contact with liquid is studied. Above T_w , perfect GB wetting is observed. Then, by increasing hydrostatic pressure, dewetting of the GB is observed. The dewetting pressures are in the range 400 – 900 MPa depending of the GB boundary misorientation. The interpretation is that GB energy, solid/liquid interfacial energy, and consequently GB wetting transition temperature, are functions of the pressure. GB wetting transition temperature increases as pressure increases. For example, the wetting transition temperature increases from 750 °C to 900 °C by increasing hydrostatic pressure from 0 MPa to 900 MPa. So the slope of the curve in the Temperature-(compressive)Stress diagram is $0.17\text{ }^{\circ}\text{C MPa}^{-1}$, as shown in figure 101 with $T_w(0\text{ MPa}) = 700\text{ }^{\circ}\text{C}$. It is also reasonable to admit that tensile stresses are probably able to decrease the GB wetting temperature, even if uniaxial stresses do not probably have the same influence than isostatic stresses. This point would need further discussion. The curve for the pressure influence on T_w has nevertheless been extended for illustration in the positive tensile stress.

Tensile strength of investigated steels (figure 43) as a function of temperature has been plotted in the diagram. According to the graphical reading, a decrease of T_w around 40 °C may be expected due to the action of tensile stress. This fact has not been experimentally observed since the wetting transition temperature has been characterized between 650 °C and 700 °C for tensile specimens and in unstressed specimens (figure 72). The uncertainty from the experimental value of T_w does not permit to see if the expected decrease is present or not.

The discussion of this paragraph shows that low strength of steels at high temperature does not induce any significant changes in wetting temperature during the tensile experiment compared to the hypothesized equilibrium situation. It means that in the present case, temperature is the main parameter for wetting transition definition. Then stress just permits crack propagation after wetting, as explained in the tentative description of a local mechanism of propagation in the paragraph below.

This paragraph just point out that it could be envisaged for hard solid metal that the wetting transition temperature will be induced under the action of stress during a tensile experiment at a temperature significantly lower than the equilibrium (zero stress) wetting transition temperature. As a consequence, it is nevertheless possible to envisage that, for hard material, temperature range of embrittlement is not correlated to the temperature range of wetting and penetration in external-stress-free experiments.

Even if this discussion is out of the scope of this experimental study and only qualitative, it is interesting to see that LME analyzed in terms of GB wetting probably permits to link what is called in the literature “corrosion-like” or “diffusive” LME, and LME resulting in the reduction in strength of brittle material.

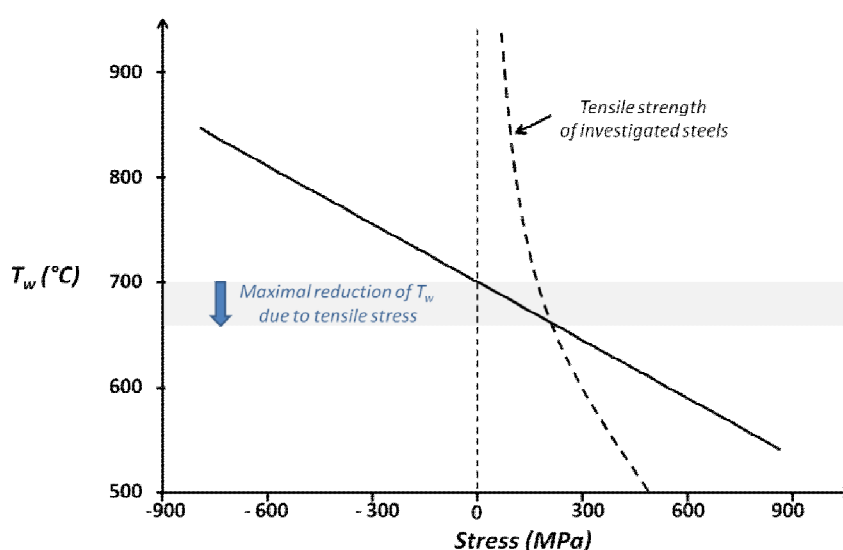


figure 101: Influence of stress on the wetting transition temperature. For an illustrative purpose, uniaxial stress has been plot on the same graph than isotstatic pressure. They have been assumed in this here to have the same influence on temperature

8.2. Kinetics of GB penetration

Because a model for LME crack propagation should agree with stress-free penetration kinetics, this paragraph shows that GB complexion can explain fast penetration rate of LM along GBs.

A very simple 1D finite element model of diffusion (with the COMSOL software introduced in appendix 3) has been used to evaluate the effect of grain boundary complexion. Without complexion, GB diffusivity of Zn at 850 °C is around $10^{-11} \text{ m}^2\text{s}^{-1}$ in Fe-5Si (figure 24). Figure 102 gives penetration profiles for $D = 10^{-11} \text{ m}^2\text{s}^{-1}$ up to 100 s.

According to the GB complexion theory, at a critical concentration the GB can experience GB complexion transition, from a monolayer adsorption to bilayer or nanometer-thick film. The diffusivity after complexion is close to liquid-type diffusivity. Thus GB diffusivity increases typically by two orders of magnitude (see section 1.2.). The figure 103 shows the results of the model for $D = 10^{-11} \text{ m}^2\text{s}^{-1}$ before complexion transition and $D = 10^{-9} \text{ m}^2\text{s}^{-1}$ after. The complexion transition occurs for . The penetration profile shows a high diffusivity slope and a low diffusivity slope, as characterized by Rabkin, et al. [RAB1991] (see figure 25).

The figure 104 shows the comparison for the penetration depth, with the complexion transition occurring at 850 °C for $\phi = 0.3$. The apparent (total) diffusivity of the GB experiencing a complexion transition is in the order of the diffusivity after complexion. The fit of the curve with GB complexion ($D = 10^{-11} \text{ m}^2\text{s}^{-1}$ before complexion, and $D = 10^{-9} \text{ m}^2\text{s}^{-1}$ after) gives an apparent diffusivity $D_{\text{eff}} = 2 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$.

The liquid-like diffusivity of complexed GBs seems able to explain the penetration kinetics described in the literature. A literature survey would be needed to validate this point by making the comparison of , existing data for “solid” GB diffusivity and liquid diffusivity for the considered couple on one side, and

penetration rate on the other side. With or without complexions, this discussion does not readily explain the observation of linear kinetics that has sometimes been made in the literature. But, as pointed out in the review, linear kinetics are probably explained by the influence of channel opening due to external, internal, or GB diffusion-induced stresses. The influence of stress, stress intensity factor on crack opening is described in paragraph below.

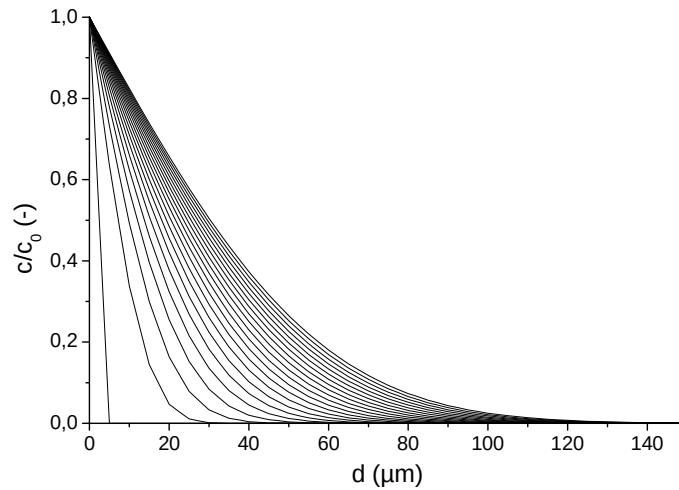


figure 102: Concentration along GB between $t = 0$ s and $t = 100$ s. Time step: 5 s

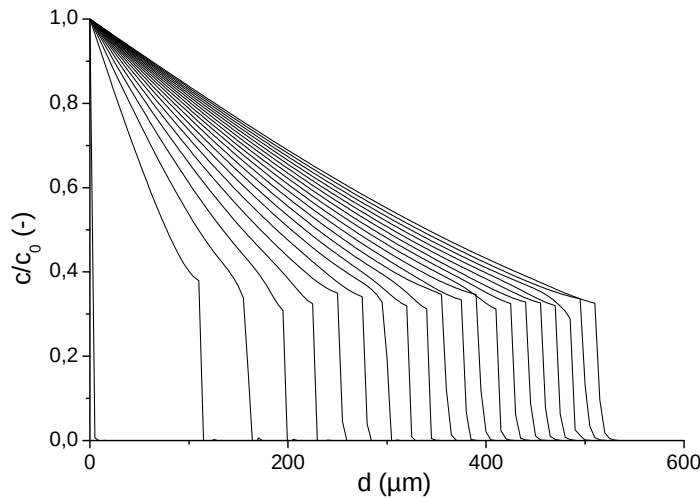


figure 103: Concentration along GB between $t = 0$ s and $t = 100$ s with GB complexion. Time step: 5 s

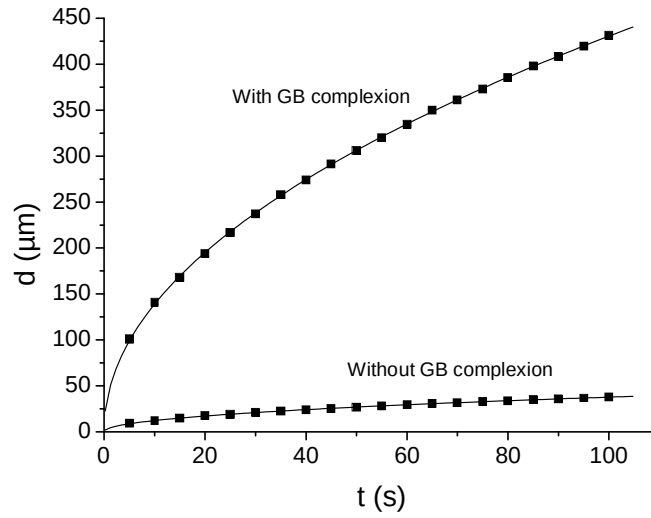


figure 104: Time dependence of the penetration depth for $c_{gb} = 0.3$ without GB complexion ($D = 10^{-11} \text{ m}^2\text{s}^{-1}$) and with GB complexion ($D = 10^{-11} \text{ m}^2\text{s}^{-1}$ before complexion, and $D = 10^{-9} \text{ m}^2\text{s}^{-1}$ after)

8.3. Crack propagation

The two paragraphs below show how diffusionnal kinetics of penetration is sufficient to explain crack propagation rate, at the condition that the GB complexion appearing for $c/c_0=0.3$ has a negligible mechanical resistance. It is demonstrated following two approaches that diffusive kinetics in the order of $10^{-9} \text{ m}^2 \text{ s}^{-1}$ can explain crack velocity of $10^{-2} \text{ m}^2 \text{ s}^{-1}$.

8.3.1. Constant diffusion profile of Zn along the GB ahead of the crack tip

Here crack tip propagation at a constant rate $V_y \text{ (m s}^{-1}\text{)}$ is considered. Ahead of the crack tip a GB diffusion profile exists. The definition of the flux is expressed in an analog manner than for a constant regime of diffusion, i.e. in the stationary situation for the crack tip associated with crack propagation at constant velocity:

$$J = -D_{GB} \frac{\partial C}{\partial y} - VyC,$$

$$\text{and } \frac{dC}{dt} = -\frac{dJ}{dy} = 0.$$

It leads to the following equation:

$$-D_{GB} \frac{\partial^2 C}{\partial^2 y} - V \frac{\partial C}{\partial y} = 0.$$

The solution of is as follows :

$$\frac{c_{GB}}{c_0} = \exp\left(-\frac{Vy}{D_{GB}}\right).$$

At 850 °C, $D_{GB} = 2 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $V = 10^{-2} \text{ ms}^{-1}$ what yields to

$$\frac{c_{GB}}{c_0} = 0.3 \Leftrightarrow y = 240 \text{ nm}.$$

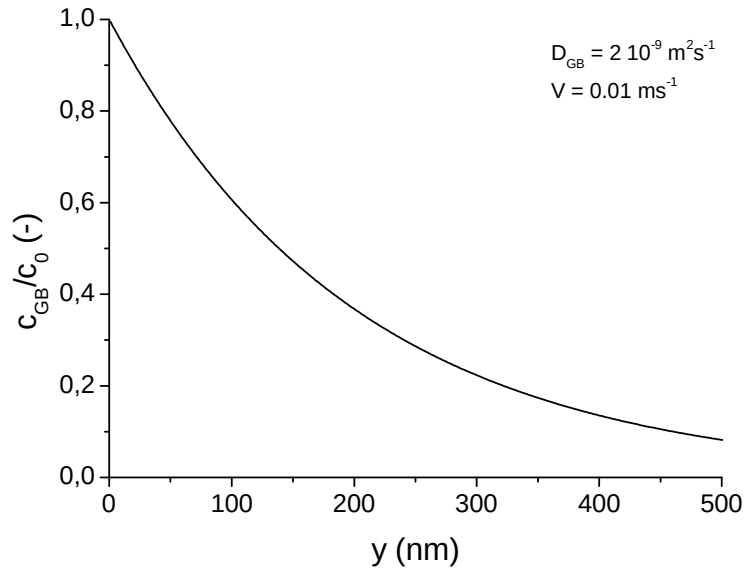


figure 105: Constant diffusion profile of Zn concentration along the GB ahead of the crack tip during propagation

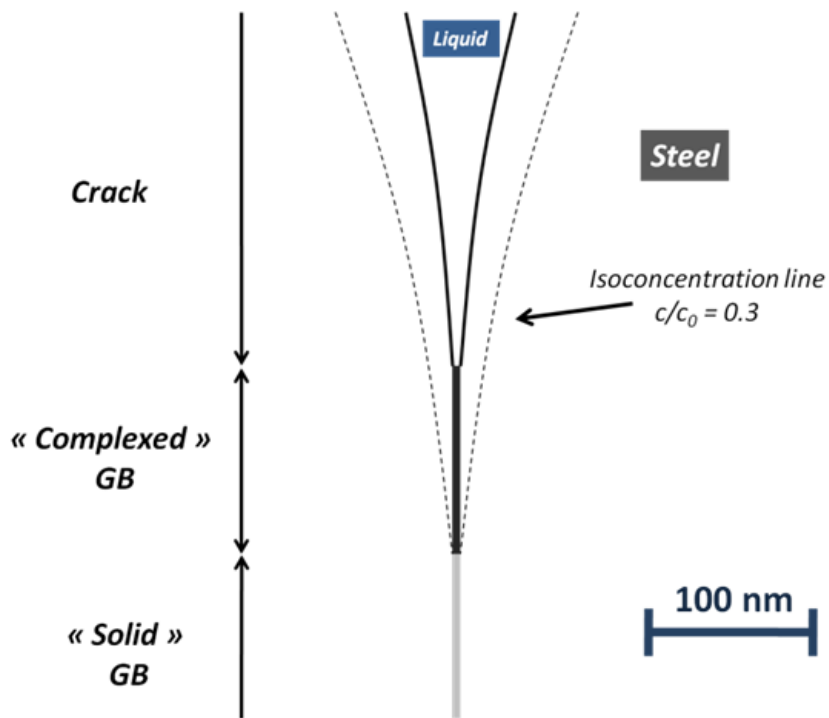


figure 106: Schematic representation of the crack tip during crack propagation

Other way to find an elementary step for crack propagation

The early stage of GB diffusion, i.e. the beginning of the penetration depth-time parabolic curve, can be fitted as high linear kinetic. The time step that corresponds to the measured crack velocity need to be identified. The root mechanism is simply GB diffusion. The penetration profile after GB diffusion, taking into account grain boundary complexion, determined for $c = c_b$ can be approximated to

$$d = \sqrt{D_{eff}t} \quad (30)$$

D_{eff} is an effective GB diffusion coefficient in the apparent diffusion coefficient after complexion. After derivation, it comes

$$\frac{dd}{dt} = \frac{\sqrt{D_{eff}}}{2\sqrt{t}} \quad (31)$$

$\frac{dd}{dt}$ is the crack velocity following pure diffusive kinetic. The time t for which this “diffusive velocity” is equal to the linear (constant) crack velocity is determined:

$$\Delta t \leftrightarrow \left(\frac{dd}{dt} \right)_{t=\Delta t} = V \approx 0.01 \text{ m s}^{-1}.$$

D_{eff} is fitted on the penetration profile (figure 104): $D_{eff} \approx 2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. According to equation (31), the elementary time step for crack propagation is given by

$$\Delta t = \frac{D_{eff}}{4V^2}. \quad (32)$$

The equation (32) gives $\Delta t = 5 \mu\text{s}$. With this value Δt , the equation (30) gives $(\Delta d)_{c_{GB}=0.3} = 100 \text{ nm}$. That means that a process zone exists with a depth of tens of nanometers, at the crack tip where GBs experience high concentration of Zn after GB diffusion, GB wetting transition and crack propagation, as shown in the figure 107.

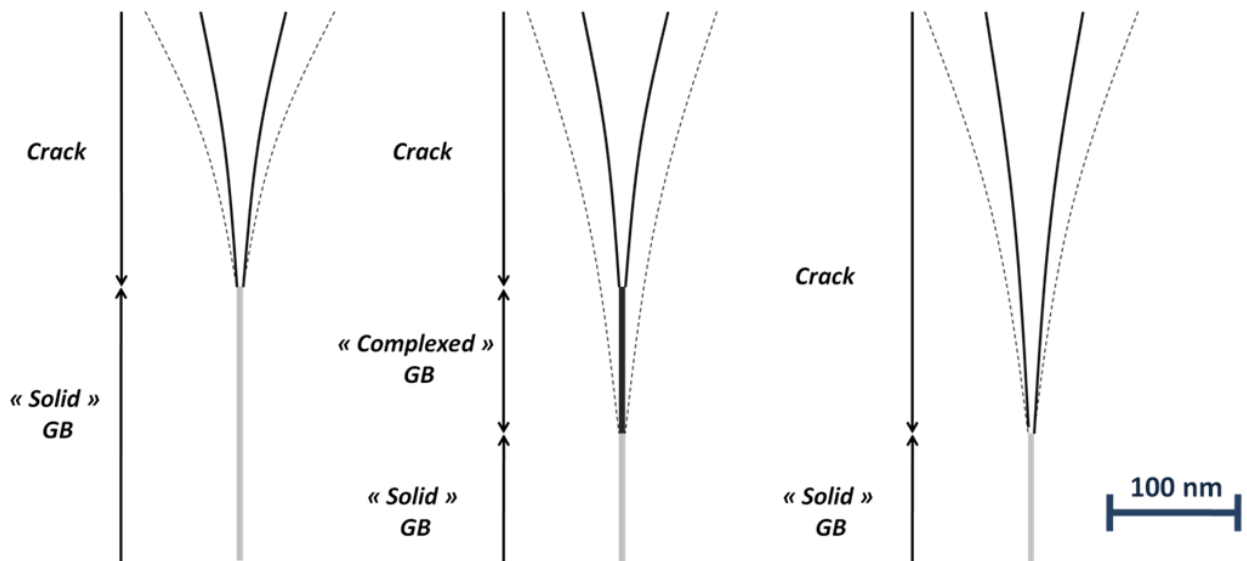


figure 107: GB diffusion-complexion model for crack propagation. 6 μs from left to right panel

8.4. Crack tip opening effect of stress

So even for fast crack propagation, a diffusion profile that may induce wetting and embrittlement of the grain boundary over a distance of tens of nanometer has been calculated. This is supposed to be the root mechanism for embrittlement and crack propagation.

Tensile stress at the crack tip has the effect to open the GB channel. In the frame of fracture mechanics, crack tip opening displacement (CTOD) refers to the opening of the crack as typically described in figure 108. In the simple case of plain strain conditions with non-hardening material, it can be derived from

$$CTOD = \frac{K_I}{E\sigma_y}.$$

For steel under investigation at 850 °C, typical parameter values are $\sigma_y = 200 \text{ MPa}$ and $E = 50 \text{ GPa}$. The evolution of CTOD with K_I is shown in figure 108. The order of magnitude of the CTOD seems in agreement with microstructural characterization (paragraph 5) as summarized as the typical crack geometry shown in figure 109, even seems if the definition of the criterion (figure 108) is difficult to apply here.

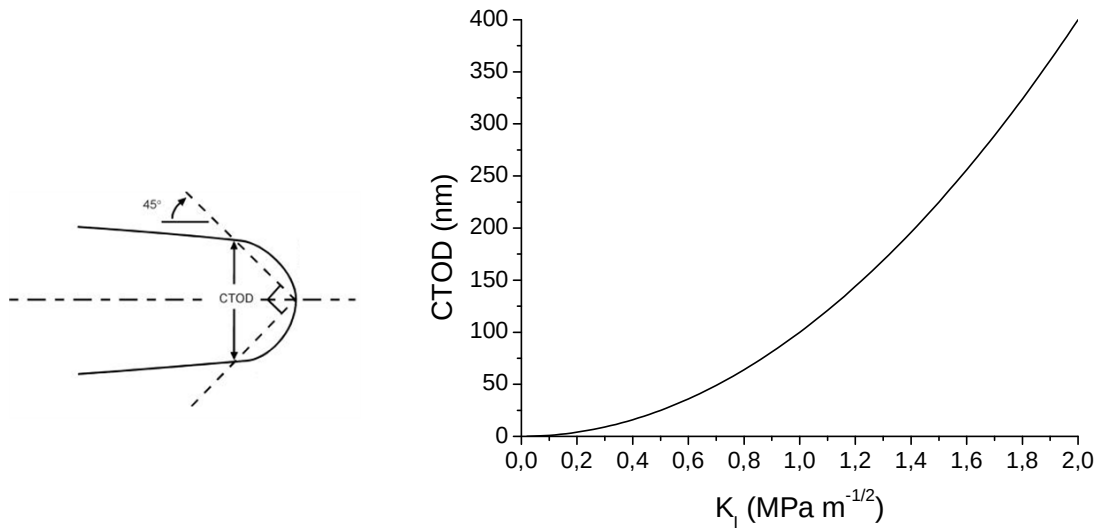


figure 108: Typical description of the CTOD in fracture mechanics (left) and CTOD vs K_I for the investigated steel at 850 °C

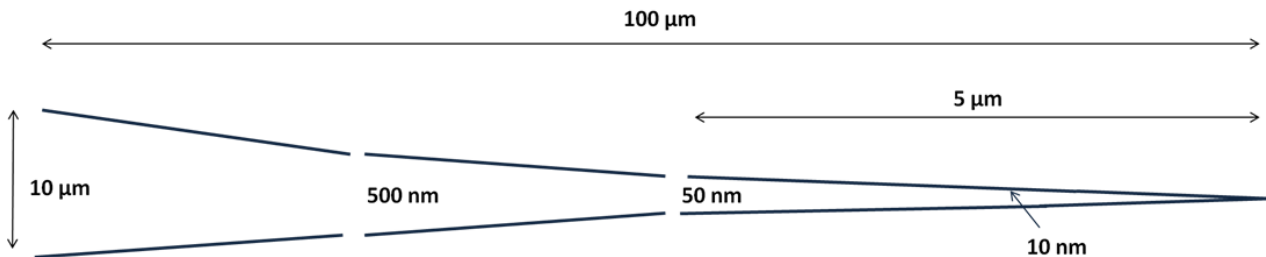


figure 109: Typical geometry of the crack according to microstructural characterization

Even if absolute values for the CTOD need probably to be corrected to capture the behavior of the material, it is an interesting indicator. It shows that, when K_I is low, the CTOD is nanometric, in the range of 10 nm or less. In such small channel, it is possible to consider that Zn transport to the crack tip is achieved by a diffusive mechanism, (complexed) GB diffusion or liquid-like diffusion, as modeled in paragraph 8.2. As K_I increases, the channel opening increases in the micrometric range (0.1 – 1 μm), the dynamic process of channel opening of this width may avoid the diffusive limitation. Zn may be transported not by diffusion, but according to a second regime which is supposed to be liquid flow, convection, or capillarity. This is supposed to be the main reason for the increase of the crack velocity for $K_I < 1 \text{ MPa m}^{1/2}$.

The interpretations of experimental results have described a second slope on the V- K_I diagram above a threshold value. Here a modification of the controlling mechanism is supposed. Since crack opening is sufficient to allow very fast Zn transport to the crack tip, the limiting mechanism should be the embrittling reaction at the crack tip itself. As described in paragraph 8.3, this is supposed to occur by grain boundary diffusion ahead of the crack tip and consecutive GB wetting transition that decrease GB cohesion to zero. The depth of the embrittling zone during propagation was estimated in the order of 100 - 300 nm. The meaning of the kinetic limitation is probably associated to this distance. Is there a minimal distance ? Is that linked to any steel microstructural parameter? This is an open discussion for further work.

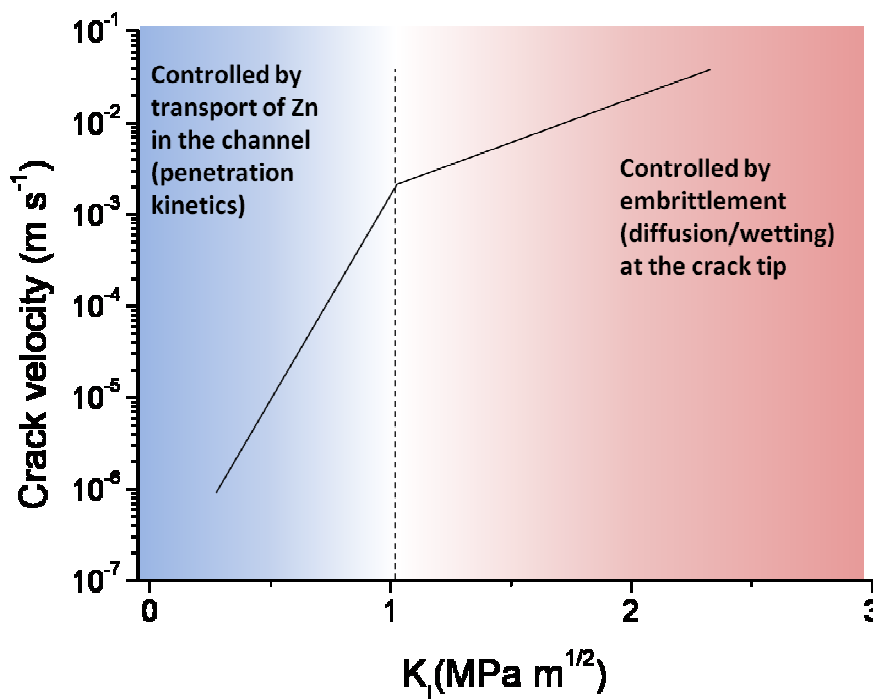


figure 110: Schematic representation of the V-K diagram considering the influence of crack opening on the different regimes of propagation

9. Conclusion and outlook

This study has described the occurrence and mechanisms of liquid zinc embrittlement for three AHSS. It has been shown that the steel/Zn couple is susceptible to LME as follows.

- A drastic loss of ductility has been observed between 700 °C and 950 °C. A ductility trough is observed for the maximal elongation on the Elongation-Temperature diagram. By comparison with bare steel specimens, the mechanical behavior is unchanged between the melting point of Zn and the beginning of the ductility trough and at very high temperature.
- Maximal elongation, in the order of 40 – 50 % for bare steel, is decrease to 5 – 10 % for Zn-coated specimens. This residual ductility seems to be constant (stays very low compared to the ductility of bare steel) in the temperature range of embrittlement. The residual ductility may vary from one grade to an other.
- The high temperature for the ductility trough corresponds to situation where no Zn is kept at the surface of the sheet, probably after vaporization.
- The low temperature for the ductility trough is described as a wetting transition temperature. It may vary from one grade to an other.

These results show also the « slow » kinetic character associated to cracking (compared to fracture of brittle material).

- Fracture cannot be described by a critical value of stress or strain.
- The incubation time before fracture (life-time) decreases as applied stress increases.
- Cracking velocity associated to fracture is measured between 10^{-2} et 10^{-1} m s⁻¹.

LME cracking seems to be close to stress corrosion cracking (SCC). Stress intensity factor has been estimated as a function of crack depth and applied stress. According to a non-conventional method for the interpretation of tests carried out at 850 °C, crack grow rate during the incubation time has been estimated. The description of crack velocity as a function of the stress intensity factor seems to be an effective way to describe LME cracking in the steel/Zn system at high temperature.

The beginning of the ductility trough, at (690 ± 20) ° C for TRIP steel, is not correlated to the melting point of Zn, or to the melting of other Fe-Zn intermetallics. Penetration (wetting) of steel GB has been observed above (680 ± 50) °C for TRIP Si steel. The correlation between these two phenomena seems to be strong. Literature review shows that rapid penetration of liquid metal should be observed above the wetting transition temperature of the investigated system. It is described by the comparison of liquid/solid interfacial energy and GB energy. That is why embrittlement is directly correlated to grain boundary wetting.

.This shows that basic mechanisms for penetration (no external stress) and embrittlement are the same. For a tentative description of local mechanism of crack propagation, several hypotheses have been made.

- Above the wetting transition temperature, GB structure is changed when Zn concentration, which increases through GB diffusion, reaches the solubility limit of the GB.

- Kinetics of rapid intergranular penetration can basically be explained by the high diffusivity after its structural transition, typically two orders of magnitude higher than the « solid » GB.
- The structure of the GB after transition has a negligible mechanical strength.

Calculations show that a diffusion profile of non-negligible depth exists ahead of the crack tip during fast crack propagation. The solubility limit of the GB is reached over typically 100 nm. According to the hypotheses above, this area is embrittled. This embrittled zone drastically decreases the toughness of the material and is assumed to be the basic reason for the embrittlement.

The major difference between stress-free penetration and cracking is that penetration is controlled by the transport of Zn along the penetration channel according to diffusive kinetics, while Zn fills crack by liquid flow (or capillarity). During penetration the source of LM atoms is maintained at the surface of the specimen, while it follows the crack tip during cracking. LME and high cracking velocity can be explained by GB diffusion and structural transition.

The difference between steel grades will be summarized at the end of the manuscript.

Several limitations exist for these results and their interpretation. Some of them are explained by the extreme complexity of materials under study.

- Influence of alloying elements on the Fe-Zn equilibrium has not really been taken into account.
- Bulk dissolution and reactions have been neglected.
- Interphase boundaries have been classed as symmetric ferrite grain boundaries.

Several quantitative results need to be more rigorously addressed.

- GB wetting depth, a function of temperature, need to be measured with lower uncertainty, and for the three grades.
- Systematical investigation of chemical composition of the coating, associated with crystallographic characterization (electron backscatter diffraction), may address the issue of the influence of intermetallic compounds.
- The temperature dependence of penetration at a constant time has been characterized. The time dependence should also be extensively studied to be discussed.
- Better model for stress intensity factor and crack tip opening displacement should be used.

The wetting transition at 680 – 690 °C has been identified after a logical analysis but has not been observed. The observation of a complexed GB after such kind of wetting transition is probably possible through high resolution transmission electron microscopy.

Investigating further kinetics of crack grow rate appears as a major outlook. For a test at constant imposed stress, arrested experiments should be carried out with the systematic measurement of crack depth. The crack grow rate would by this way be characterized precisely and without doubt.

The expression of the modeled mechanism of crack propagation, based on GB diffusion/wetting transition/crack opening, should be worked further.

- What is the influence of the size of the embrittled zone at the crack tip? What is it linked to?

- In this frame, is it possible to find a single equation to link
 - o cracking velocity,
 - o diffusion coefficients (GB, complexed GB, liquid),
 - o GB solubility limit,
 - o stress intensity factor or crack opening displacement ?

As a validation of this model, study on model material need to be carried out, for example on pure Fe-Zn or Fe-5Si alloy (already investigated by Rabkin, Straumal and coworkers). The method consisting in systematical comparison of stress-free penetration and cracking under external stress seems to be relevant. A bibliographic review of experimental data on model systems such as Al-Ga, Cu-Bi or Ni-Bi is probably needed.

Chapter II Surface cracking during RSW

The previous chapter has given the description of the occurrence of liquid Zn embrittlement of steels. Since resistance spot welding involves high temperature and deformation, the correlation is a priori evident between surface cracks detected in spot welds and the conditions of occurrence characterized in the 0. This chapter wants to quantify the occurrence of surface cracks (depth, frequency, localization in the weld, etc.) depending on the process parameters (current, force, time,...) and weld attributes (size, geometrical feature).

After introducing basics of RSW and weld characterization, two innovative methods for welding characterization are described: surface temperature measurement by infrared thermography and high speed camera monitoring of electrode displacement. The results for weld characterization (weld size, temperature, indentation) and the correlation with cracking extent in spot weld is given. The discussion of the influence of strain and stress is carried out and a description of the probable scenario for surface cracking during RSW is given.

1. Basic notions about resistance spot welding

1.1. Principle

1.1.1. Heat production

RSW involves Joule effect when a high current flows, in a concentrated manner, through the metal parts to be welded. Fundamentals of the process are summarized for example in [MIL2012]. A French language introduction to RSW can be found in [CAZ1993][DUP2000][CLA2005]. One can roughly estimate the heat Q produced during the welding cycle, i.e. heat input, by [CAZ2000]

$$Q = \int_0^{t_w} RI^2 dt. \quad (33)$$

Here R is the total electrical resistance of the assembly, I is the welding current intensity, t_w the welding time. Electrical continuity of the assembly is achieved through the application of a force F to keep steel sheets in contact. Usually high heat input leads to metal melting. RSW has the special feature that melting occurs internally at the interface between the steel sheets. Figure 111 gives a schematic representation of the homogeneous RSW of two steel sheets. The term “homogeneous” refers to the symmetric welding of two identical steel sheets (steel grade, composition, coating and thickness).

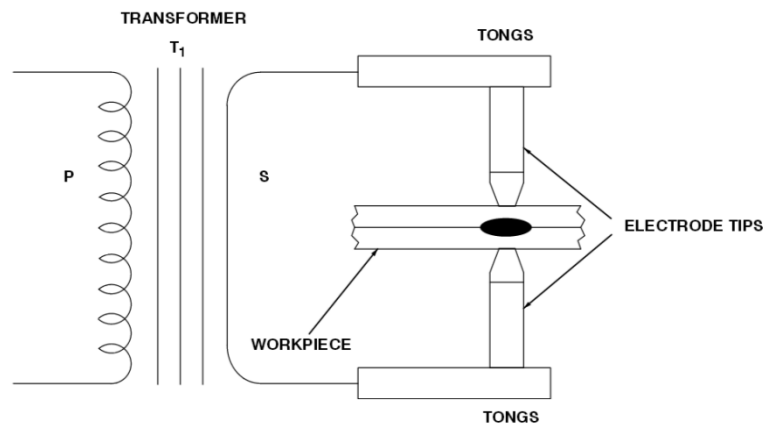


figure 111: Principle of RSW. Transformation occurs in the transformer T_1 between the primary (P) and secondary (S) circuit. Reprinted after [MIL2012]

A typical welding cycle is shown in figure 112. It is composed of four specific moments.

- Squeeze time: electrode approach and pressure application.
- Welding time: current flows.
- Holding time: pressure is maintained without current.
- Off time: electrode separate for moving of steel sheets before next weld.

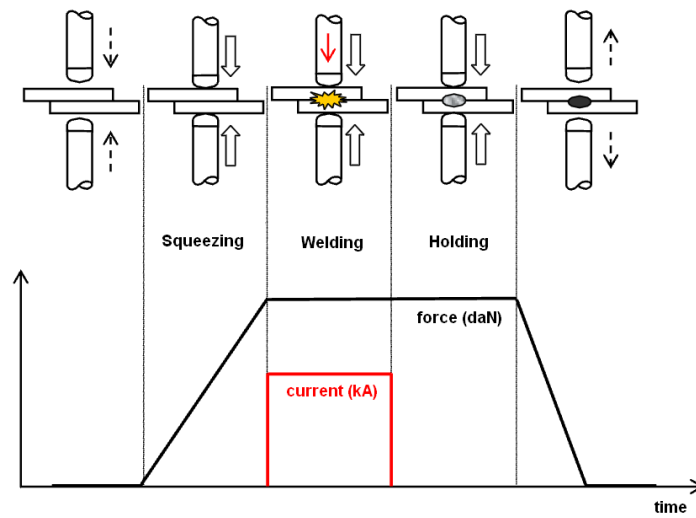


figure 112: welding cycle. Reprinted after [SIB2003]

The total electrical resistance is the sum of metal bulk resistances and interfacial contact resistances, as shown in figure 113 for a homogeneous assembly of two sheets. Steel bulk resistance depends on steel grade electrical conductivity (chemical composition and microstructure). Usually steel bulk resistance increases with the temperature and depends on phase transition and melting of the material. Contact resistance depends on surface roughness and coating of the steel (bare, electrogalvanized, hot dip galvanized, etc.). It usually decreases with temperature and welding force. As a rough description, interfacial resistances are the main heat sources at the beginning of the welding cycle and cause preferential heating and melting at the steel/steel interface. The dynamic evolution of interfacial resistances is the main difference between welding of coated and bare steel sheets [SIB2003]. Going further in the welding cycle and increasing average temperature, steel bulk resistances represent the main heat source.

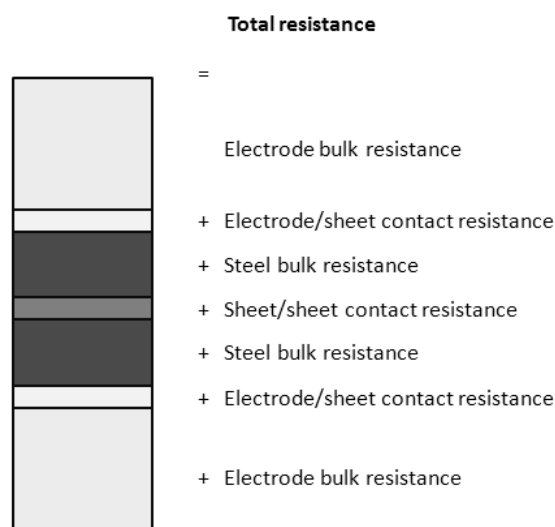


figure 113: Schematic representation of electrical resistance sources in the assembly

1.1.2. Welding machine

The RSW machine is basically composed of a current transformer (figure 111), a pneumatic system for force application, a water cooling system for electrode cooling, and electrode holders. An electric and electronic system controls all the welding parameters: current, pressure and time. The current from the primary circuit is transformed for working in the secondary circuit. 50 Hz alternative current is mainly used in RSW and time unit is sometimes periods P (50 periods = 1 s). Direct current can also be used. The welding machine used in the study will be described in the section 2. of this chapter.

1.1.3. Process parameters

Current, force, welding time, holding time, and electrode tip curvature and diameter represent the main process parameters. They need to be adjusted in function of material parameters (bulk and interfacial, sheet thickness) to obtain an adequate heat generation and molten nugget growth. Because the influences of these parameters interact, there detailed description is out the scope of this manuscript. Rough description for a specific assembly configuration can be made as following [SIB2003].

- Average temperature (and nugget diameter) increases as current increases and/or as time increases, according to equation (33).
- Average temperature decreases as force increases, as the consequence of the interfacial resistances decrease.

The definition of the weldability of steels and the influence of process parameters are described in the paragraph 1.2.

1.1.4. Weld final structure

A geometrical description of the weld is shown in figure 114. Weld surface has been deformed due to the application of the welding force. It results in the indentation, or electrode imprint, of the weld. The edge of the indentation has the curvature of the edge radius of the electrode.

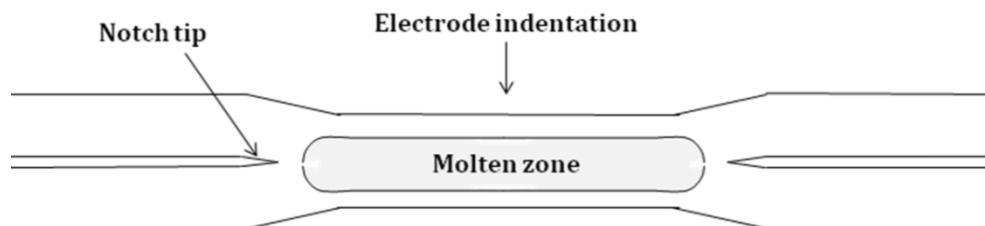


figure 114: Geometric description features of the spot weld

Steel experiences phase transition at different temperatures (Ac_1 , Ac_3 , T_m , see paragraph 3.4 of the Chapter I). The microstructure observed at different points in the weld is function of the maximal temperature T_{max} reached at this point.. The holding time at high temperature is very small. This means that the molten nugget ($T_{max} > T_m$) and the heat-affected zone (supercritical for $T_{max} > Ac_3$ and intercritical for $T_{max} > Ac_1$) can be identified through the microstructure observation for low alloy steel as those investigated

in this thesis. Figure 115 shows a typical weld cross section. The correlation between the thermal welding cycle and the existence of different zones in the weld is schematically described in figure 116.

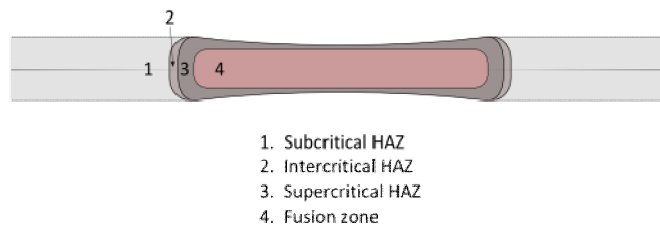


figure 115: Schematic representation of the weld final structure observed on the cross section

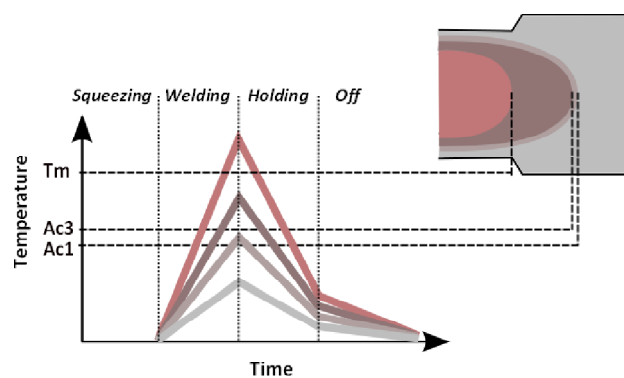


figure 116: Temperature during the welding cycle. Schematic. Each curve represents a point of the area with the same color

1.2. Weldability of high strength steels

1.2.1. Weldability: definition

The material weldability is the facility that one has to weld this material. It is high for a material which would keep good mechanical properties after being molten and rapidly cooled, and so form a weld with sufficient strength by comparison with the base metal mechanical properties. As a consequence the weldability refers to the size of the process parameter window to have appropriate welding conditions, and so sufficient strength. Actually one can rigorously detail the metallurgical weldability (material behavior, apparition of specific defects), the operative weldability (process parameters) and structural weldability (properties of the weld). These different features can be intimately linked.

For the example of carbon steels, very fast cooling rates involved in RSW will results in hard microstructure in the molten nugget and in the heat-affected zone. When increasing carbon content, steels will have the tendency to form brittle welds. For low alloy steel (C and other elements: Mn, Si, Cr, etc.) the current required to have sufficient molten nugget diameter will be lower since alloying tends to increase the electrical resistivity.

The appropriate process parameters for RSW of specific steel and assembly are obtained after the determination of the lobe diagram.

1.2.2. Determination of the lobe diagram

Figure 117 shows an example of time-current diagram with the position of the acceptable welding range. For specific materials and assembly, this diagram has been obtained by making numerous welding tests at different (time, current) points. When the welding energy is too low, the weld is undersized. The upper limit of the lobe is the expulsion of molten metal from the nugget at the interface between the two steel sheets or at the electrode corner. Expulsion is most of the time visually characterized.

A typical evolution of weld nugget diameter as a function of the current is given in figure 118. The lower limit corresponds to a minimal value d_{min} for the nugget diameter (mm). Weld strength, characterized in kN for example by a tensile test after welding, can be assumed to be proportional to the weld diameter. So the lower limit of the welding range also corresponds to acceptable weld strength. When expulsion occurs, weld diameter does not increase further, but tends to decrease. When all other process parameters are chosen and kept constant, the welding current range $[I_{min}-I_{max}]$ (process window) characterizes the operative weldability of the material.

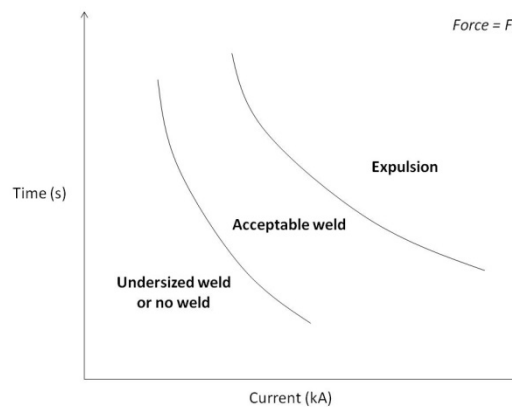


figure 117: Schematic example of a time-current lobe diagram for a constant force

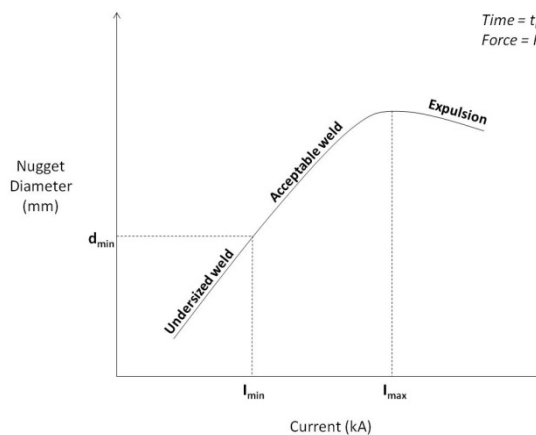


figure 118: Schematic example of the influence of the current on weld diameter

1.2.3. Weldability of AHSS

Special features for the weldability of AHSS

AHSS are generally considered as readily weldable. There are nevertheless slight differences for RSW of AHSS compared to low carbon steels [SHI2003]. The main differences are caused by the higher carbon content but also because of high Si and Al alloying, in particular for TRIP steels. Furthermore the complex microstructure of AHSS is subject to higher modifications than low carbon steel. Typically, welding AHSS need higher electrode force and lower current intensity.

The increase of C content, but also hardening elements like Mn, has a direct effect on weld hardness. For example TRIP steel can reach hardness around 500 – 600 HV in the molten nugget, while it is usually around 400-450 for DP steel. As a basic description, high hardness in the weld promotes interfacial brittle failure and reduction in tensile strength of the weld, possibly leading to unacceptable weld performance. The propensity of AHSS for interfacial failure has been related to the extreme notch sensitivity of these materials. Great effort has been conducted to change the failure mode from interfacial failure to plug or partial plug failure. In this second case the fracture occurs in the HAZ or the base metal and the ductility and toughness of the weld is usually improved. Nevertheless the fracture strength can be reduced. For very high strength (> 800 MPa) parent metal, the HAZ potentially becomes softer than the parent metal and may contribute to a decrease of weld mechanical properties. The issues of high quality RSW of HS automotive steels can be roughly summarized as follows: avoiding interfacial failure but without HAZ softening. This implies control of cooling rate, for examples by geometrical specifications for the assembly, or by designing complex welding cycle with additional pulses of current. These basic pieces of information do not always describe specific steel grades behaviors and dedicated study need to be conducted to link microstructures, hardness and mechanical properties of the weld, as made for automotive steels during RSW in [KRA2010].

Coating effect

On one's hand galvanized coating significantly affects welding behavior of AHSS in two different ways. First the presence of the low melting point metal drastically reduces the evolution of the contact resistance as temperature increases. As a consequence, welding current is often higher for coated steels. Then the welding lobes are found at higher current, but are also usually narrower than for uncoated products.

One the other hand, electrode life is significantly reduced when welding Zn-coated products. Electrode life is usually defined as the number of welds that can be made before the weld size falls below the minimal acceptable diameter, because of electrode face enlargement. Alloying between Zn and copper from the electrode is the main reason for electrode tip wear. As a consequence, electrode material softens leading to electrode enhanced face enlargement. Brass alloy layer formed on the electrode face also changes electrical resistance. Even if electrode life depends on various factors, it can typically decrease from several thousands of welds for bare steel welding, to few hundreds for Zn-coated steels.

The metallurgy of Zn-coated AHSS leads to specific problems considering RSW. Examples of welding windows for zinc-coated DP and TRIP steels, and different methods for weld characterization, will be given in the section 2 for the three investigated steel grades.

1.3. Comments on RSW introduction

1.3.1. Specificity of RSW process

The complete cycle for a welding operation is less than 1.5 s. It involves very high current density, thermal gradient, heating and cooling rate, and fast modifications electrical, thermal and mechanical properties. Then RSW involves interactions between electrical, thermal, mechanical and metallurgical phenomena. Furthermore interfacial resistances are parameters very difficult to measure and simulate, but they are considered as key parameters for early time nugget growth. To finish weld grows up internally avoiding direct observation and constituting additional difficulty for process characterization.

Recent advances in finite element simulation of the process have given new insights into the mechanisms of weld growth and temperature prediction. But main knowledge on RSW is still mainly empirical.

1.3.2. Industrial implementation and expulsion occurrence

Industrial problem for the implementation of RSW

The welding lobe for steel grades can be experimentally described for various materials following international standards and after an experimental studies of the weld diameter, for example, as a function of welding current. Nevertheless in industrial conditions, in particular in the automated production lines of carmakers, welding is not carried out as in lab experiments. Indeed several difficulties such as squeezing problems (for example: electrode misalignment), or the necessity of using auto-adaptive robot due to multiple welding assembly types, are met with industrial welding. As a result, expulsion is very often observed for a significant amount of spot welds made in industrial conditions.

Consequence of expulsion

As already written, expulsion refers to the projection of molten metal from the weld into the air. It may occur both at the notch tip, i.e. between the two steel sheets, or at the edge of the electrode/sheet interface. Expulsion is found when too high heat input is applied to the weld. But geometric feature such as the presence of a gap between the two steel sheets (due to, for example, to specific set up of the assembly in industrial conditions) or electrode misalignment significantly increase expulsion occurrence.

Expulsion means that the volume of material in the weld under the electrode is reduced during welding. As a consequence, increased indentation depth is measured after welding with expulsion.

2. RSW methods

2.1. Welding of investigated steel grades

2.1.1. Welding machine and specimen geometry

Machine

The welding machine is an ARO 1000 series pedestal as shown in figure 119. It is equipped with a pneumatic jack of 10 kN and an electric power transformer of 64 kVA. All tests are performed with 50 Hz alternating current. The voltage in the secondary circuit is typically between 1 V and 2 V.

Current, voltage, displacement of the welding head and force can be recorded. A typical welding cycle is shown in figure 120. First, force profile is not exactly as the ideal one (compared to figure 112). In particular the effective force varies during welding time. The insert shows the alternating current profile regulated by the thyristors (power control device) bridge of the primary circuit.

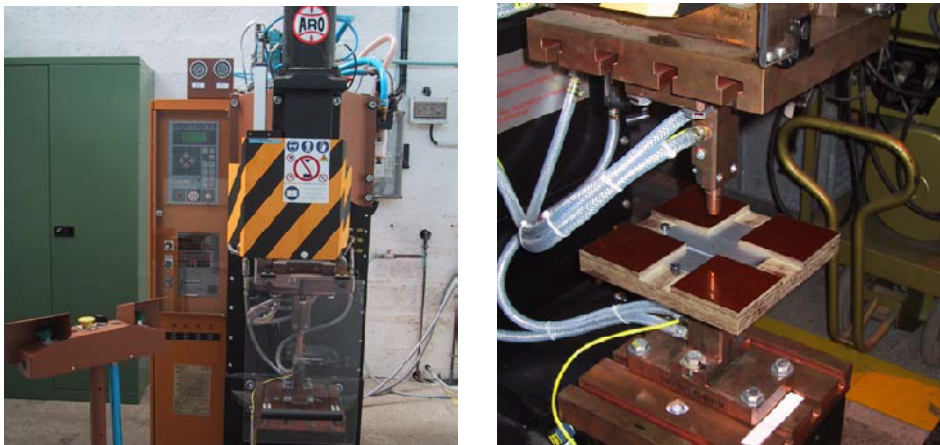


figure 119: Pedestal welding machine used in the study. Reprinted after [SIB2003]

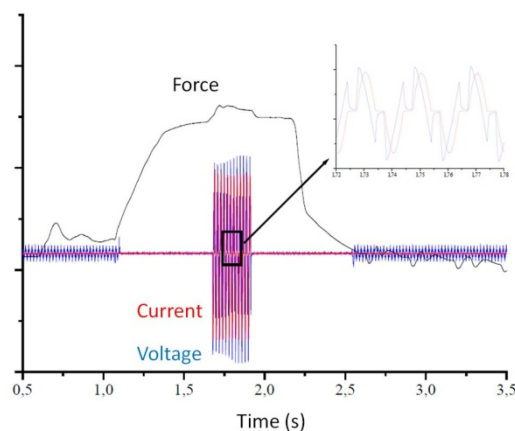


figure 120: Example of welding cycle recorded by the instruments implemented in the welding robot. Reproduced after [SIB2003]

Electrodes

G type electrodes (ISO standard designation) with 6 mm tip diameter described in figure 121 are used in this study. Electrode material is a copper alloy dedicated to resistance welding, composed of 0.65 wt% Cr and 0.08 wt% Zr, and commercially named Elbrodur HF. Before each test series, electrode conditioning is carried out through 20 welding operations at 7 kA with 1mm TRIP Si EZ in homogeneous configuration.

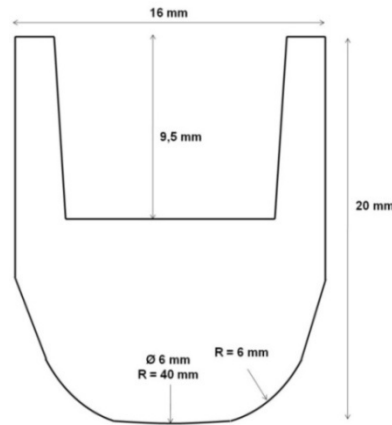


figure 121: Geometry of the electrode used in the study

Specimen geometry

As already described in Chapter 1, 1 mm thick electrogalvanized steel grades are studied: DP, TRIP Si and TRIP Al Si. Steel sheet has been prepared in 20 x 250 mm bands to facilitate further cutting operation for metallographic preparation. So the specimen size specified by ISO norms is not followed. Spacing between two subsequent spot welds is higher than 40 mm, which is considered high enough to neglect any shunting effect. Spot welding design guidelines show that spacing higher than 20 times material thickness is sufficient to avoid shunting effect [PMA2004][WAN2013].

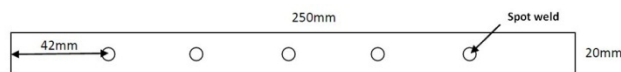


figure 122: Steel sheet specimen geometry used for welding tests. 42 mm spacing between two welds

2.1.2. Process parameters and testing plan

Process parameters

Investigated steel grades have been already studied in ArcelorMittal lab. Process parameters indicated in table 16 follow international standard ISO 18278-2 for RSW. Welding current ranges have also been determined. I_{min} and I_{max} are given in table 16. As written told in the paragraph about the weldability of AHSS, the DP steel range should be found at higher current because C and (Si+Al) contents are lower than in TRIP steel.

table 16: Process parameters for 2 x 1 mm homogeneous assembly of EG steel

Grade	Electrode	Squeeze time (P)	Welding time (P)	Holding time (P)	Force (daN)	I _{min} (kA)	I _{max} (kA)
TRIP Si	TH6	20	14	20	350	6,5	7,9
TRIP AISi	TH6	20	14	20	350	6,8	8,7
DP	TH6	20	14	20	350	unknown	unknown

Test plan

In this study the influence of current is investigated, below and above I_{max}. All other parameters are kept constant according to table 16. The welding current has been investigated from 6 kA to 9.5 kA for TRIP grades, and from 6 kA to 12 kA for DP. For each current level, 10 welds are made. The total is 190 welds. This is supposed to be enough to give good statistical information.

table 17: Number of welding operations carried out for the study

Grade	6 kA	7 kA	8 kA	9 kA	9,5 kA	10 kA	11 kA	12 kA
TRIP Si	10	10	10	10	10	10	0	0
TRIP AISi	10	10	10	10	10	10	0	0
DP	10	10	10	10	0	10	10	10

2.2. Measurements of weld geometrical parameters

Cross section measurements

Quantitative measurement of weld geometrical parameters will be needed for the discussion about racking occurrence. After welding, spot welds are cut in the middle plan with a metallographic cut-off machine as shown in figure 123.

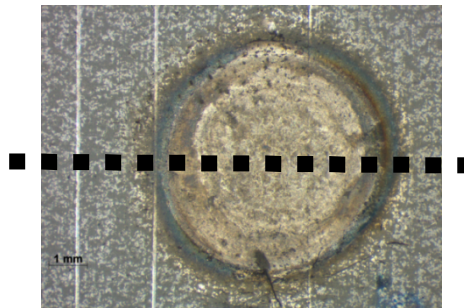


figure 123: Top view of the spot weld and position of the cut-off plan. DP, 7 kA.

Cross section are polished until a 1 µm diamond paste, etched in EtOH solution with 5 wt% of nitric acid during 4 s, and observed in the optical microscope. The macrographic observation of the whole weld is obtained by automated assembly of several images thanks to the acquisition software and the motorized sample holder. An example of cross section observation is given in figure 124.



figure 124: Example of a spot weld cross section observation after nitric etching. DP, 7 kA.

From the cross section observation, indentation depth on each face and molten zone diameter are extracted, as shown in figure 125. Because of process imperfections such as minor electrode misalignment or expulsion, the weld is not perfectly symmetric, in particular for high current. That is why the indentation is not the same for top and bottom faces of welds. Indentation depth is measured at the center of the weld after drawing a straight line supposed to represent the initial steel sheet surface.

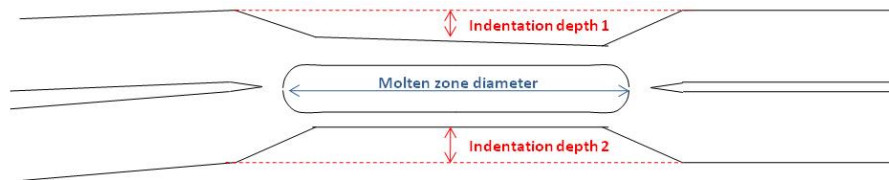


figure 125: Measurement of indentation depth and molten zone diameter

Measurement on indentation depth by topographic reconstruction

When observing a rough surface, the optical microscope and the associated processing software are able to make a 3D topological reconstruction of a surface. So it is possible to investigate the weld surface profile without cutting and cross section observation. An example of 2D profile of the indentation extracted from the 3D surface is shown in figure 126. The indentation depth can be measured from this profile and give the same results than cross section measurements.

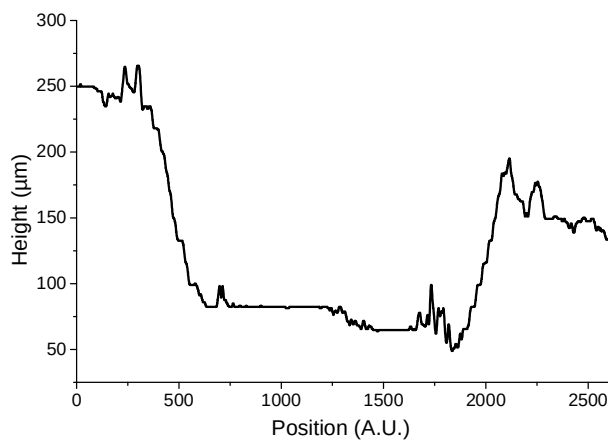


figure 126: 2D profile reconstruction of the weld indentation. TRIP AISi, 7 kA

3. Innovative methods for RSW characterization

In this section two characterization methods implemented during the study for better RSW characterization are introduced: infrared thermography for quantitative surface temperature measurement, and high speed camera monitoring of electrode displacement for in-process indentation depth measurement.

3.1. Infrared thermography

It is obvious that temperature is an important parameter during welding. Furthermore Chapter I has shown that LME cracking occurs in a specific temperature range. So temperature information is needed to describe the welding cycle. The infrared thermography method has been adapted to RSW for this study. The paper “Infrared quantitative analysis of welding processes” submitted and accepted in the journal *Science and Technology of Welding and Joining* reports the implementation of the technique [FRA2014]. In this paper it is demonstrated that reliable temperature measurement can be obtained with a reasonable uncertainty after preliminary measurement of material surface emissivity. The main features of the paper are summarized in this paragraph.

3.1.1. Principle

Infrared (IR) thermography refers to the detection of infrared energy emitted from surfaces, and its conversion into temperature, to obtain a two-dimensional image of temperature distribution. The camera detects the infrared intensity I_i emitted from surface and converts it into temperature T according to

$$T = f\left(\frac{I_i}{\varepsilon_{app}}\right) \quad (34)$$

Here the function f is calibrated by the camera producer depending on optical configuration, and hardware and software parameters, in particular the integration time (exposure time). The apparent surface emissivity ε_{app} is a parameter comprised between 0 and 1. For the Zn-coated steel sheet it has been characterized as shown in figure 127. The estimation of the uncertainty on T has been carried out in [FRA2004]. Results for the relative uncertainty are shown in figure 128. For example it corresponds to absolute error around 15 °C at 700 °C.

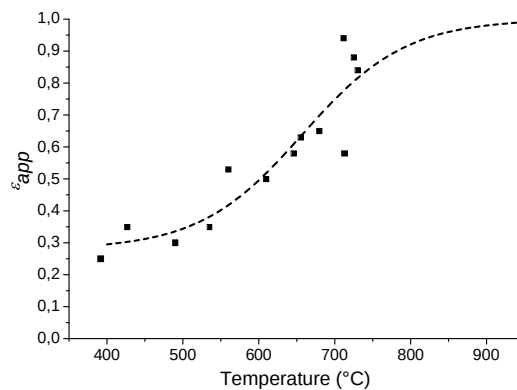


figure 127: Apparent emissivity of electrogalvanized steel

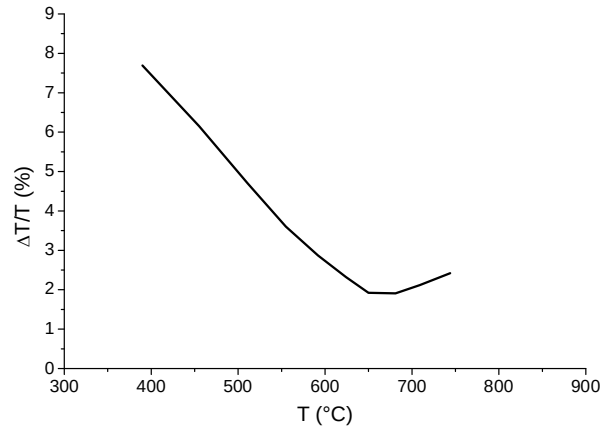


figure 128: Relative uncertainty to consider on temperature results

3.1.2. Experimental set up

Recording specifications

The IR camera is a FLIR Orion SC7500 with an InSb detector calibrated by the manufacturer for each optical configurations, and hardware and software parameters. The pixel resolution is 320 x 256 with a 30 μm pitch. The camera was equipped with a close-up having a magnification ratio of 1 at a working distance of 300 mm. Figure 129 shows the set up and the angle necessary to observe the weld. The observed zone has 9.60 mm x 7.68 mm space dimensions. A 3.97 - 4.01 μm wavelength filter and an integration time of 300 μs were used. The acquisition frequency was 50 Hz. This frequency was imposed by the special set up of the camera and supposed to be sufficient for RSW application (50 Hz alternating current). A temperature per alternative current period will be obtained. As a consequence, temperature variation during each period is not observed.

Post-processing was made with the Altair software developed for FLIR cameras. The correlation between temperature and infrared intensity level is implemented and calculations are automatically done as a function of the emissivity of the material.

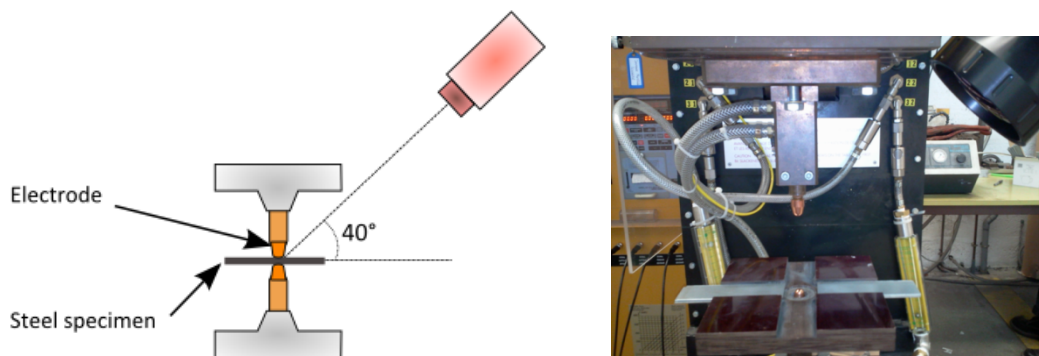


figure 129: Set up for temperature measurement

Observed area

Figure 130 gives the description of which surfaces are observed with the camera. There is not any direct access to temperature inside the weld or at the surface of the weld since electrode hides the main part of the weld. The temperature gradient observed at the surface of the steel sheets beside the weld is the interesting part of the thermograph.

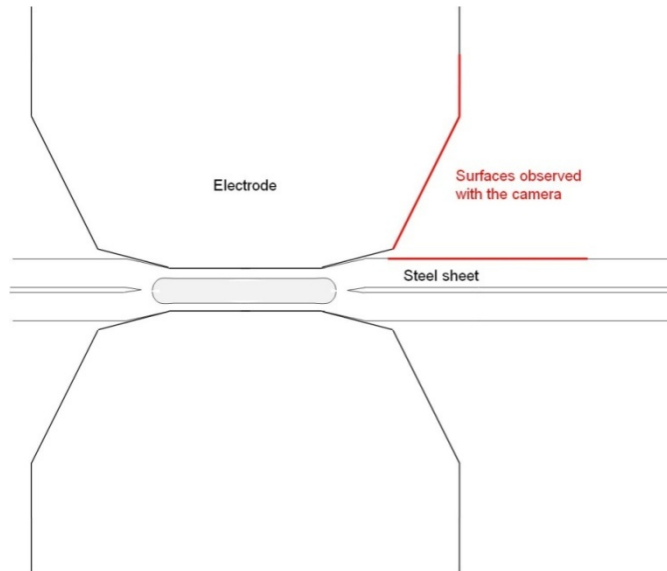


figure 130: Surfaces observed with the camera

3.1.3. Example of measurement

Thermogram and temperature

Figure 131 shows a typical thermographic image obtained during RSW. This image is taken at the end of the welding time, i.e. when the temperature is maximal in the weld. At the top of the image, the electrode is colder (water cooling inside the electrode). The colors representing the infrared intensity show the thermal distribution at the surface of the steel sheets. High infrared intensity is detected just around the electrode tip. High thermal gradient, well-known in RSW, is illustrated by this map. The signal decreases on the sides because the electrode corner shape hides the sheet surface just at the radius of the electrode. Sampling is always made in the middle.

Graphs show the evolution of the infrared intensity during the welding cycle, but not directly temperature. Intensity increases to during weld time and decreases during holding time and after. According to equation (34) infrared intensity (figure 131) can be converted into temperature. The maximal temperature observed during the welding cycle is found to be 729 °C, 586 °C, 446 °C respectively for sampling position A, B and C.

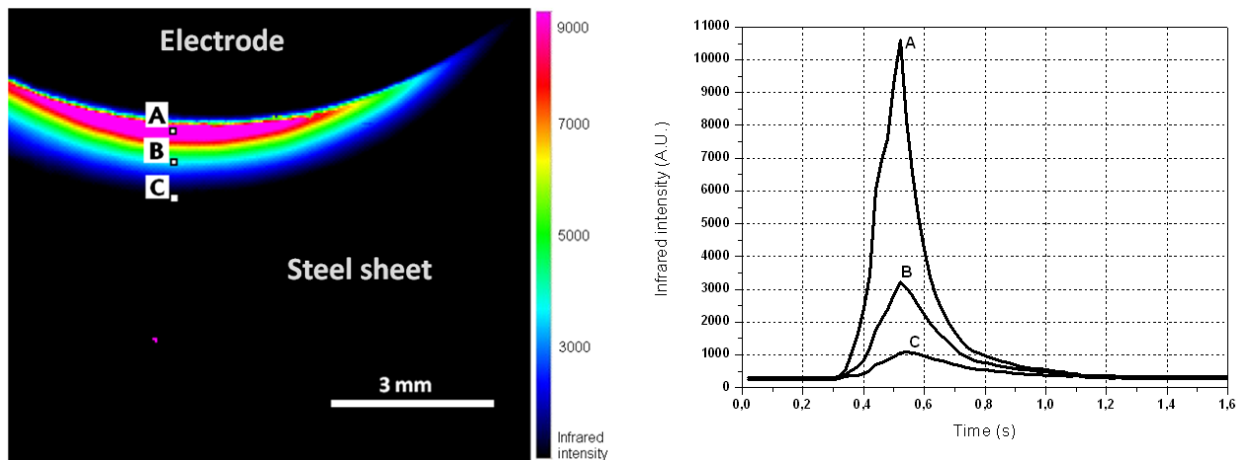


figure 131: Typical thermogram at the end of the welding time (left) and infrared intensity detected at the sampling positions A, B and C (right). TRIP Si, 9 kA.

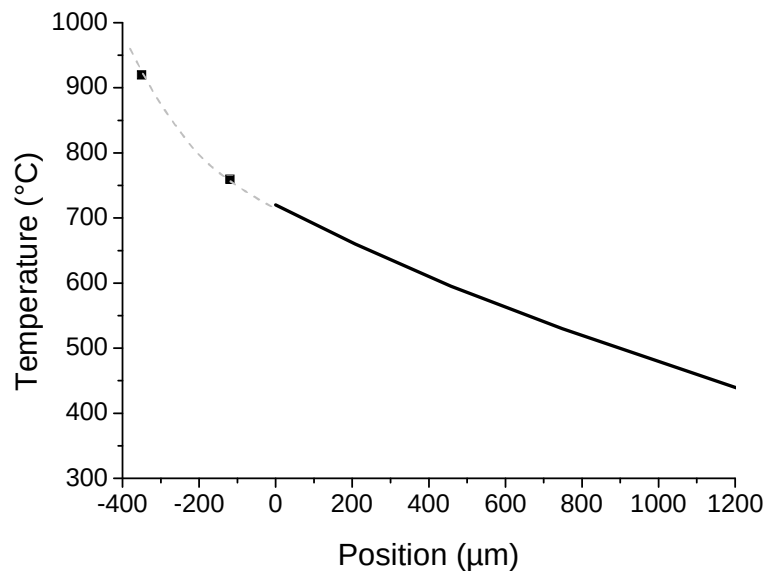


figure 132: Maximal temperature reached at the steel sheet surface observed with the camera (straight line). The two isolated point indicate Ac1 and Ac3 positioned after microstructure identification in figure 133. TRIP Si, 9 kA.

Metallographic validation

Figure 133 shows the macrograph and micrograph of the RSW weld cross section. The different microstructure of the base metal and the heat affected zone (HAZ) are visible. Thanks to these microstructural modifications, the boundaries between subcritical (1), intercritical (2) and supercritical (3) microstructures have been located on the cross section. Transitions between these microstructures correspond to Ac1 and Ac3 temperatures. There were found to be $(760 \pm 5)^\circ\text{C}$ and $(920 \pm 10)^\circ\text{C}$, respectively (see paragraph 3.4 in Chapter I). These two points have been added in the graph of maximal reached temperatures (figure 132). The origin “0 μm” of the observed surface has been located on the cross section thanks to a

groove line made at the surface of the sheet. The metallographic examination shows that the temperatures found by infrared thermography are in relative good agreement with the metallurgical analysis.

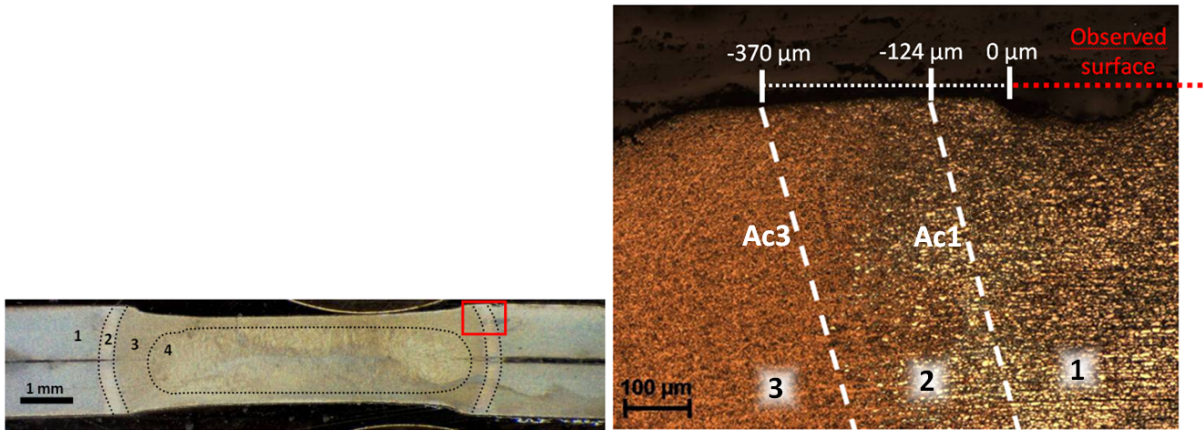


figure 133: Cross section of the weld and enlarged view of the surface out of the electrode imprint with positions of the observed surface, Ac1 and Ac3. Distance scale refers to the graph in figure 132

3.1.4. Selection of a temperature criterion

This method does not provide direct information of temperature at the electrode/steel sheet interface, nor internal temperature. The characterization of surface temperature is nevertheless supposed to provide relative, but quantitative, information on overall heat input.

Each welding operation of the study has been monitored with the camera. So information equivalent to what is given in figure 131 and figure 132 can be extracted. For comparison between steel grades and welding current levels, the maximal temperature detected during the welding cycle has been chosen. It is actually the temperature at “0 μm ” position in the figure 132. Making this choice the distance between the center of the weld and the “0 μm ” position is supposed to be constant for all welding operations.

The uncertainty on temperature consecutive to the uncertainty on emissivity is 2 % at 700 °C, namely 14 °C. An other source of uncertainty is coming from the variation of the “0 μm ” origin position. An estimation of this sensitivity can be carried out. After the estimation of the thermal gradient at 700 °C (derivative of the curve in figure 132), an error of 100 μm (1/10 mm) results in a basic error of 30 °C.

3.2. High speed camera monitoring of electrode displacement

As pointed out in paragraph 1.3 indentation depth and expulsion are correlate and of high importance for weld quality. Indentation depth can be measured on the final weld cross section. High speed camera monitoring has been implemented to RSW to get in-process measurement of the electrode displacement and indentation depth. Because expulsion is associated with an increase of the indentation depth, this method is also expected to give information about expulsion occurrence.

3.2.1. Description of the method

This paragraph describes the implementation of the camera for RSW monitoring and the sequences of post processing to obtain the displacement of the electrode during the welding cycle.

The camera is placed at the height of steel sheets at a distance of 40 cm from the weld as shown in figure 134. Focus is made on the electrode surface thanks to the optical adaptative zoom system. Additional light is also needed. A mark has been made on the electrode side surface at 1.5 mm from the tip face of the electrode.

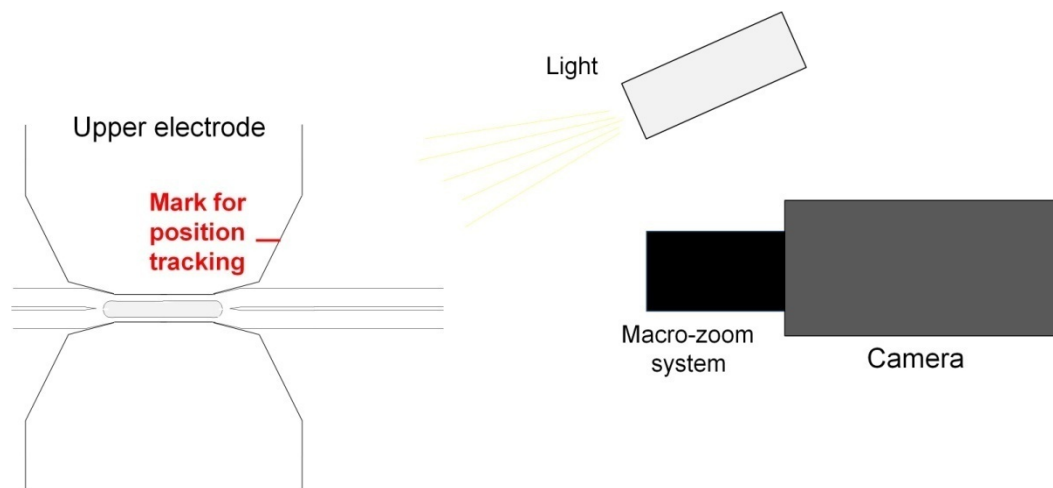


figure 134: Set up for high speed camera monitoring

The recording frequency is 4000 Hz. Image processing tool of the camera software allows the automated start of the motion capture. A 4 s long motion is obtained.

Figure 135 shows a typical image from motion and the principle of the method to get the displacement of the electrode during the welding cycle. The two steel sheets and the electrodes can be observed. The mark made on the upper electrode surface has been highlighted by a red line. Image processing tools track the (red) mark by comparing contrast and colors in the (green) area in the succession of images. Knowing optical configuration, the software convert the pixel position of the mark in Y coordinate, that can be plotted as a function of time. The Y coordinate (in mm, arbitrary origin) of the mark is assumed to describe the displacement of the electrode during the welding cycle. For that the position of the bottom electrode is assumed as constant. This is in agreement with preliminary trials made to characterize the displacement of the bottom electrode with the same camera method. Note that the bottom electrode is fixed while the top electrode is on the mobile frame driven by the pneumatic jack.

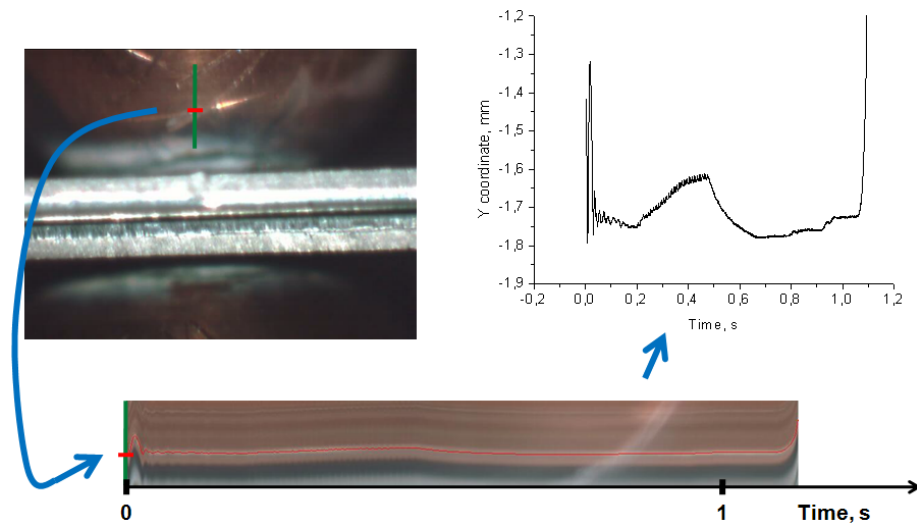


figure 135: Method for electrode position tracking during the welding cycle. 1/ Detection the mark made at the electrode (red line) surface. 2/ Automated tracking of the mark during the welding cycle thanks to the image analysis software. 3/Processing of the image to get the vertical position of the upper electrode as a function of time

3.2.2. Example of measurement

Electrode displacement during the welding cycle

Figure 136 shows the displacement of the electrode during the welding cycle. Squeezing, welding and holding times programmed in the welding robot have been added to the graph after identification of these different steps on the movie. During squeezing, electrode comes down in contact with the steel sheet. After first electrode contact, several bounces are observed. Oscillation amplitude rapidly decreases indicating that the contact is effectively obtained. During welding thermal expansion of the assembly is observed. During holding shrinkage is observed. After holding the electrode withdraws.

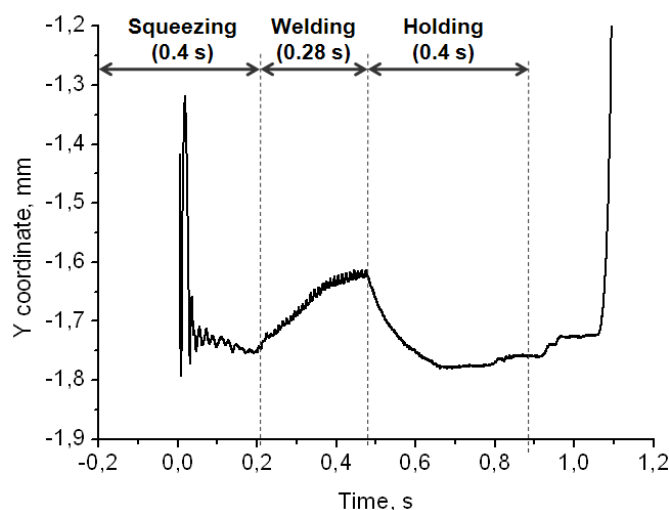


figure 136: Displacement of the electrode during the welding cycle. TRIP AISi, 6 kA

Pulsation of the weld

As an example of the accuracy of the characterization, figure 137 shows the welding part of the previous graph (figure 136). The full expansion extent is around 130 μm . The contribution of the electrode expansion is neglected (temperature in the electrode is supposed to be lower than in steel assembly) this dilation represents 7.5 % of the initial thickness of the assembly (2 mm). Furthermore the sinusoidal shape of the curve is observed. These 28 peaks correspond to the 14 periods of 50 Hz alternating current used for welding. The peak height is between 8 μm and 10 μm . It gives an indication on the order of magnitude for the minimal displacement that can be observed with the camera in RSW conditions. It should be in the order of a few microns.

This observation is in good agreement with what typically observed experimentally [WAN2009] and also in finite element simulation of the process, as shown for example in figure 138.

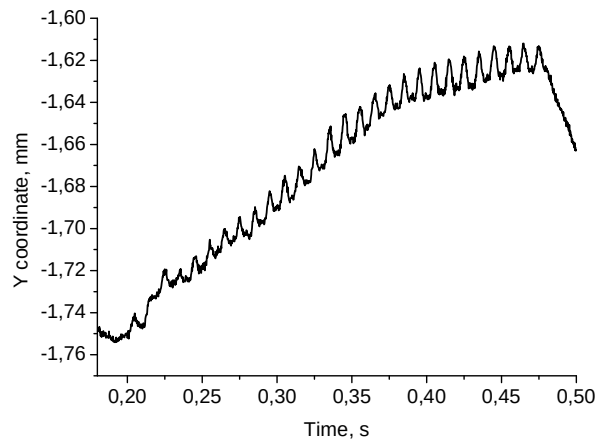


figure 137: Thermal dilation during welding. 28 peaks corresponding to 14 periods of 50 Hz alternating current can be identified. TRIP AISi, 6 kA

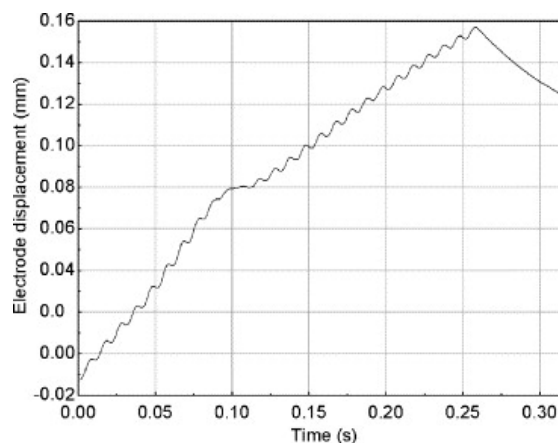


figure 138: Displacement of the electrode by FE simulation. Current: 12.2 kA, welding: 13P, holding: 3P, force: 300 daN. Reprinted after Z. Hou, et al. [HOU2007]

4. Preliminary characterization of welds

The influence of welding current on weld attributes is characterized: nugget diameter, indentation depth and surface temperature. Expulsion is also characterized through high speed monitoring of the electrode displacement.

4.1. Influence of current on weld attributes

4.1.1. Influence of current on nugget diameter

Figure 139 shows the effect of welding current on nugget diameter. Nugget diameter increases as current increases. Nugget diameter increases further up to 12 kA and exceeds the electrode tip diameter (6 mm). No significant difference is found between grades, except for the first point at 6 kA where TRIP Si diameter is significantly higher than for TRIP AISi and DP. There is poor correlation between this graph and differences between welding lobes (table 16).

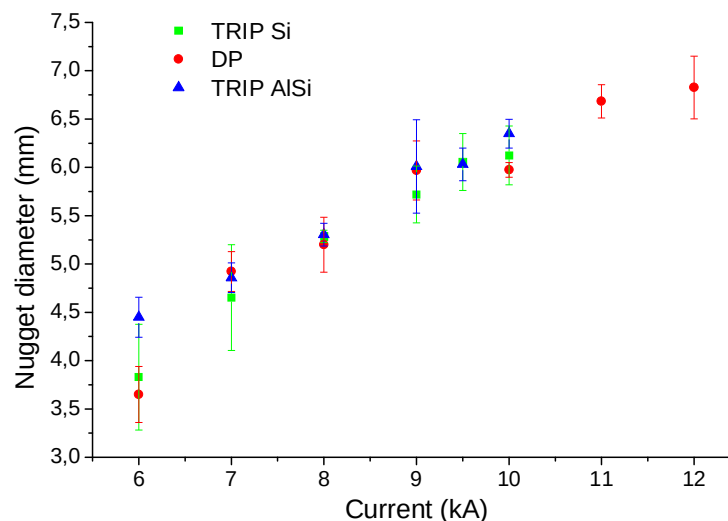


figure 139: Nugget diameter vs. welding current

4.1.2. Influence of current on surface temperature

Figure 140 shows the effect of welding current on maximal surface temperature measured by thermal camera. Surface temperature increases as current increases. Even if scatter is high, surface temperature is often found lower for DP than for TRIP steels. This would be in agreement with the fact that DP needs more current to get the same heat input.

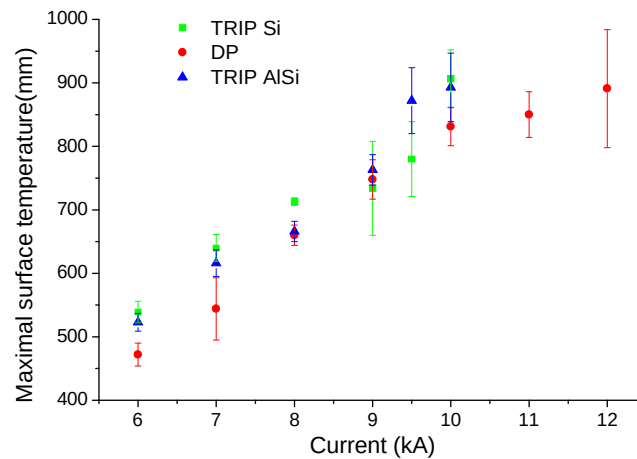


figure 140: Maximal surface temperature vs. welding current

4.1.3. Influence of current on indentation depth

Influence of current on indentation depth

Figure 141 shows the effect of welding current on indentation depth. Indentation depth increases as current increases. Indentation depth is significantly lower for DP than for TRIP for equivalent current, at least between 9 kA and 10 kA. Increasing current for DP leads to indentation as high than what observed for TRIP at lower current. Indentation depth up to almost 40 % (400 μ m) of the sheet thickness can be found for high current. Indentation average values and standard deviations are significantly higher above 9 kA. The same is observed for DP above 11 kA. This can be correlated to expulsion occurrence for current levels outside the welding current range defined for each grades (table 16). Indeed expulsion refers to a loss of metal from the molten nugget and, consequently, to higher indentation. In this sense, the higher the metal volume loss is, the more the indentation depth is. This fact will be also investigated in paragraph 4.2. Expulsion appears as a random phenomenon since it increases standard deviation for the indentation depth.

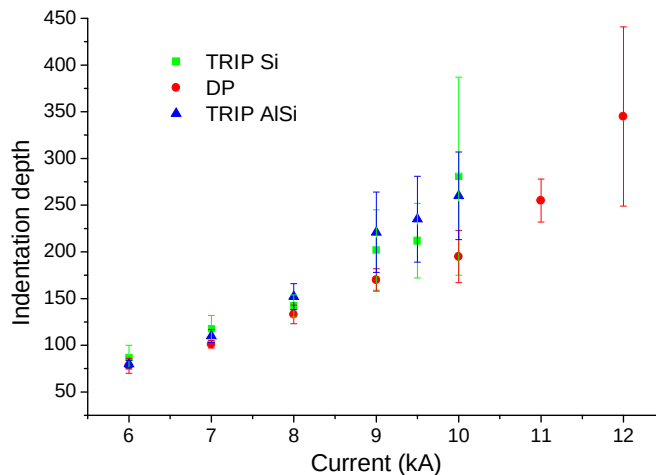


figure 141: Indentation depth vs. welding current

Correlation of indentation depth with surface temperature

Slight difference has been found between DP on one side, and TRIP Si and TRIP AlSi on the other side. In figure 142 the dependence of indentation with surface temperature is shown. Average values are given, but also the detail of each weld. These graphs show that average values for the indentation depth increases with surface temperature, remotely without any distinction between the three grades.

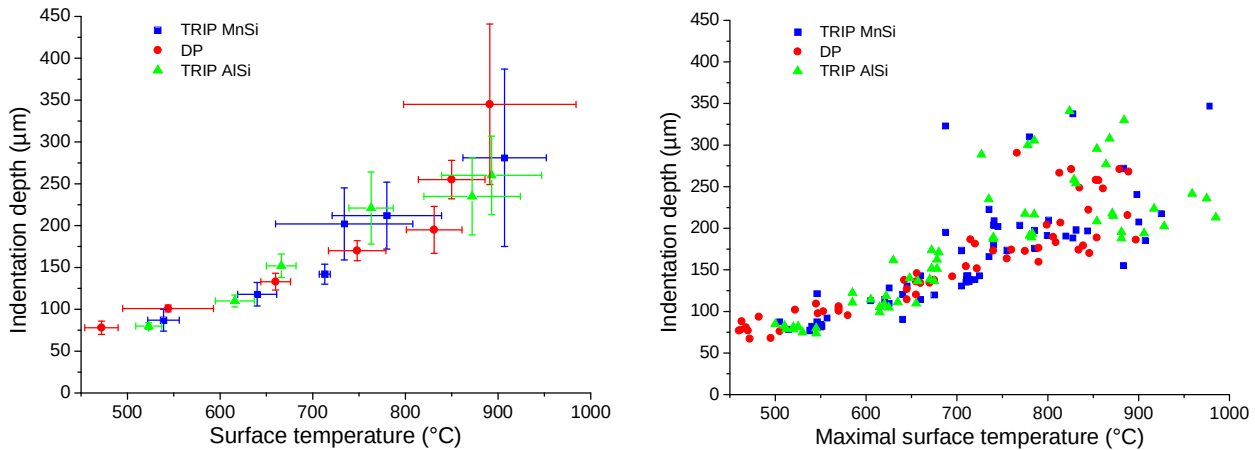


figure 142: Indentation depth vs. maximal surface temperature. Left: average values. Right: detail

4.2. Characterization of indentation and expulsion

In this subsection results for high speed camera characterization of the electrode displacement are given. They don't have been carried out on the same samples than studied above, but in addition to the test plan described in paragraph 2.1.2. Only TRIP AlSi grade is characterized.

4.2.1. Occurrence of expulsion

Figure 143 shows examples of electrode displacement characterization during welding of TRIP AlSi at different current levels. For 6 kA continuous thermal expansion during weld time (approx. between 0.2 s and 0.48) is observed with a slight saturation in the end. For 7 kA an abrupt fall of the electrode is observed. This corresponds to expulsion. Fall about 94 μm occurs during an interval of $8.5 \cdot 10^{-3}$ s. It corresponds to an average velocity of 11 mm s^{-1} . Characteristics of the other expulsion events are detailed in table 18. It seems that for high current, several single events of expulsion occur during one welding operation.

table 18: Characteristics of expulsion events (figure 143)

Current (kA)	Event n°	Δd (μm)	Δt (ms)	V (mm s^{-1})
6	-	-	-	-
7	-	94	8.5	11
8	1	112	2.8	40
	2	308	7.0	44
10	1	153	14	11
	2	48	2.5	19
	3	58	3	19

As a confirmation that what just described, the direct observation of molten metal expulsion at the exact moment of electrode fall is shown in figure 144.

Here it has to be kept in mind that the electrode displacement describes the sum of indentation depths on both faces of the weld. So the indentation depth measured on one face should be two times lower, as described in graphs of for the dependence of indentation depth with current, temperature, etc. (paragraph 4.1.3).

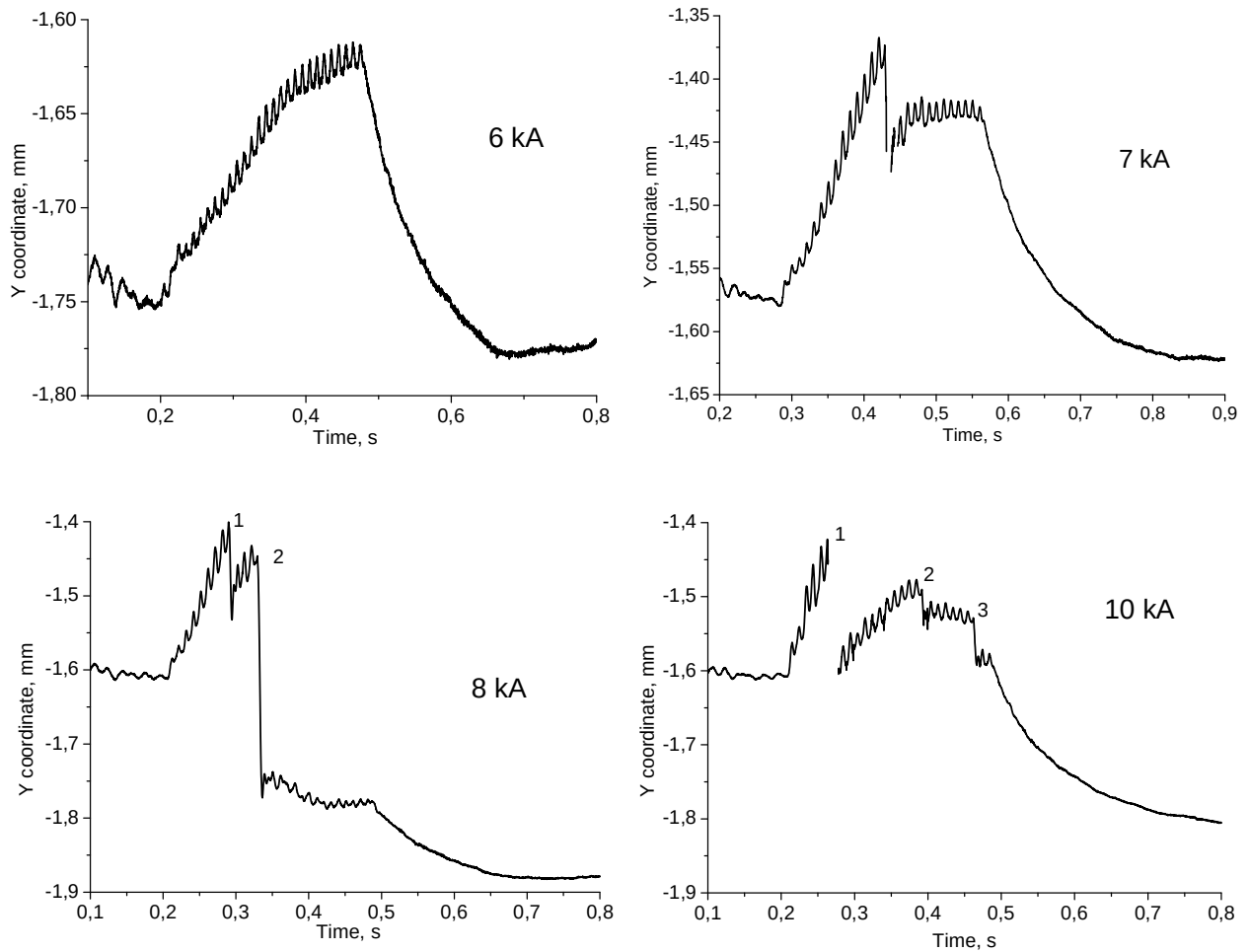


figure 143: Observation of expulsion events during welding: abrupt displacement of the electrode. TRIP AISi

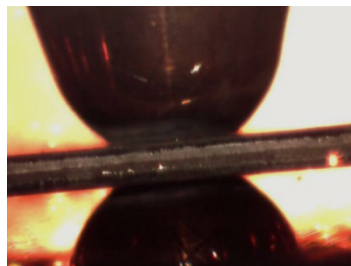


figure 144: Expulsion of molten metal (flash behind the electrode from this point of view). TRIP AISi, 8 kA

4.2.2. Final indentation depth

From electrode displacement graph it is possible to extract the final indentation depth by computing the difference between electrode position after squeezing and after holding. For example for 6 kA (figure 143), electrode position is - 1.751 mm and - 1.779, respectively at 0.2 s and 0.7 s. Here indentation depth is estimated to be

$$\frac{1779 - 1751}{2} = 14 \mu m$$

The factor 2 is to take into account that the electrode displacement describes the indentation on both faces of the weld. Results for the indentation depth measured according to this method are given in figure 145. Only two spots were welded per current step. Results are compared to measurements made by 3D reconstruction with the optical microscope (method described in paragraph 2.2).

First, results from the camera are underestimated compared to those from the microscope. It is probably due to the fact that at the end of holding time, the weld is still hot, especially internally. So further thermal shrinkage will occur, what will increase indentation depth. So microscope observation made when the weld is cold gives deeper indentation than camera measurement just at the end of holding time. In that sense, it is possible that a slight indentation exists also at the end of squeezing time.

Then these results are in relative agreement with those found above for TRIP AlSi where the indentation depth was between 50 μm and 300 μm , for current between 6 kA and 10 kA. As a simple observation, these additional results show that indentation increases further for very high current (11 kA and 12 kA). These current levels have not been investigated in the basic test plan.

The agreement between electrode displacement and indentation directly observed with the microscope measurement consist in a validation for camera method.

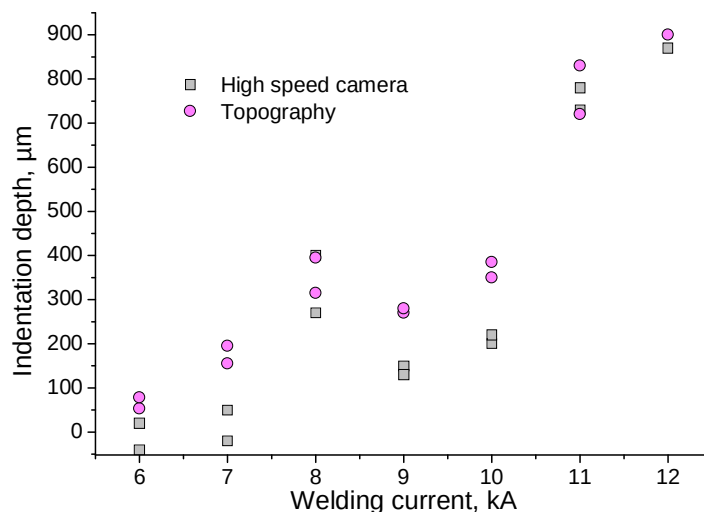


figure 145: Final indentation depth. Comparison between high speed camera and topographic measurement with the optical microscope

4.1. Comments on weld characterization

Nugget diameter, surface temperature and indentation depth increase as current increases. For the same current, DP has slightly lower indentation than TRIP steels. This is in particular due to the fact that expulsion may occur for TRIP and not for DP in a relative wide range of current levels (8 – 11 kA). A good correlation between indentation depth and surface temperature has been found without making any distinction between steel grades. In other words: the indentation depth can be directly correlated with heat input characterized for example by surface temperature measurement.

High indentation depth has been found to be caused by expulsion of molten metal from the weld. The moment of the welding cycle at which expulsion occurs has been characterized. Expulsion results in very abrupt increase of the indentation depth. The velocity of the electrode displacement has been estimated between 10 mm s^{-1} and 45 mm s^{-1} . As a consequence, expulsion and indentation probably promote high deformation in the weld with high strain rate.

In the next section, cracks in the weld are observed and cracking extent as a function of welding current and weld characteristics is determined just above.

5. Quantification of surface cracking occurrence

This section shows qualitatively where cracks are observed in the weld and the method for crack depth measurement. Then cracking extent is quantitatively correlated to welding current and weld characteristics.

5.1. Detection of cracks

5.1.1. Surface observation

Cracks can be detected by surface examination of the weld as shown in figure 146. Cracks are visible in the zone called “center of the weld” since it can be considered as approximately flat (horizontal). Cracks are along both radial and circumferential directions.

This method is not used for quantitative detection of crack since the depth of the crack cannot be measured. Furthermore the Zn coating, even if partially removed during welding, may hide small or not opened cracks, like secondary cracks observed in tensile specimens (Chapter I).

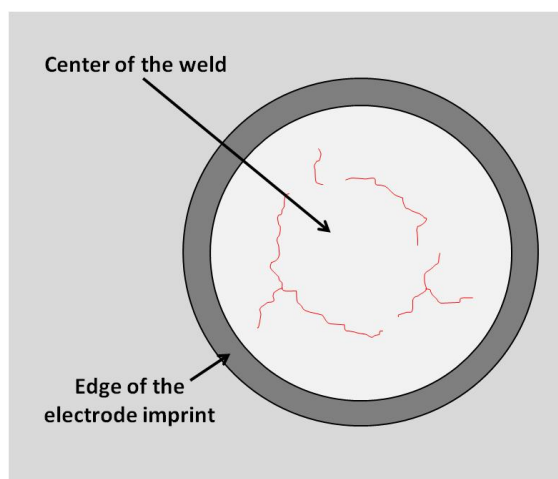
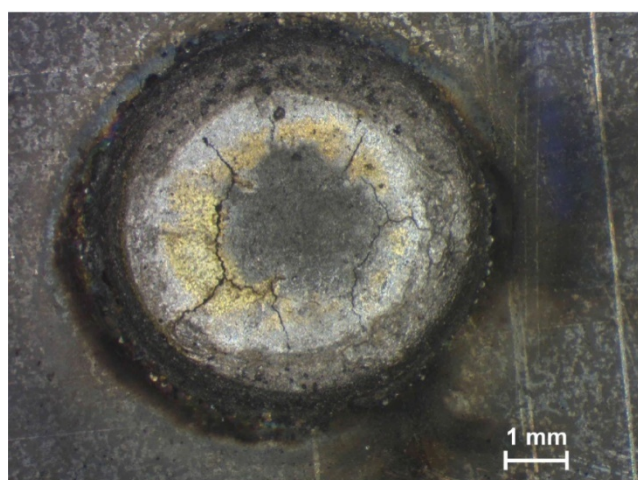


figure 146: Surface observation of the spot weld with cracks. TRIP AISi, 10 kA

5.1.2. Cross section observation

Cross section observation after nital etching in figure 147 clearly shows multiple surface cracks in a weld. They can be both in the center of the weld and at the edge of the electrode imprint as schematically drawn in figure 148. Very deep cracks but also multiple secondary cracks can be observed. These cracks are intergranular and filled with Zn exactly in the same manner than cracks found inside tensile specimens in Chapter I. The identification of microstructure found to be cracked will be performed in section 5.3.

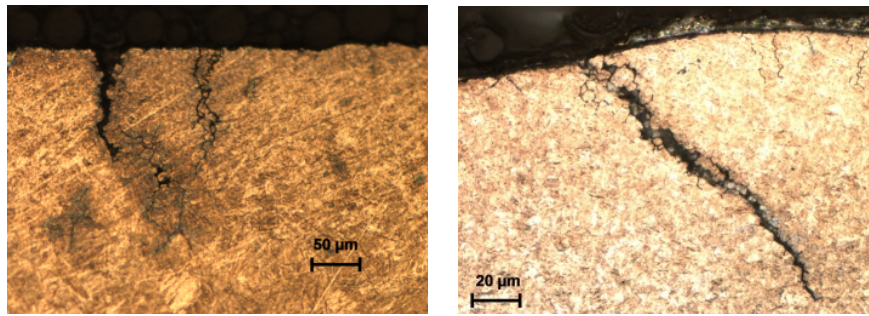


figure 147: Examples of cracks found in the center of the weld (nital etching). Left: center cracks. Right: corner cracks

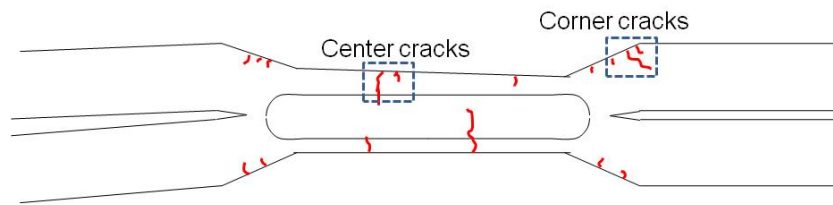


figure 148: Schematic representation of the cross section with cracks. Distinction between center cracks and corner cracks can be made

Cross section measurement

The method for crack depth measurement on polished cross section after nital etching is displayed in figure 149. Only cracks deeper than 20 µm are taken into account.

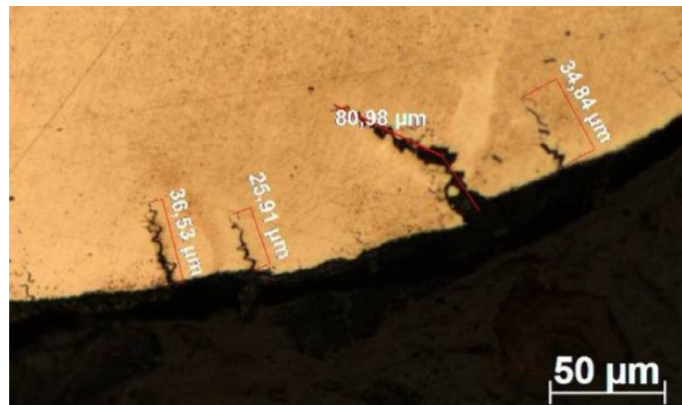


figure 149: Examples of crack depth measurement

Comment on crack depth measurement

First, a depth (1D) measurement is performed on the cross section (2D) while the crack extent should be measured as a surface (2D) in the weld volume (3D). Then, the main question is how representative is this cross section? Indeed it is clear that the cross section doesn't cross all cracks visible in the top surface (). The number of observation (10 welds, i.e. 20 faces per current) is expected to give enough statistics to get quantitative information for cracking occurrence.

5.2. Characterization of cracking occurrence

5.2.1. Influence of welding current on crack depth

Figure 150 shows the effect of welding current on crack depth. For the three grades the crack depth is zero for small current (6 kA and 7 kA). Then crack depth increases as current increases. Crack depth seems to stabilize for high current. For the two TRIP grades, cumulated crack depth is found around 2000 μm for current above 9 kA. As for the correlation between current and indentation, an abrupt increase of the cumulated crack depth is observed for TRIP steels increasing current from 8 kA to 9 kA, due to excess current, compared to higher limit of the welding current range, and expulsion occurrence. For DP, the maximal crack depth is found around 700 μm for current above 11 kA, which is significantly lower, even considering high standard deviation values.

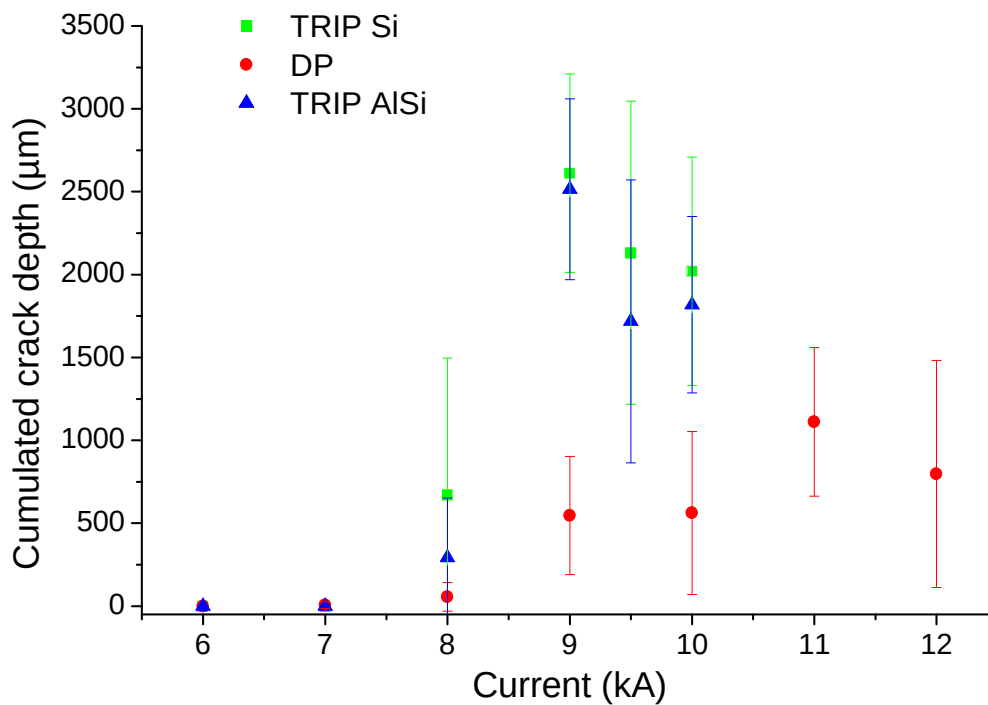


figure 150: Crack depth for the weld vs. welding current

In the next paragraph the influence of the indentation on crack depth is described.

5.2.2. Influence of indentation depth on crack depth

Figure 151 shows the effect of indentation depth on cracking. For the three grades the crack depth is zero for small indentation ($< 130 \mu\text{m}$). Then crack depth increases as indentation depth increases. But it increases more for TRIP than for DP. For the two TRIP grades, crack depth is found around 2000 μm for a 200 μm deep indentation. For DP, maximal crack depth is found around 1000 μm , which is significantly lower, even considering high standard deviation values.

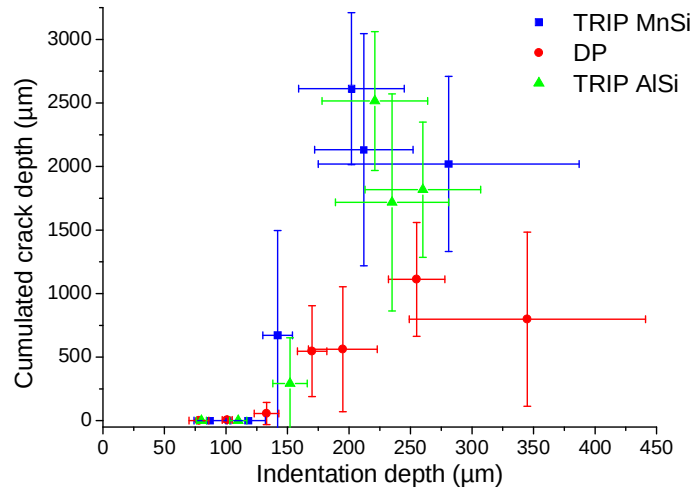


figure 151: Crack depth for the weld vs. indentation depth

Figure 152 shows the detail of indentation depth and crack depth measurements on each face of spot welds. It means that there are two points in this graph for each spot weld. The extreme scatter of results is indicated above by high standard deviation. As a consistent result, no cracked weld is found for indentation depth lower than 130 μm . The continuous increase of crack depth with indentation depth, approximately described by average values (figure 150), is not really observed here.

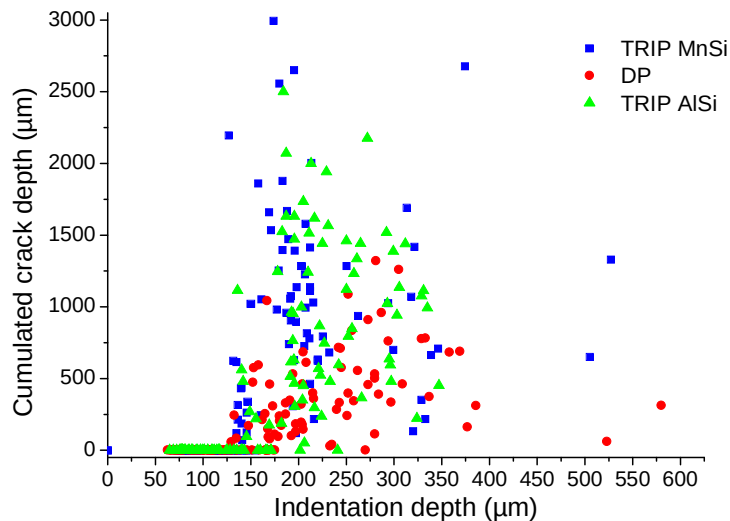


figure 152: Crack depth for one face vs. indentation depth

5.2.3. Influence of surface temperature on crack depth

As above with indentation depth, crack depth can be correlated to surface temperature, as shown in figure 153 and figure 154. Similar description as for the influence of indentation depth can be drawn. The threshold temperature for cracking occurrence is 640 $^{\circ}\text{C}$.

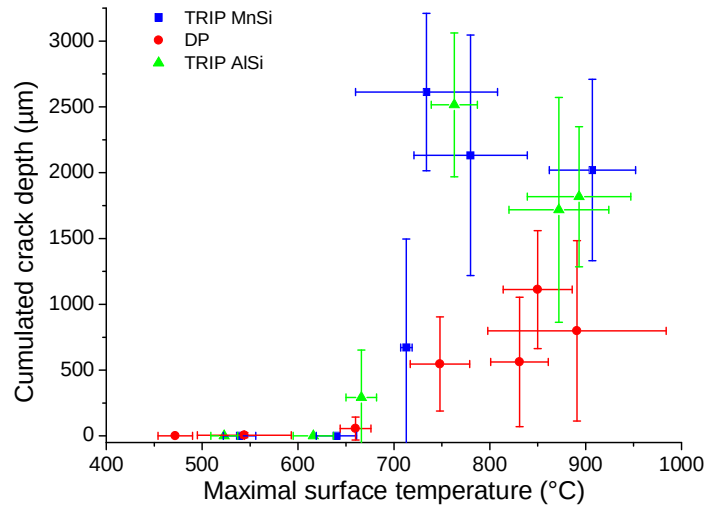


figure 153: Crack depth in the weld vs. maximal surface temperature

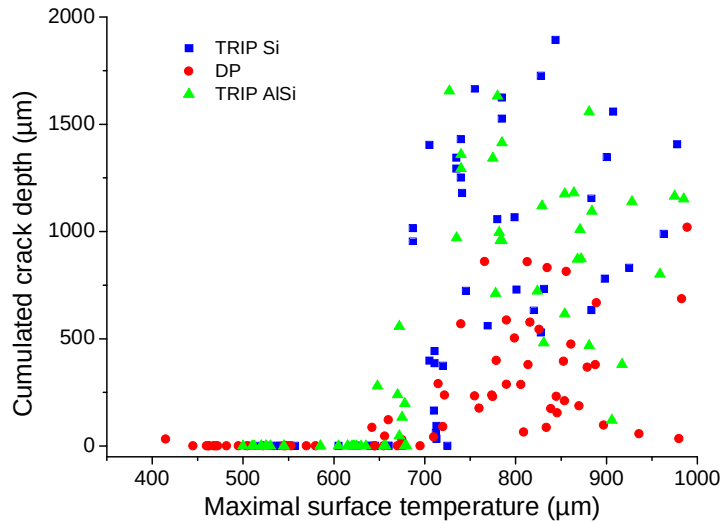


figure 154: Crack depth for one face vs. maximal surface temperature

5.2.4. Influence of other process parameters

As pointed out in welding methods paragraph, welding tests have been carried out following standards process parameters, current being the only parameter to be modified. The influence of other process parameters can be questioned.

Welding force

The influence of welding force, from 150 daN to 1000 daN, has been studied in addition to the test plan given in paragraph 2.1.2. No significant results have been found, but many difficulties for studying the welding force itself are involved. Indeed by increasing welding force, heat input is reduced as the result of the decrease of interfacial resistance. This makes difficult the comparison between different force levels. A tentative adjustment of the current to study different force has been carried out but the results were not

successful. Nevertheless too few tests have been carried out to give significant information. The indentation depth decreases as force increases for constant current. As already told, it is the result of the decrease of the heat input. Here, as a rough interpretation, it seems that welding force is not a key parameter to describe the indentation depth, while the correlation with surface temperature was in direct and good agreement.

Holding time

The influence of holding time, from 2 P to 80 P, has been studied in addition to the test plan given in paragraph 2.1.2. No significant influence on cracking extent has been found. It should be emphasized that this result is less statically relevant since only two welding operations per holding time have been carried out, and the results scatter is high.

Electrode tip face geometry

The influence of the tip face geometry has not been investigated carefully in this study. Some pieces of evidence have shown that welding with higher tip radius and higher face diameter results in decreasing cracking extent. Nevertheless nor significant reports have been found, and no validation of this hypothesis has been performed.

5.2.5. Comments

Even if numerous spot weld operations have been carried out for the characterization of cracking occurrence as a function of welding current, scatter is high. It results in difficult interpretation of detailed results and in high standard deviations on average values. Nevertheless significant difference for cumulated crack depth has been found between TRIP Si and TRIP AlSi on one side, and DP on the other side. DP steel is found to be less sensitive to surface cracking. Furthermore crack depth in the weld can be roughly correlated to the indentation depth (and also to surface temperature characterizing heat input). A threshold indentation depth exists for cracking occurrence, keeping in mind that only cracks deeper than 20 μm have been measured. So it is possible that small cracks exist nevertheless for lower indentation depth. To investigate this part of the problem and to identify microstructure where cracks are found, the next paragraph shows micrographic characterizations of weld cross sections.

5.3. Characterization of crack location and morphology

At this point of the description of surface cracking occurrence, only numerical data have been considered. Even if all cracks that have been measured cannot be described here (it would represent hundreds of figures), some overall observation about the different “types” of cracks observed during the study are given, regarding in particular their location in the weld macro-structure.

5.3.1. Location of cracks and microstructure identification

Figure 155 shows cross sections of weld structures between 6 and 9 kA. Surface cracks and expulsions have been indicated. As already characterized, cracking extent increases as current increases. Here also, increase of weld diameter and indentation depth as current increases is observed.

As a general observation, it is difficult to discriminate two mechanisms of cracking, separately for edge cracks and center cracks. Indeed sometimes deep edge cracks are found with only very few and shallow

center cracks. The opposite (numerous center cracks and only very shallow edge cracks) is also possible and maybe observed more often. But neither discrimination nor quantification has been made. Even if the situation at the edge or in the center appears *a priori* different, the numerous observations do not allow discriminating one from the other. This result is valid for the three grades as DP steel at higher current level (11 kA, 12 kA) can also show deep edge cracks.

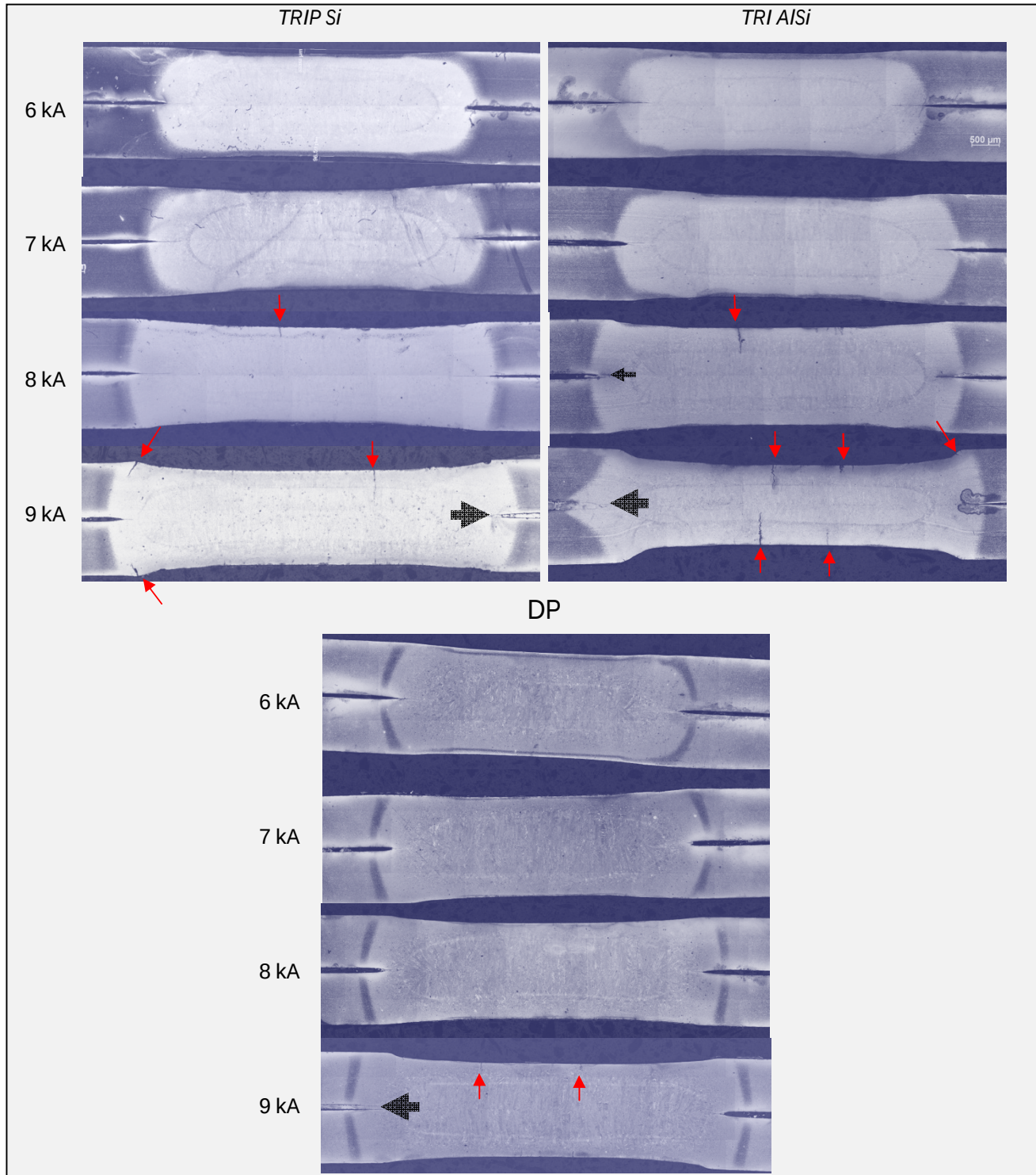


figure 155: Spot welds cross sections for TRIP Si at 6, 7, 8 and 9 kA. Red arrow: surface crack. Black arrow: expulsion

Examples of very shallow cracks and deep cracks at the edge of the electrode imprint are given in Figure 156. Shallow cracks, not deeper than 30 μm , are found in the base metal microstructure meaning that the maximal temperature has not reached A_{c1} . These shallow cracks are several and distributed at the surface. One important observation is that a single deeper crack, say deeper than 50 μm , can be observed only if the supercritical microstructure (T_{max} higher than A_{c3}) is observed at the sheet surface as schematically described in figure 157. In other words HAZ must exceed the indentation width (wider than the electrode tip diameter, namely 6 mm) to observe deep corner cracks.

Examples of very shallow cracks and deep cracks in the center of the weld are given in figure 158.

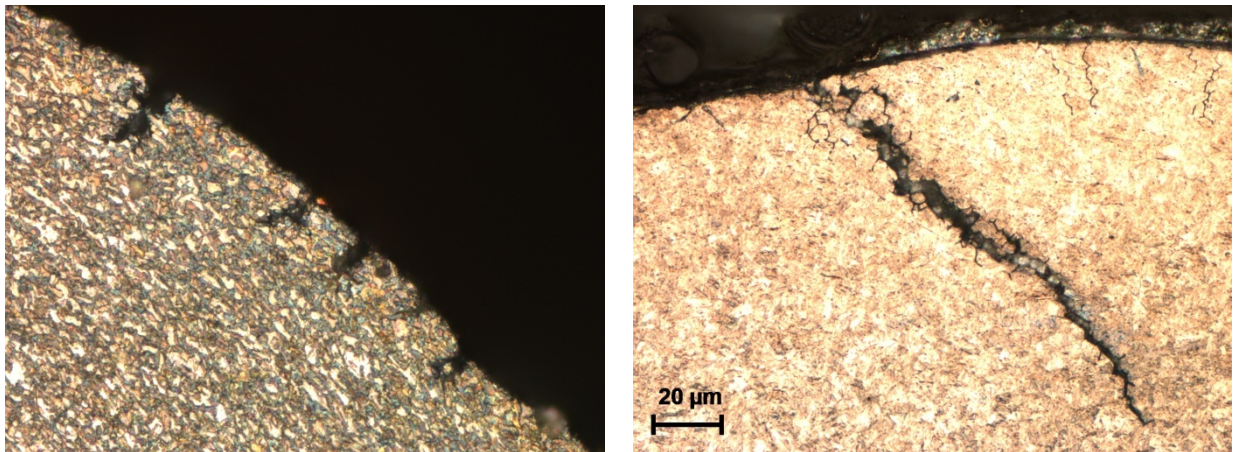


Figure 156: Examples of cracks found at the edge of the electrode imprint. TRIP Si

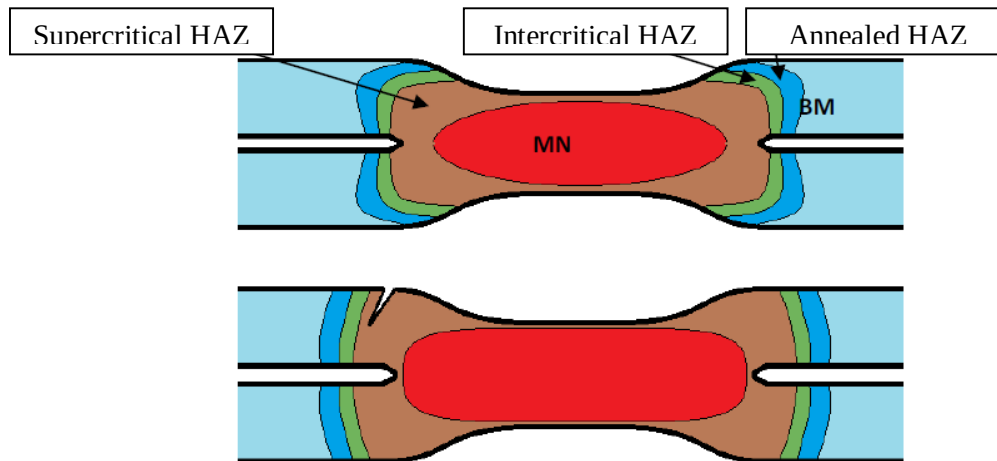


figure 157: Comparison of two spots. Schematic. Deep schematic corner cracks appear when HAZ width exceeds the indentation width. Legend: MN, molten nugget; BM, base metal

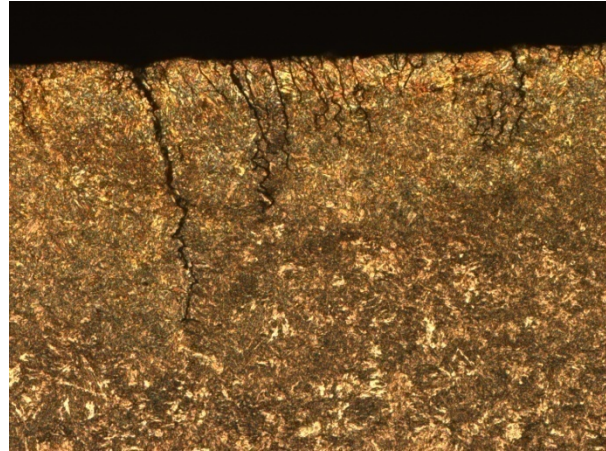
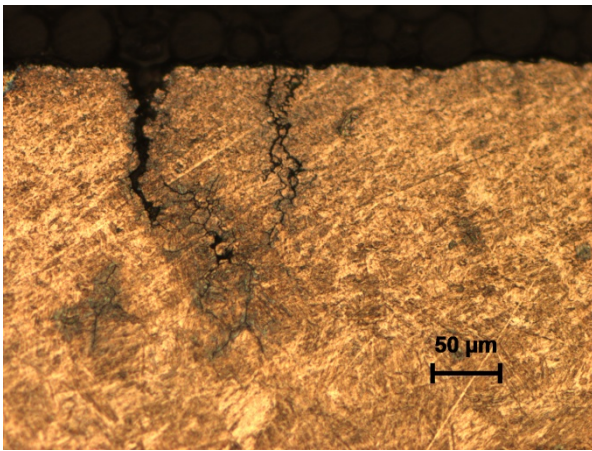
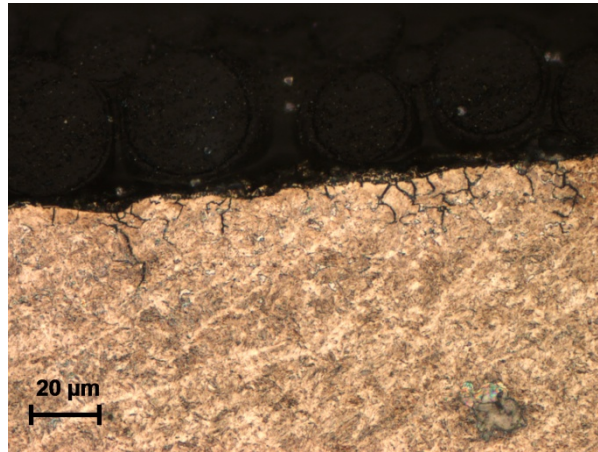


figure 158: Examples of cracks found in the center. TRIP Si

5.4. Surface characterization

5.4.1. Presence of Zn under the electrode

In the center of the weld, SEM-EDX analyses shows that Zn is still present even for high welding current. Figure 159 shows examples for welding TRIP Si at 7 kA and 10 kA. Significant thickness of coating with high concentration of Zn is found whether for high or low current.

Not shown here, the residual coating layer is not constant at the surface, Zn is only present on certain zones in the weld center. It means that liquid Zn is not totally expelled from the steel sheet and can be kept under the electrode, probably due to roughness of electrode and steel sheet surfaces.

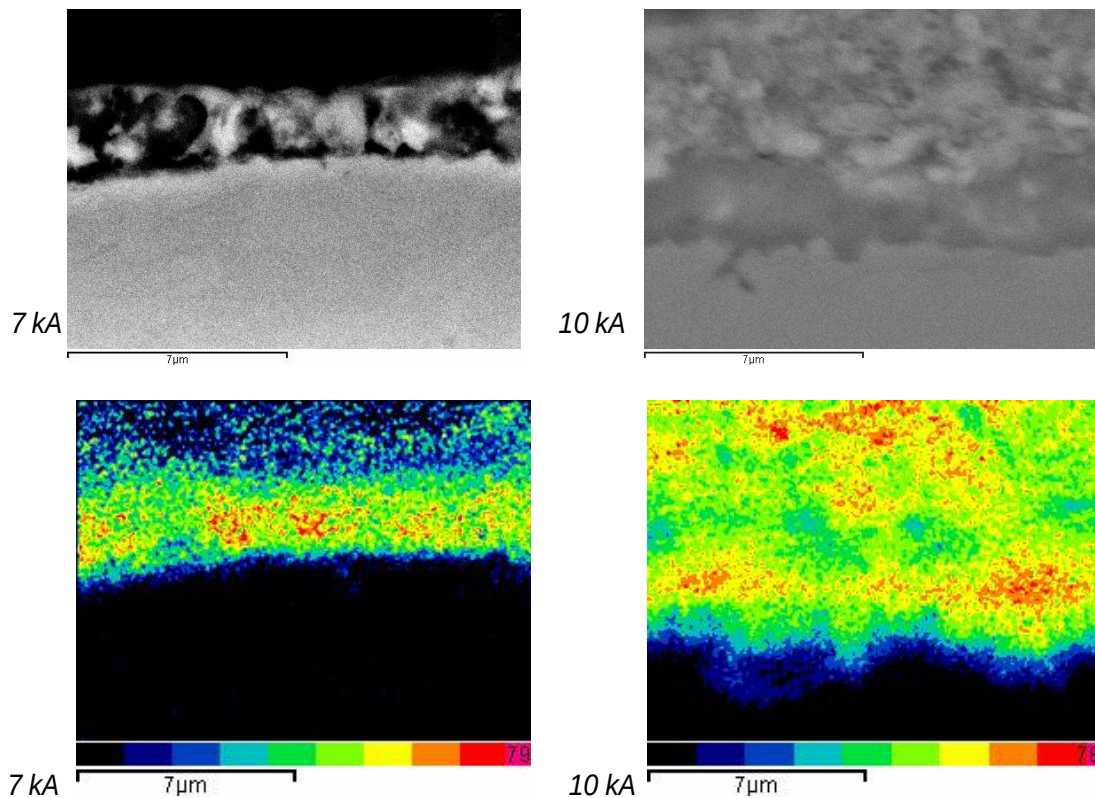


figure 159: Surface analyses shows that Zn is present at the sheet surface in the center of the weld after welding. Top (se2), bottom (Zn wt% by EDX analysis)

5.4.2. Identification of microstructure in the center

Figure 160 shows microstructures typically found at the sheet surface in the center of the weld for TRIP Si and different current levels. In the SEM after etching of polished surfaces, martensite grains of the quenched microstructure appears lighter than ferrite from the base metal. Crystalline contrast is also easier to identify in ferrite grains. Thus Ac1 and Ac3 lines are positioned manually. Ac1 and Ac3 lines go closer to the steel sheet surface (sheet/upper electrode interface during welding) as current increases. Observed thermal gradients are extremely high since, for example for 6 kA, a temperature drop of 270 °C in approximately 70 μm is observed. Cracks have been detected for TRIP Si spots welded with current of 8 kA and more (figure 155). In these spots surface microstructure shows that maximal temperature close to Ac3 is reached during the welding cycle. Figure 161 shows the example of a crack nucleating in intercritical microstructure.

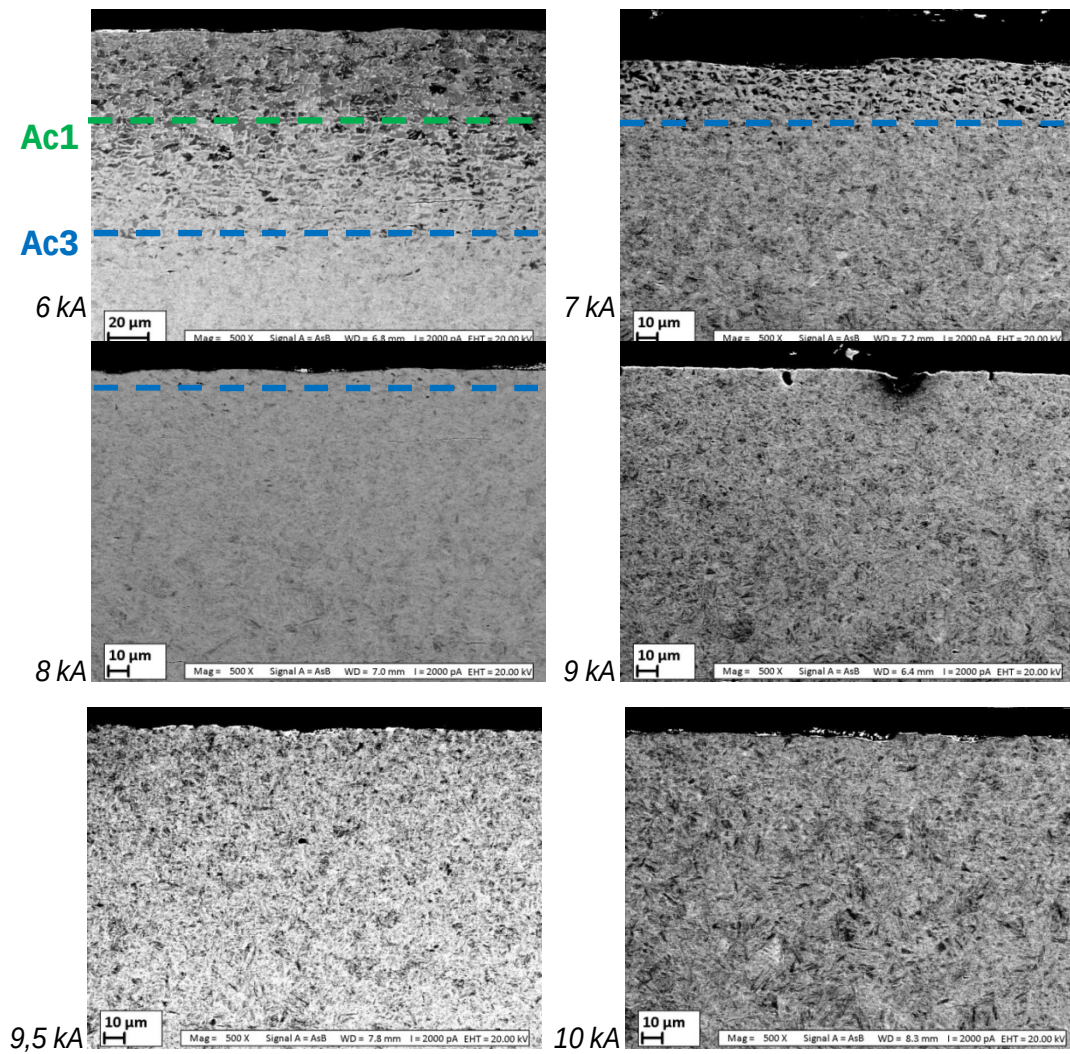


figure 160: Steel microstructure at the sheet surface in the center of the weld (out of cracked areas). TRIP Si. Ac1 = 760 °C, Ac3 = 930 °C

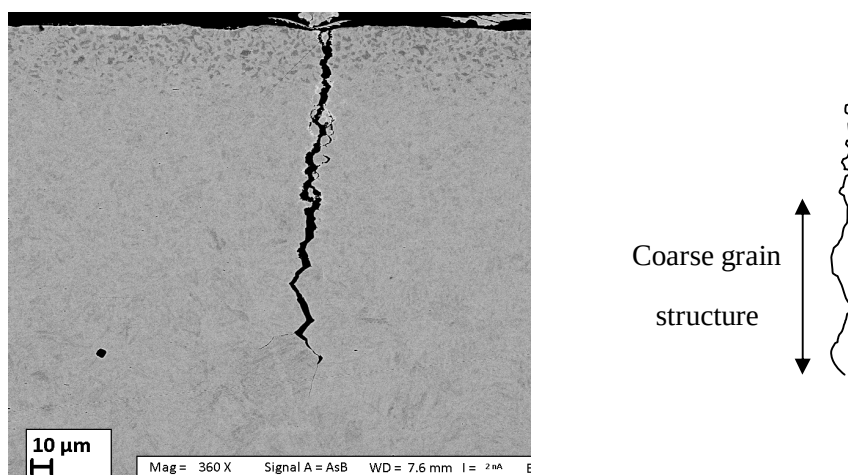


figure 161: Center crack nucleating in intercritical microstructure and propagating further in coarse grain HAZ. TRIP Si, 8 kA

5.4.3. Identification of microstructure at the edge

Figure 162 shows microstructures typically found at the edge of the electrode imprint for TRIP Si and different current levels. Ac1 and Ac3 have been approximately positioned after microstructure identification. Ac1 and Ac3 lines shift further from the center of the weld as current increases. This is in agreement with the temperature measured with the camera in a neighboring area of the weld (figure 140). In other words, the diameter of the heat-affected zone increases as current increases. It seems that deep cracks are only observed if Ac3 line is further than the edge of the electrode imprint, as the examples for 9 kA, 9.5 kA and 10 kA.

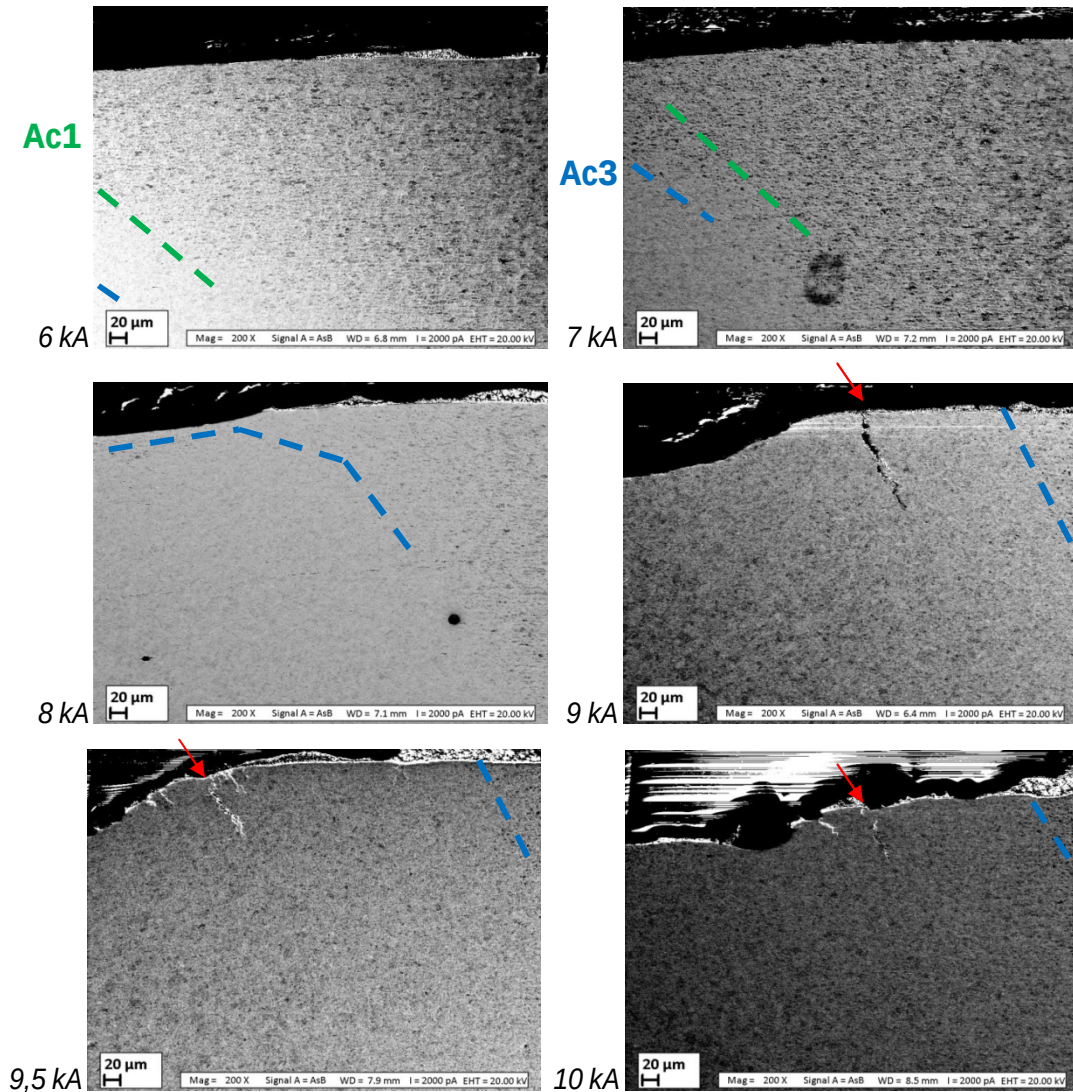


figure 162: Steel microstructure at the edge. TRIP Si. Ac1 = 760 °C, Ac3 = 930 °C

5.4.4. Direct agreement with results from chapter I

Figure 163 shows a corner crack which propagates from the surface in a zone where all GBs are penetrated by Zn, as observed in Chapter I. This observation indicates that temperatures corresponding to the range for wetting and embrittlement described in Chapter I have been reached in the area of cracking.

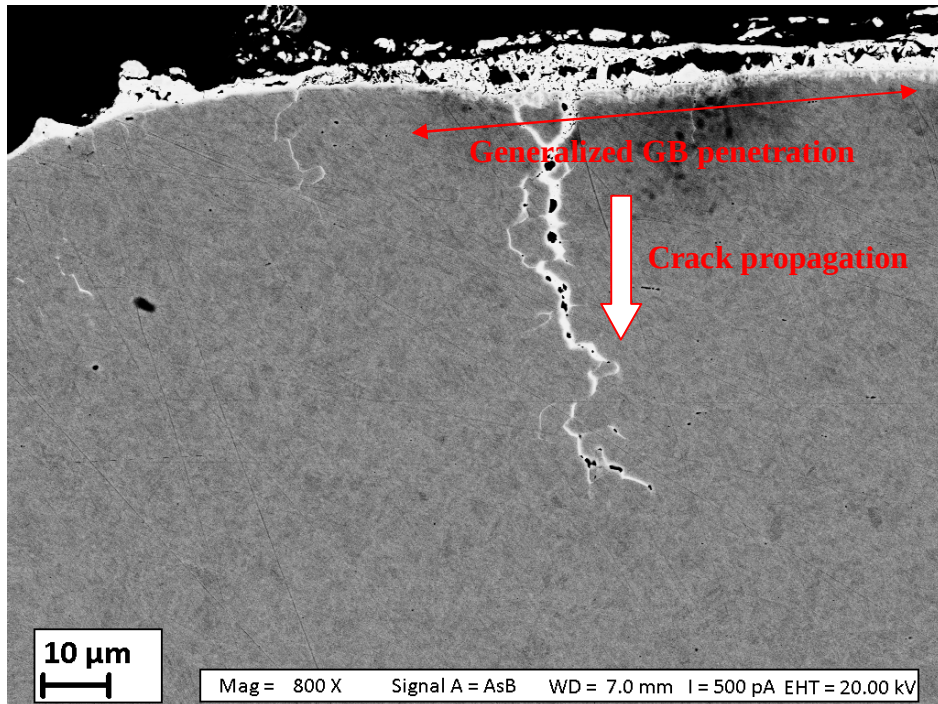


figure 163: The crack propagates in the area where all GBs under the coating are penetrated by Zinc

6. Discussion on surface cracking occurrence

Several experimental results describe cracking occurrence as a function of welding current. Cracking occurrence can also be correlated to surface temperature observed at the edge of electrode imprint, indentation depth, or particular microstructure observed at the surface of the weld.

Here a discussion is carried out to understand the scenario of surface cracking during RSW and the interpretation of the dependence of cracking extent with the parameter just cited above. For that experimental results are correlated with literature data from study of simulation of RSW by finite element (FE).

6.1. About the role of surface strain induced by the indentation

A dependence of cracking extent with indentation depth has been found. Indentation causes deformation, in particular at the surface of the weld. The influence of surface strain induced by the indentation for an explanation of cracking is discussed.

6.1.1. Evaluation of surface strain

Since cracks nucleate at surfaces surface strain is evaluated here assuming that this is mainly caused by the electrode indentation. As in discussion from Chapter I, cracks are supposed to be opened in a tensile mode (mode I in fracture mechanics), not shear.

Surface strain direction

Strain direction need to be questioned. Localization of cracks (figure 146 and figure 148) shows that edge cracks are circumferential, meaning that the circumferential strain should be neglected. So strain involved for surface cracking at the edge of the electrode has a radial and a vertical component. The direction of center cracks seems to have a random character. So strain involved for center cracks has a radial and a circumferential component (center surface is “horizontal”, i.e. no vertical component). In the paragraph below, the 3D axisymmetric geometry is described by analyzing 2D cross sections of welds. The evaluation of surface strain should be considered in what follows as a total (or equivalent) plastic strain without directional information.

Simple geometrical evaluation of surface strain

A simple geometrical analysis on the indented face of a cracked weld shown in figure 164 is carried out. The indentation depth is 299 for a 9 kA weld, which is relatively high (see figure 141). The geometry of the weld surface has been approximated manually through 7 straight lines as shown in figure 165. The diameter of the center, where surface strain is assumed to be homogeneous, has been measured to be 5 800 μm .

After indentation the initial surface diameter w_0 of the weld has been strained to have a diameter w . The average strain $\varepsilon_{average}$ is as follows:

$$w_0 = w_{edge1,0} + w_{center,0} + w_{edge2,0} ,$$

$$w = w_{edge1} + w_{center} + w_{edge2} ,$$

$$\varepsilon_{center} = \frac{w_{center}}{w_{center,0}}, \varepsilon_{edge} = \frac{w_{edge1}+w_{edge2}}{w_{edge1,0}+w_{edge2,0}}, \text{ and } \varepsilon_{average} = \frac{w}{w_0}.$$

The numerical result for the average strain is 0.6 % in the center and 11.4 % at the edges (1.6 % overall). In the center the result is 0.6 %. As expected, surface strain caused by the indentation is mainly localized at the edge of the electrode corner. The present situation can be roughly compared to a stamping test where edges of the indentation are walls and the center of the weld is the bottom of the cup.

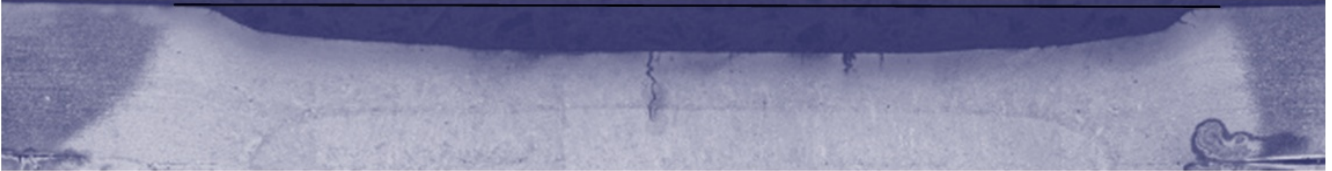


figure 164: Weld face. TRIP AISi, 9 kA

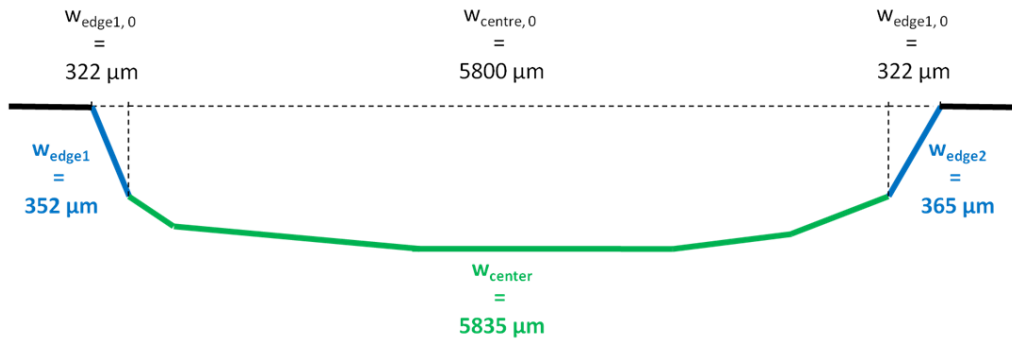


figure 165: Geometrical description of the indented weld face (figure 164). Vertical scale exaggerated

Strain rate

It has been demonstrated that the main contribution for indentation in high current welds is the expulsion of molten metal. Expulsion involves increase of the indentation depth in a time interval of 10 ms (paragraph 4.2.1). If the total indentation is considered to be caused by a single expulsion event, the associated tensile strain rate can be calculated. It is 11.4 s^{-1} and 0.6 s^{-1} respectively for the edges and for the center.

Comments: depth affected by surface strain?

The simple analysis carried out here describes tensile strain at the surface only for a thin thickness. Deeper in the material strain should turn into compression, especially in the center of the weld. The depth where the above analysis is valid is not really known.

The formulation of simplified FE model for a qualitative analysis of the mechanical behavior has been envisaged. As described in this Chapter, RSW is an electrical, thermal, mechanical and metallurgical process. In addition to computational means and know-how, material data in all these fields are needed for a right description of the material behavior during welding. Thus this kind of experiments has not been carried out during the thesis. Literature data about strain found in the literature with FE model are introduced below.

Comparison to literature data from FE model

In the literature many reports of investigations on RSW through FE model can be found. Based on commercial or home-made numerical methods, they are often dedicated to the study of nugget growth or residual stresses after welding. RSW modeling involves many difficulties. About mechanics, the description of material behavior at high temperature seems to constitute one of the main challenges.

Experimental data (data from simulation being interpreted and validated) of stress and strain in the spot weld during weld time are very scarce, in particular regarding the present need of material for discussion.

According to Hou, et al [HOU2007], figure 166 gives the distribution of plastic strain in the weld at the end of welding time for the assembly of two 1.5 mm mild steel sheets. Orange and red areas correspond to plastic strain in the range 2.8 – 3.6 %. The higher strain is found at the steel surface just at the edge of the electrode imprint. Causes of relative high plastic strain level are not detailed by Hou, et al. It may correspond to the mechanical effect of the electrode indentation, exactly as what has been described above. Blue areas at the steel surface in the center of the weld correspond to strain in the range 0.4 – 1.2 %.

So the plastic strain found in this study of RSW through FE simulation is compared to the tensile strain level evaluated with the simple geometric analysis carried out just above. Strain values found at the surface in the center of the weld, between 0.4 % and 1.2 %, are very close to what was found with the very simple geometrical analysis carried out just above, namely 0.6 %.

At the edge of the electrode imprint strain from FEM is less than 3.6 % while it was 11 % in the simple geometrical analysis above. As a general observation about FE model for RSW, expulsion (loss of a material volume) is never taken into account for weld deformation description. In Hou, et al. study the electrode vertical displacement is positive after thermal expansion during and at the end of weld time. In welds studied here, the electrode displacement is negative at the end of weld time due to expulsion during welding time. As a consequence, if expulsion could be taken into account in FE model, it would lead to high values of strain at the edge of the electrode imprint, at least as high as what found with the geometrical analysis of the indentation, namely 11 %.

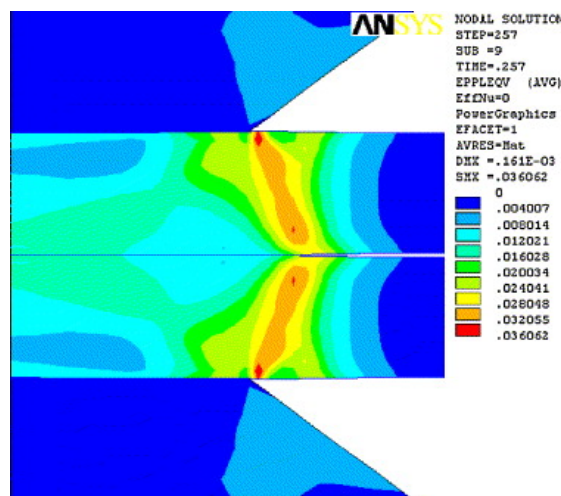


figure 166: Typical plastic strain distribution at the end of weld time. 2 x 1.58 mm mild steel. Current: 12.2 kA, welding: 13P, holding: 3P, force: 300 daN. Reprinted after Z. Hou, et al. [HOU2007]

6.1.2. Temperature of surfaces being strained

Spot weld surfaces are expected to experience strain at relative high strain rate during weld time, in particular at the edge of the electrode imprint when expulsion occurs. In this paragraph the temperature experienced by weld surfaces is evaluated according to information from the experimental characterization of welds.

Maximal temperature reached at the surface

The temperature criterion characterized with the infrared camera describes surface temperature just after the edge of the electrode imprint. Basically, the same information is given by positioning Ac3 boundary at the edge of the electrode imprint (figure 162), since HAZ width increases as camera temperature increases.

Cracked welds are found only if the camera temperature is higher than 640 °C (figure 154) what corresponds to situation where Ac3 has reached the edge of the electrode imprint (observed for TRIP Si steels in figure 162). In the same time observation in the center of the weld shows that Ac3 has also reached the surface (figure 160). So for sufficiently high current the temperature at the surface of the weld can be roughly considered to be homogeneous with a maximal value at the end of weld time around 950 °C or higher (for TRIP Si, Ac3 = 930 °C)

Simple estimation of surface temperature at the moment of straining

Expulsion occurs for TRIP AlSi not exactly at the end but during welding time (figure 144). From those results, expulsion occurs most of the time after half of the total weld time for all steel grades.

On the experimental infrared camera characterization of the welding cycle for TRIP Si at 9 kA given in figure 131 (modified after data processing with equation), the temperature at half of the weld time is 550 °C while the final maximal temperature is 730 °C. This example shows that surface temperature increases not linearly during weld time, but reaches relatively high value at the early stage of welding (here $550/730 = 0.75$). As a rough estimate, surface temperature at the half of weld time can be considered to be around 70 % of the final surface temperature.

Considering (i) the discussion about maximal temperature reached at the surface of weld showing cracks, (ii) the typical evolution of surface temperature during weld time, and (iii) the time of expulsion occurrence resulting in surface strain, surface temperature during straining should be higher than 665 °C (70 % of 950 °C)

Comparison to literature data from FE model

According to [EIS2010], a typical temperature distribution at the end of weld time is shown in figure 167. Temperature at weld surfaces is not exactly homogeneous since overheating is visible after the edge of the electrode, while steel temperature is lower in the center of the weld because of electrode cooling. The temperature during the welding cycle at the electrode sheet surface in the center is shown in the graph. Maximal temperature at the end of weld time is 1000 °C. After half of the weld time it is about 750 °C what is in agreement with the simple estimation made in paragraph just above.

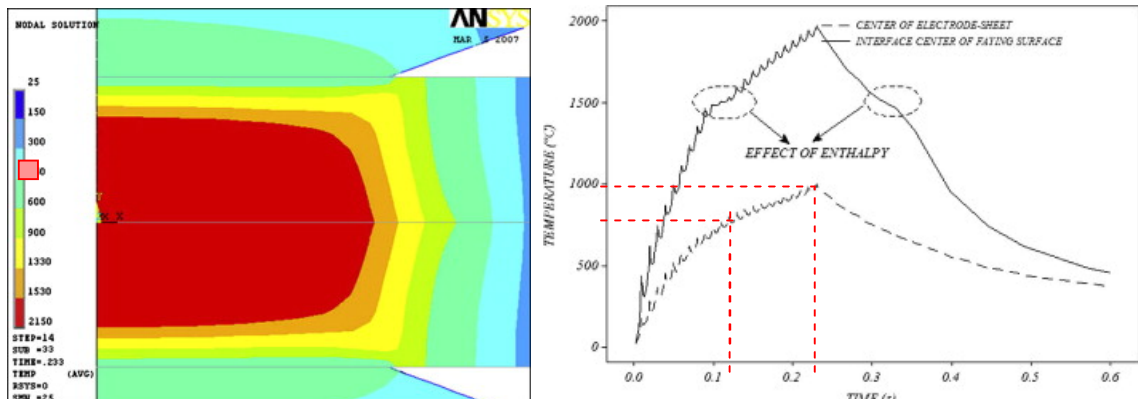


figure 167: Typical temperature (°C) distribution at the end of weld time. 2 x 1.58 mm AISI 1008 steel. Current: 14.2 kA, welding: 14P, force: 467 daN. Reprinted after Eisazadeh, et al [EIS2010]

6.1.3. Comments

The discussion shows that weld surface is being strained during welding. At the edge of the electrode imprint, the representation in figure 168 is proposed for strain due to the electrode indentation based on the argument of the discussion. For welds showing cracks, surface strain is as follows.

- At the edge of the electrode imprint: around 10 %, with 10 s^{-1} of strain rate during 10^{-2} s
- In the center: around 0.5 %, with $5 \cdot 10^{-1} \text{ s}^{-1}$ strain rate during 10^{-2} s

It has been demonstrated that temperature at the moment of straining is probably higher than 650 °C for weld showing cracks.

The correlation with Chapter I can be made. For TRIP grades and DP grade the ductility trough in tensile tests was found for temperatures higher than 700°C and 750 °C, respectively. Indeed it is clear that there is high probability for the material to be strained during welding in the temperature range for LME cracking. Furthermore the strain extent and strain rate involved seem to be relatively high. At the edge of the electrode imprint it is clear than 10 % of strain at 10^{-1} s^{-1} is enough for large cracks propagation. The depth of cracks found after welding may only be limited by the depth in the material affected by the indentation. The plastic strain of figure 168 can explain crack depth from tens of microns to several hundreds of microns.

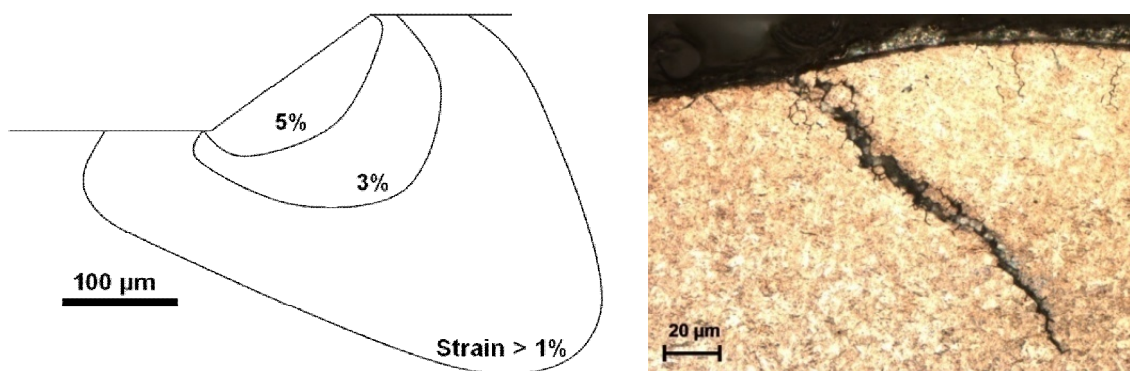


figure 168: Schematic map of plastic strain in the weld at the edge of the electrode imprint for explanation of surface cracks

In the weld surface center, it seems that surface strain caused by the indentation is too low to explain deep cracks. Indeed modeled kinetics of crack propagation from Chapter I, considering strain extent in the center (strain rate $5 \cdot 10^{-2} \text{ s}^{-1}$ during 10^{-2} s), lead to insignificant crack depth. Next section will evidenced that center cracks may propagate during cooling, not during weld time as proposed for edge cracks.

Here the role of surface strain has been approached. It is clear that robust FE simulation of RSW in configurations studied here would be needed for further discussion.

6.2. The role of stress during cooling

In figure 155, deep center cracks propagate in the fusion zone of the weld. In the fusion zone these cracks do not look like solidification cracks. That is why it can be assumed this kind of cracks propagates in fusion zone after solidification. In figure 161 it can be seen that crack shape is not the same close to the surface in the intercritical microstructure or in the supercritical HAZ. This is because grain size is coarser in the supercritical microstructure for sufficiently high temperature (austenite grain growth). So this crack propagates after grain growth, i.e. at the very end of weld time.

These are pieces of evidence to say that such crack do not propagate because of surface strain caused by the indentation. They may propagate during weld cooling.

During cooling tensile stresses exist because of thermal shrinkage of the weld that has been plastically deformed during welding [JOA2007][KOC2008]. Furthermore differential thermal shrinkage coefficient between liquid, austenite and ferrite may also involve high stress level. These stresses probably constitute the cause of deep crack propagation.

Crack propagation in coarse grain austenite microstructure or in the solidified microstructure may not be described by the results of tensile tests from Chapter I. Indeed it is clear that microstructures during cooling (and consequently structural and chemical properties of grain boundaries) are far from microstructures found between $700 \text{ }^{\circ}\text{C}$ and $950 \text{ }^{\circ}\text{C}$ during heating, as investigated during tensile tests.

Here the role of stress during cooling has been approached. It is also clear that robust FE simulation of RSW in configurations studied in this thesis would be useful for further discussion.

6.3. Difference between investigated grades

Surface strain during weld time promotes deep cracking at the edge of the electrode imprint, but is probably only responsible for crack nucleation in the center. Propagation in the center, characterized to occur during cooling, may be driven by tensile stress caused by thermal shrinkage.

Results have shown that cracking extent in DP steel is significantly lower than in TRIP steels. It has been demonstrated that this difference cannot be explained by a lower indentation or lower surface temperature, and remained unexplained if only the present characterization of material behavior during RSW is considered.

Chapter I has shown that the ductility trough area (in the elongation-temperature diagram) is lower for DP than for TRIP steels. This is explained in particular because LME cracking occurs only for temperature

higher than around 740 - 780 °C for DP steel, while it for temperature higher than 690 – 700 °C for TRIP steels. This difference in the temperature range of the ductility trough may be considered for the discussion of cracking sensitivity in RSW.

The probability for DP that an expulsion event takes place in the temperature range for LME cracking is lower than for TRIP steels. This can lead to less cumulated crack depth in the weld. Furthermore the time in the temperature range for liquid zinc penetration and crack growth is lower for DP than for steels leading to less time for subcritical crack growth. Then propagation of cracks during cooling could be supposed to be more difficult in DP.

7. Conclusion and outlooks

The issues resulting from liquid zinc embrittlement of steels at high temperature during resistance spot welding have been addressed.

First characterization of the welding process has been carried out by usual welding metallurgy means, and through innovative techniques: surface temperature measurement through infrared thermography and electrode displacement characterization through high speed camera monitoring.

- The effect of an increase of welding current is :
 - nugget diameter increases from 4 mm to 6,5 mm ;
 - surface temperature increases from 550 °C to 900 °C ;
 - indentation depth increases from 80 µm to 300 µm for each side of the weld,
- These parameters are correlated together.

For welding current above the welding range, expulsion decreases the volume of the weld and consequently increases abruptly the indentation. Expulsion occurs typically during the second half of the welding time.

Cracks are identical to that observed into tensile specimens. They appear from the surface in center of the weld and at the edge of the electrode imprint. Cracking has been quantified by measuring a cumulated crack depth on the cross section of the weld. For low welding current, the cumulated crack depth is zero. Cracking appears as current increases. Above the welding range and with the expulsion, cracking extent becomes high.

The increase of cumulated crack depth is correlated to :

- the increase of indentation depth ;
- the increase of surface temperature ;

A discussion based on simple analyses of temperature and deformation has been carried out.

- Surface deformation (caused by the indentation) from 1 % to 10 % has been estimated with strain rate from 0.5 s^{-1} à 10 s^{-1} . Deformation is particularly high at the edge of the electrode imprint.
- During straining, temperature is in the range of 650 °C 1000 °C for welds found susceptible to crack.

These results are in very good agreement with those from Chapter I for the occurrence of embrittlement. Cracking appears at the moment of expulsion during the second half of the welding time before cooling starts. This scenario is able to explain the cracking extent at the edge of the electrode imprint. In the center, it seems that deformation extent is not sufficient to explain deep cracks. The influence of stresses during cooling due to weld shrinkage is probably involved for further crack propagation.

Chapter III Analyse de la sensibilité des nuances : vers des solutions industrielles

Le Chapitre I a décrit l'occurrence de la fragilisation en fonction des caractéristiques des matériaux et des contraintes mécaniques. Le Chapitre II a caractérisé l'influence des paramètres process et des caractéristiques des points soudés sur l'apparition de la fissuration de surface. A ce stade de l'étude, une différence intrinsèque de sensibilité de la nuance vis-à-vis de la fissuration est observé entre les deux aciers TRIP d'une part, et l'acier DP d'autre part.

L'acier DP est moins sensible. Le puits de ductilité commence seulement à partir de 750 °C alors qu'il commence dès 700 °C pour les aciers TRIP. Toutes caractéristiques égales des soudures (température et indentation), la fissuration est moins importante pour le DP que pour les TRIP au cours du soudage. Ceci peut d'ailleurs être relié à la largeur du puits de ductilité caractérisé en traction.

Dans ce dernier chapitre, la différence de sensibilité entre les nuances est discutée en fonction de l'influence de la microstructure et de la composition chimique.

Des hypothèses basées sur les apports des chapitres I et II sont d'abord formulées.

Pour aller plus loin, une base de données établie au centre de recherche ArcelorMittal de Maizières-lès-Metz est introduite. Elle présente les résultats d'essais de traction à chaud (protocole proche de celui du Chapitre I) réalisés sur de nombreuses nuances DP et TRIP avec des compositions chimiques variées. La composition chimique et la sensibilité à la fissuration seront liées de manière quantitative.

A partir de ces résultats et interprétations, quelques lignes directrices sont formulées pour le développement futur des aciers vis-à-vis de la fissuration induite par le zinc liquide.

Pour finir sur des perspectives concrètes, deux solutions pratiques conçues pour supprimer la fissuration seront présentées.

1. Analyses des différences entre les nuances étudiées

A partir des mécanismes décrits dans le Chapitre 1, les conséquences des différences de microstructure et de composition chimiques entre les 3 nuances étudiées sont discutées. Ceci sera fait pour les trois critères supposés avoir une influence sur la fragilisation.

- La température de transition de mouillage. Le lien avec les différentes énergies interfaciales et la nature des joints de grains dans les deux types d'aciers sera discuté.
- Les paramètres influençant le mécanisme de propagation locale:
- la concentration limite pour la transition de pré-mouillage. Le lien avec la solubilité de Zn dans l'acier sera discuté.
- les contraintes en fond de fissure. L'influence de la résistance mécanique de l'acier à haute température sera discutée.

1.1. Influence de la nuance d'acier sur la transition de mouillage

A propos des nuances caractérisées pendant la thèse, la première différence entre TRIP et DP est leur microstructure, en supposant que les vitesses très rapides de chauffage n'entraînent pas de modification de la microstructure (dénaturation de l'austénite ou de la martensite) avant d'atteindre le point critique Ac1. Le DP est composé de martensite et de ferrite. Les joints de grains sont en fait des joints interphases ferrite/martensite. Les TRIP sont composés de ferrite, bainite et d'austénite résiduelle. La plupart des joints de grains sont donc des joints interphases ferrite/austénite retenue. Le terme générique joint de grains est utilisé pour désigner les différents joints interphases.

Nous avons analysé la limite basse pour la gamme de température de fragilisation comme une transition de mouillage caractérisée par les énergies interfaciales solide/liquide et les énergies des joints de grains. En dessous d'Ac1, les deux inéquations suivantes décrivent la situation de fragilisation

$$TRIP : \gamma_{ferrite/austenite} > \gamma_{ferrite/Zn} + \gamma_{austenite/Zn}.$$

$$DP : \gamma_{ferrite/martensite} > \gamma_{ferrite/Zn} + \gamma_{martensite/Zn}.$$

La chute de la ductilité a été observée à plus haute température pour le DP que pour les TRIP. C'est-à-dire que, grossièrement entre 700 °C et 750 °C, l'inégalité ci-dessus pour les TRIP est vérifiée mais pas celle pour le DP. Ceci peut s'expliquer de plusieurs manières, en considérant soit l'influence de la phase cristallographique (martensite ou austénite) sur l'énergie des joints de grains, soit l'influence sur l'énergie de l'interface avec le Zn liquide, soit les deux.

1.1.1. Différences entre les énergies des joints de grains

Hypothèse

Il est possible que le décalage vers les hautes températures de la transition de mouillage soit dû au fait que l'énergie des joints ferrite/austénite soit plus grande que celle des joints ferrite/martensite comme l'indiquerait l'inégalité :

$$\gamma_{ferrite/austenite} > \gamma_{ferrite/martensite} \quad (35)$$

L'interface ferrite/austénite serait plus instable que celle ferrite/martensite en présence de Zn. Il est très difficile de trouver des données dans la littérature qui permettraient de confirmer cette hypothèse. Les paragraphes suivant comparent ces deux types d'interface.

Discussion : structure et incohérence de l'interface

La structure de l'interface pour un joint général, *i.e.* de forte désorientation, peut être approximer par la différence de paramètre de maille entre les deux phases en contact. Pour les paramètres de maille à 700 °C, les données ont été regroupées dans la table 19. Ces valeurs sont valables pour des taux de carbone de 0,1 – 0,2 %m. L'influence des autres éléments d'alliages sur les paramètres de maille n'a pas été prise en compte. Les paramètres de maille de la martensite sont beaucoup plus proches de la ferrite, que ne le sont ceux de l'austénite. L'appréciation qualitative suivante peut être envisagée. Vu la ressemblance de la structure cristalline entre la martensite et la ferrite par rapport à l'austénite, il est probable que l'énergie d'un joint général ferrite/martensite soit inférieure à celle d'un joint ferrite/austénite. Mais il semble impossible de dire dans quelle mesure vu les nombreux paramètres mis en jeu dans la description de l'énergie interfaciale. Même s'ils sont très qualitatifs et nécessitent de plus profondes discussion, ces éléments tendent à confirmer l'inégalité (35).

table 19: Données pour les paramètres de maille dans les aciers

Phase	Type	Paramètre	T (°C)	Paramètre (nm)	Réf
Ferrite	cc	a	700	0.289	[ONI1993]
		a	20	0.286	[BAB2005]
Martensite	h	a	20	0.285	[CHE1991]
		a	20	0.290	[RAM2006]
		a	20	0.285	Cité dans [CHE1990]
		c	20	0.299	[CHE1991]
		c	20	0.297	Cité dans [CHE1990]
Austénite	fcc	a	700	0.366	[ONI1993]
		a	700	0.365	[RAM2006]
		a	20	0.359	[YAS2009]
		a	20	0.357	Cité dans [CHE1990]

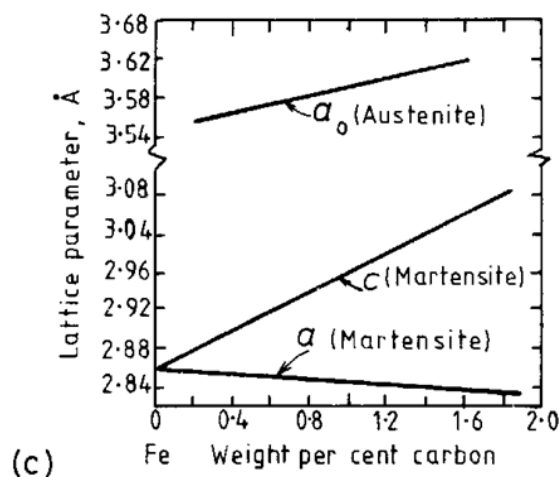


figure 169: Paramètres de maille de la martensite et de l'austénite. Influence du taux de carbone. Reproduit après [ROB1953]

Discussion : influence chimique (ségrégation de soluté) sur l'énergie du joint de grain

Un autre facteur vient modifier les énergies des joints de grain : la ségrégation interfaciale de certains éléments d'alliages. La ségrégation d'espèces à faible limite de solubilité dans le fer diminue l'énergie des joints de grains. C'est le cas par exemple du phosphore [HON1965] ou du bore [MORTIMER1975]. Il est très difficile d'avoir une hypothèse quantitative à propos de l'énergie des joints de grains de nos aciers. Cette discussion n'est pas menée dans ce manuscrit. Par contre les indices qui montrent qu'une solution peut-être envisagée à l'aide d'un élément ségrégeant aux joints de grains sont donnés en fin de chapitre.

Données chiffrées sur l'énergie des joints de grains de l'acier

La table 20 présente les données récoltées dans la littérature à propos des énergies des joints ferrite/ferrite et ferrite/austénite. Aucune donnée n'a été trouvée concernant les joints ferrite/martensite. Il est difficile de tirer des conclusions sur les différences entre les interfaces ferrite/martensite et ferrite/austénite dans les aciers de l'étude. Ce tableau donne néanmoins l'ordre de grandeur des énergies interfaciales.

table 20: Données pour les énergies des joints de grains dans les aciers

Interface	Température (°C)	Energie (J m ⁻²)	Référence
ferrite/ferrite	700 – 1000	1,0	[CHO2013]
	700 – 1000	0,8	[TONG2004]
ferrite/austénite	700 – 1000	1,0	[CHO2013]
	700 – 1000	0,56	[TONG2004]
	-	1,0	[LOG2004]
	-	0,2 – 0,8	[BOT1998]
	-	0,4	[THI2006]
austénite/austénite	700 – 1000	1,9	[CHO2013]
	700 – 1000	0,79	[TONG2004]
	-	0,7	[THI2006]
	1050	0,5 – 0,8	[MOR1975]

1.1.2. Différence entre les énergies solide/Zn liquide

Hypothèse

Il est possible que le décalage vers les hautes températures de la transition de mouillage soit dû au fait que l'énergie de l'interface austénite/Zn liquide soit plus petite que celle de l'interface martensite/Zn liquide comme l'indiquerait l'inégalité suivante :

$$\gamma_{austenite/Zn\ liquide}(TRIP) < \gamma_{martensite/Zn\ liquide}(DP). \quad (36)$$

L'interface austénite/Zn liquide favoriserait plus le mouillage que l'interface martensite/Zn liquide. Aucune donnée n'a été trouvée dans la littérature. Ici cette énergie interfaciale est métastable : le contact entre le Zn liquide et l'austénite ou avec la ferrite en dessous de 780°C (point de fusion de l'intermétallique Γ) n'est pas explicitement décrit. En effet le diagramme de phase décrit la formation d'intermétalliques. La relation entre solubilité et énergie interfaciale est discutée dans le paragraphe suivant.

Discussion : lien entre solubilité mutuelle et énergie de l'interface

Dans le diagramme de phase Fe-Zn, la boucle austénitique est très petite. De plus l'ajout de silicium (comme dans certains alliages de l'étude), alphagène, réduit encore le domaine austénitique. La solubilité du Zn dans l'austénite est très faible $< 1\%$. Pour la ferrite la solubilité est beaucoup plus grande. La cristallographie de la martensite est plus proche de la ferrite que de celle de l'austénite. La solubilité du Zn dans la martensite est supposée plus grande que dans l'austénite.

Or il a été montré que l'énergie interfaciale diminue quand la solubilité mutuelle augmente à température constante. Ceci est indiqué par exemples dans [GIR1957][FRE1922][DON1952] et plus récemment dans [HIN2011]. Vu ces arguments, l'énergie interfaciale martensite/Zn liquide semble plus faible que celle austénite/Zn liquide. Ceci va dans le sens de l'équation (36). Les variations d'énergie indiquées dans les références citées semblent néanmoins faibles.

1.1.3. Résumé sur les énergies interfaciales

Dans les paragraphes précédents, l'influence de la microstructure sur l'énergie des joints de grains de l'acier a été discutée. La figure 170 illustre l'hypothèse de la plus grande énergie de l'interface ferrite/austénite par rapport à celle ferrite/martensite. La conséquence est que la température de transition de mouillage est trouvée à plus basse température. Ceci explique le décalage observé pour le puits de ductilité.

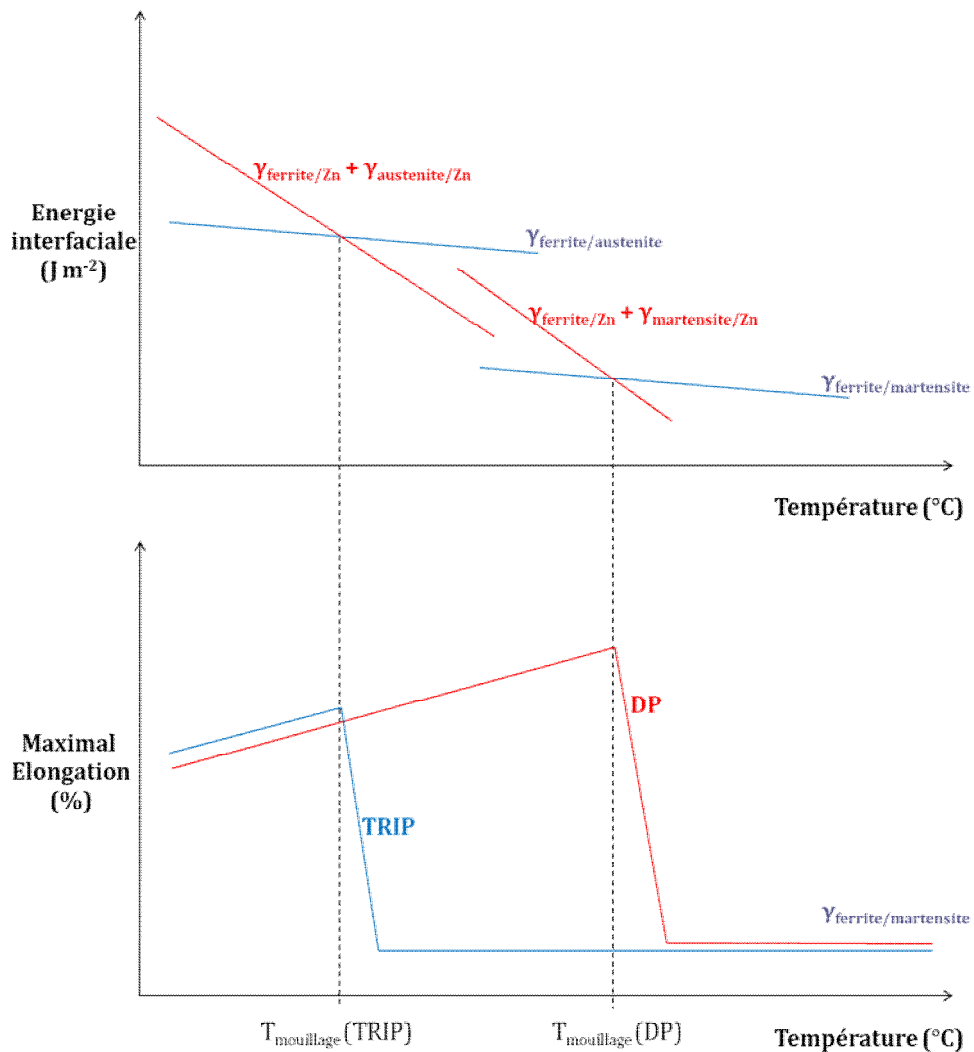


figure 170: Représentation schématique des énergies interfaciales, des températures de transition de mouillage, et des conséquences pour la ductilité de l'acier en contact avec Zn.

1.2. Influence de la nuance d'acier sur le mécanisme de propagation

1.2.1. Influence sur la concentration limite pour le mouillage

Le Chapitre 1 s'est terminé par la définition d'un mécanisme local de propagation de fissure, valable lorsque l'on se trouve au dessus de la température de transition de mouillage. Un incrément de la longueur de fissure se produit lorsque la concentration en Zn en pointe de fissure atteint une valeur entraînant la transition de mouillage du joint de grain. En d'autres termes, il faut que la concentration volumique en Zn atteigne localement la limite de solubilité du joint de grain pour poursuivre la propagation de la fissure.

La composition chimique a une influence sur la limite de solubilité de Zn dans le fer alpha. Par exemple, le taux de Si diminue fortement la solubilité de Zn dans la ferrite (voir paragraphe 2.4.1). Or le taux de Si est plus élevé pour les aciers TRIP que pour l'acier DP. Ceci constitue la principale différence de composition chimique entre ces deux types de nuances.

On peut ici supposer que la baisse de la limite de solubilité en volume entraine la baisse de la limite de solubilité pour le joint de grain. Ainsi, au dessus la température de transition de mouillage, l'acier DP aura tendance à fissurer moins vite que les aciers TRIP.

1.2.2. Influence sur les contraintes en fond de fissure

Dans le chapitre 1, le facteur d'intensité de contrainte K_I en fond de fissure influe directement sur la vitesse de fissuration. Celui-ci est fonction de la contrainte appliquée et de la profondeur de la fissure. Dans le chapitre 1, la contrainte appliquée a été assimilée à la limite d'élasticité (ou contrainte d'écoulement) décrivant le comportement mécanique parfaitement plastique à haute température.

Donc à température et vitesse de déformation constante (le cas des essais de traction du Chapitre 1), une nuance avec une contrainte d'écoulement plus grande présentera un K_I plus grand pour la même profondeur de fissure. La littérature indique que des relations entre la dureté et la sensibilité à la fragilisation par les métaux liquides existent. La figure 171 présente par exemple le cas de la gravité de la fragilisation par le zinc d'acier de structure aux températures de galvanisation à chaud.

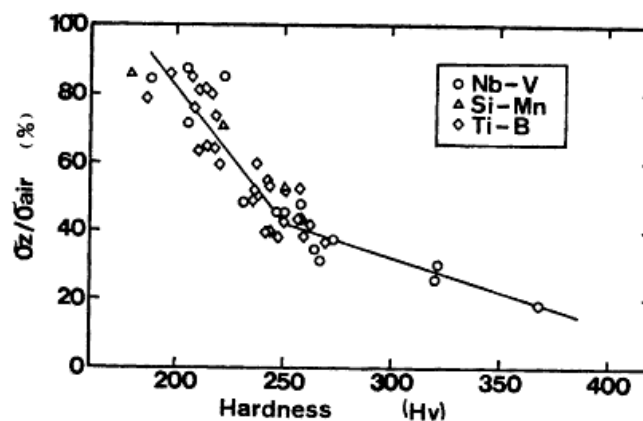


figure 171: Corrélation entre la dureté et la sévérité de la fragilisation

Il est possible de modéliser la contrainte d'écoulement en fonction de la composition chimique (voir paragraphe 2.4.2). Néanmoins les essais n'ont pas montré de différences notables entre les contraintes d'écoulement ou les contraintes à rupture entre les aciers TRIP et l'acier DP (figure 44). Il semble donc peu probable qu'une faible différence de contrainte ait une influence de premier ordre.

Il faut aussi noter le point suivant. Si l'interprétation de l'influence de K_I est faite seulement en considérant son influence sur l'ouverture en fond de fissure (CTOD) et que le matériau est parfaitement plastique (pas d'écrouissage, écoulement à contrainte constante), alors l'influence de la limite d'élasticité (ou contrainte d'écoulement) à module d'Young constant est nulle.

1.2.3. Résumé sur le mécanisme en fond de fissure

La solubilité et le facteur d'intensité de contrainte peuvent probablement indiquer que l'acier DP présentera des vitesses de fissuration plus faible que les aciers TRIP étudiés. Ce résultat est présenté sur la

figure 172. Les plus faible vitesses de fissuration supposée pour l'acier DP ont pour conséquence que la descente dans le puits de ductilité est moins rapide. De manière apparente, le niveau atteint dans le puits est plus haut.

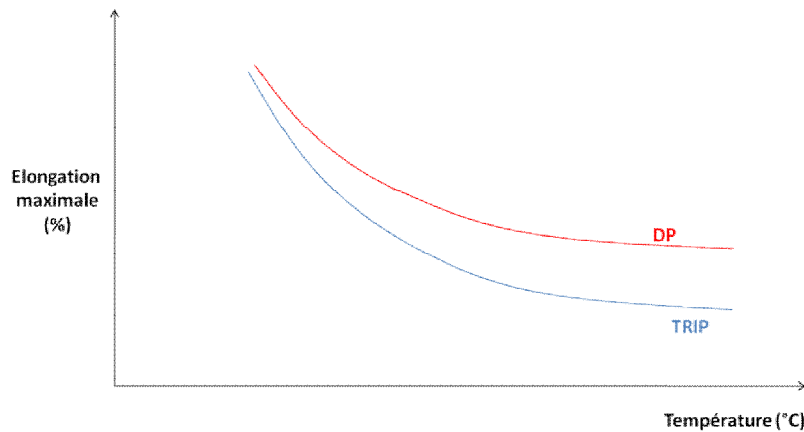


figure 172: Représentation schématique de la différence de la forme du puits entre les aciers TRIP et l'acier DP

1.3. Résumé des hypothèses pour la différence entre TRIP et DP

La microstructure influence la température de transition de mouillage et modifie la gamme de température de fragilisation. Ainsi la présence de martensite à la place de l'austénite semble réduire la sensibilité à la fissuration par le zinc. La caractérisation expérimentale du mouillage n'a cependant pas été faite sur l'acier DP et l'acier TRIP AlSi. De plus des données sur les énergies interfaciales seraient nécessaires pour poursuivre la discussion. D'autre part l'influence de la chimie locale et les différences à ce propos entre TRIP et DP sont inconnues.

La composition chimique influence la vitesse de propagation de fissure. Ainsi, l'acier DP, moins allié en Si, semble potentiellement moins sensible de ce point de vue aussi. Comme cela a déjà été dit dans le Chapitre 1, une vérification expérimentale du mécanisme en fond de fissure est très difficile.

La plupart des hypothèses pour la différence entre l'acier DP et les aciers TRIP a été listée dans cette section. Une discussion qualitative de ces hypothèses a été tentée.

Il est très difficile de conclure sur l'influence de la microstructure et de la composition chimique simplement à partir de l'étude de trois nuances. L'étude d'un grand nombre de nuances a été impossible dans le temps de la thèse. Pour préciser et confirmer ces hypothèses, l'analyse d'une base de données de résultats provenant d'ArcelorMittal Maizières qui porte sur de nombreuses nuances d'aciers DP et TRIP de diverses compositions chimiques est effectuée.

2. Classification de la sensibilité des nuances ArcelorMittal

2.1. Bases de données

2.1.1. Contexte

Une étude plus large est nécessaire pour préciser certaines des hypothèses émises pour expliquer la différence de sensibilité entre les nuances étudiées. La fissuration de surface est étudiée depuis plusieurs années chez ArcelorMittal. De nombreux essais de soudage ont donc été effectués. Les essais de soudage sont difficiles à utiliser pour quantifier la sensibilité à la fissuration d'une nuance vue la forte variabilité du procédé, de l'apparition et de la quantification du défaut. Le Chapitre 2 a permis de montrer la forte dispersion des résultats individuels et la forte incertitude sur les valeurs moyennes.

Un essai de type traction à chaud a été conçu pour mieux étudier la sensibilité à la fissuration par le Zn.

2.1.2. Méthode

L'essai est effectué sur une machine Gleeble 3500, du même type que celle utilisée dans le Chapitre I. Après chauffage à la température d'essai en 1 s, l'éprouvette est déformée immédiatement jusqu'à atteindre une déformation visée. Cette déformation cible est atteinte en 1 s. La déformation est maintenue et le chauffage de l'éprouvette est interrompu. Cela consiste de fait à un essai de traction interrompu. Les vitesses de déformation varient entre 0.02 s^{-1} et 0.3 s^{-1} . Par observation visuelle de l'éprouvette, la présence de fissure est déterminée. Des essais à différentes valeurs de déformation imposée et à plusieurs températures sont réalisés. Sur le diagramme Elongation-Température, la ligne correspondant à la déformation critique en fonction de la température est tracée entre les éprouvettes fissurées et non fissurées, comme le montre la figure 173. La déformation minimale, appelée déformation critique, est utilisée comme critère de sensibilité à la fissuration pour la nuance. Celle-ci est arrondie au pourcent près.

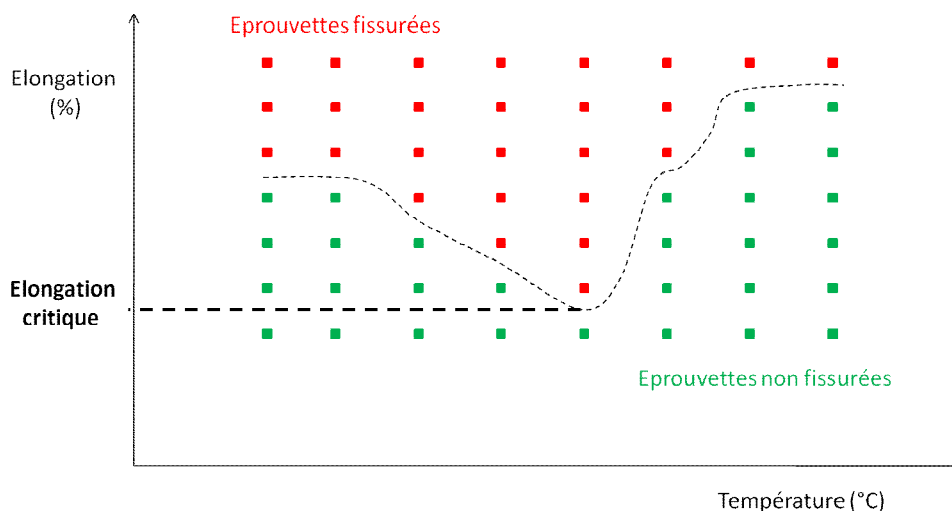


figure 173: Représentation des essais et de l'élongation critique

2.1.3. Comparaison avec les résultats du chapitre I

Pour l'acier TRIP Si, les résultats du Chapitre I (élongation à rupture en traction monotone), et les résultats obtenus à Maizières (« élongation critique ») sont comparés. La figure 174 montre que les résultats sont très proches. La déformation critique relevée pour le TRIP MnSi sur la courbe de Maizières est 5 %.

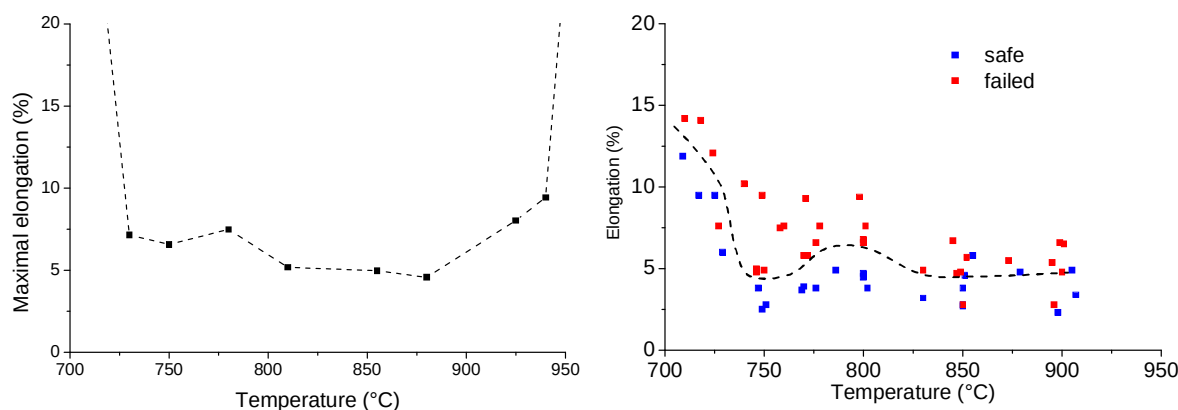


figure 174: Comparaison des résultats du Chapitre I (gauche) avec ceux obtenus à Maizières (droite)

Commentaire

Comme cela a été dit, le critère « élongation critique » obtenu avec l'essai de Maizières mesure en fait la ductilité résiduelle dans la gamme de température de fragilisation, c'est-à-dire le niveau du fond du puits de ductilité. Dans le Chapitre I, l'élongation critique est sensiblement la même : entre 5 et 7 %. Il est montré plus loin que le fond du puits pour les nuances caractérisées à Maizières peut varier entre 4 % et 25 %. La capacité de l'essai effectué à Maizières pour différencier le niveau du fond du puits est remarquable.

Après plusieurs essais, il semble qu'un essai de traction classique, i.e. monotone jusqu'à rupture de l'éprouvette, ne soit pas capable de différencier aussi bien le comportement des nuances. La différence entre les deux essais est pourtant faible. Le fait que l'essai de Maizières soit un essai arrêté, ajouté au caractère cinétique « lent » de la fissuration décrit au Chapitre I, explique peut-être cette différence.

2.1.4. Nuances étudiées et composition chimique

30 nuances d'aciers de microstructure de base TRIP et DP ont été étudiées. Ces nuances ont des résistances mécaniques à froid comprises entre 700 MPa et 1000 MPa. Les compositions chimiques des principaux éléments d'addition sont présentées dans la table 21.

Les autres éléments de microalliage (Ni, Cu, Ti, B, etc.) ainsi que les traces et impuretés (Sn, P, S, etc.) seront aussi étudiés dans la suite. Les compositions chimiques ne sont pas données pour des raisons de confidentialité.

table 21: Gammes de composition étudiées

Elément	Composition min (%m)	Composition max (%m)
C	0.08	0.25
Mn	1.50	2.00
Si	0.06	1.70
Al	0.02	1,60
Cr	0.02	0,29
Mo	0.00	0,19

2.2. Résultats

La figure 175 présente les résultats obtenus à Maizières sur les 30 nuances de microstructure TRIP et DP réalisés par la méthode présentée ci-dessus. Les aciers TRIP étudiés ont une elongation critique comprise entre 5 et 25 %. Les aciers DP ont une elongation critique est comprise entre 15 % et 25 %.

Pour essayer de trouver des critères qui permettent de décrire la sensibilité des deux familles d'aciers, l'influence de la composition chimique est étudiée dans le paragraphe suivant.

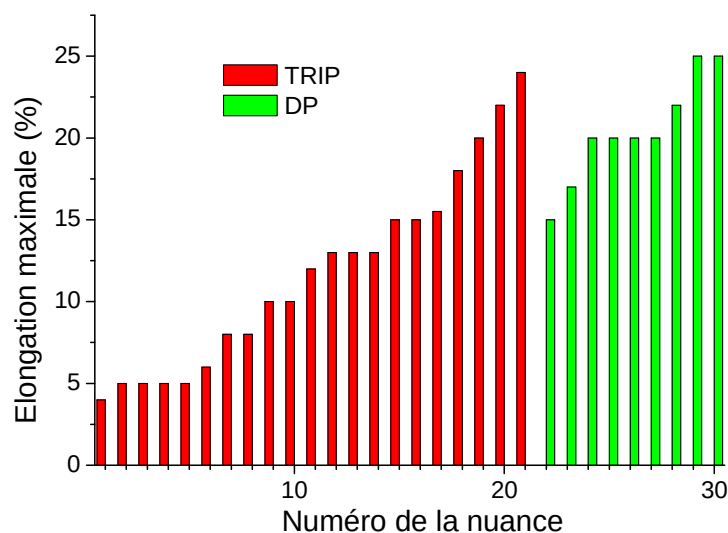


figure 175: Elongation critique pour les 30 nuances étudiées à Maizières

Commentaire

L'essai mécanique de Maizières est capable de différencier les nuances. Pour validation, des corrélations ont été faites entre l'elongation critique ici caractérisée et des mesures de fissures sur les points soudés. Les informations recueillies à Maizières (non détaillées dans ce manuscrit) montrent une corrélation relativement bonne sur quelques nuances, en particulier lorsque les mesures des fissures sur les points soudés ont été répétées un grand nombre de fois. Aucune corrélation forte sur l'ensemble des nuances n'a cependant été trouvée. Ceci est dû en particulier à la grande difficulté de la quantification de l'apparition des fissures au cours du soudage, comme indiqué dans le Chapitre II.

Pour la suite, le test de Maizières et le critère de l'élongation critique est admis comme mesurant bien la sensibilité d'une nuance à la fissuration par le Zn liquide.

2.3. Influence de la composition chimique

2.3.1. Influence individuelle des éléments

Si

L'influence de la teneur en Si sur l'élongation critique est donnée par la figure 176. L'élongation critique diminue clairement quand la teneur en Si augmente. Cette courbe permet de caractériser de manière cohérente, sur une même tendance, les aciers DP et les aciers TRIP. Trois groupes de points sont identifiés. Le premier entre 0,1 % et 0,3 % de Si regroupe tous les aciers DP et les aciers TRIP peu alliés en Si. Ces nuances sont donc peu sensibles. Le deuxième à environ 0,7 % de Si regroupe des nuances du type TRIP AlSi. Le troisième groupe regroupe des nuances du type TRIP MnSi. La dispersion des résultats au sein de chacun des groupes peut être expliquée de deux manières. Premièrement elle correspond certainement à l'incertitude sur le résultat de l'essai. Une incertitude relative constante d'environ 25 % sur le résultat pour l'élongation critique permettrait d'expliquer la dispersion. Par exemples :

- pour Si = 1,6 %, l'élongation critique est de (5 ± 1) % ;
- pour Si = 0,75 %, l'élongation critique est de (11 ± 3) % ;
- pour Si = 0,20 %, l'élongation critique est de (20 ± 5) %.

Deuxièmement, l'influence d'autres éléments au sein de chacun des groupes définis par la teneur en Si pourrait être significative au deuxième ordre. Ce type d'influence est discuté dans les paragraphes 2.3.2. et 2.3.3. Pour affiner la courbe de tendance arbitrairement choisie de type $y = A + Bx^n$, il faudrait tester Fe pur et trouver ainsi l'intersection avec la droite des ordonnées.

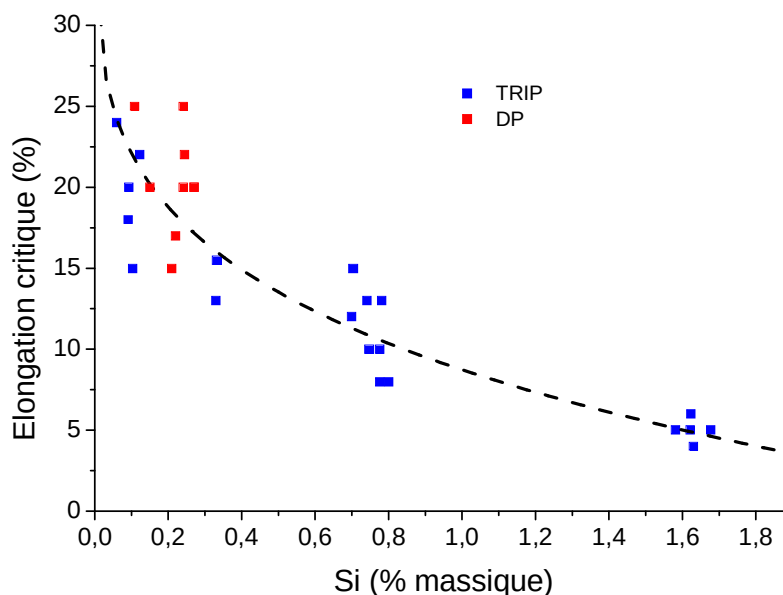


figure 176: Influence du silicium sur l'élongation critique

Al

L'évolution de l'élongation critique en fonction de la teneur en Al est donnée par la figure 177. La teneur en Al ne permet pas de décrire de manière satisfaisante la sensibilité des aciers, contrairement à la teneur en Si. Une évolution monotone peut être observée les aciers TRIP sont considérés séparément. Pour ceux-ci, l'évolution pour le développement des produits a été de remplacer en partie Si par Al, principalement pour améliorer la revêtabilité et la soudabilité [LI2007]. La somme (Al + Si) est maintenue constante. Ainsi l'influence apparente de Al peut être simplement considérée comme l'effet de la réduction de Si.

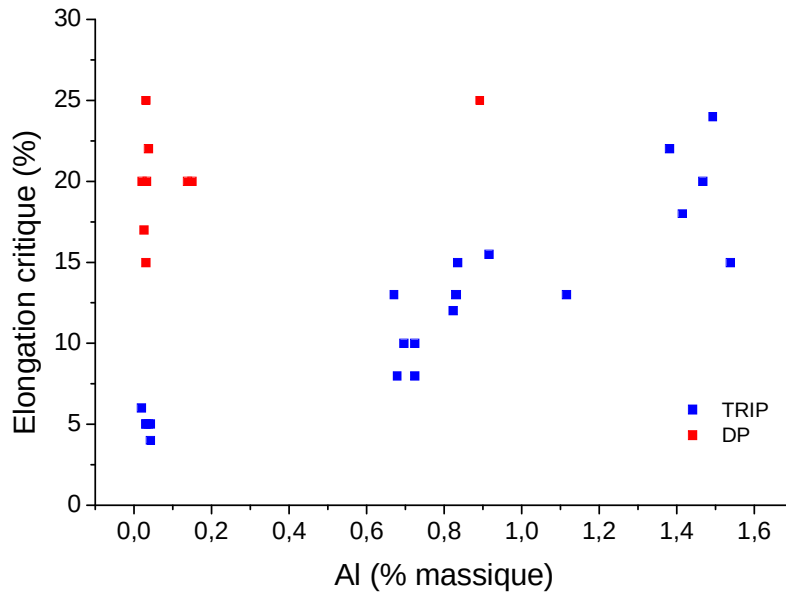


figure 177: Influence de Al sur l'élongation critique

Autres principaux éléments : C, Mn, Cr, Mo

L'évolution de la déformation critique en fonction de la teneur en C, Mn, Cr et Mo de manière individuelle est donnée dans la figure 178. Aucune dépendance ne peut être déduite de ces courbes. Ceci montre que ces éléments n'ont pas d'influence de premier ordre sur la sensibilité à la fissuration par le Zn.

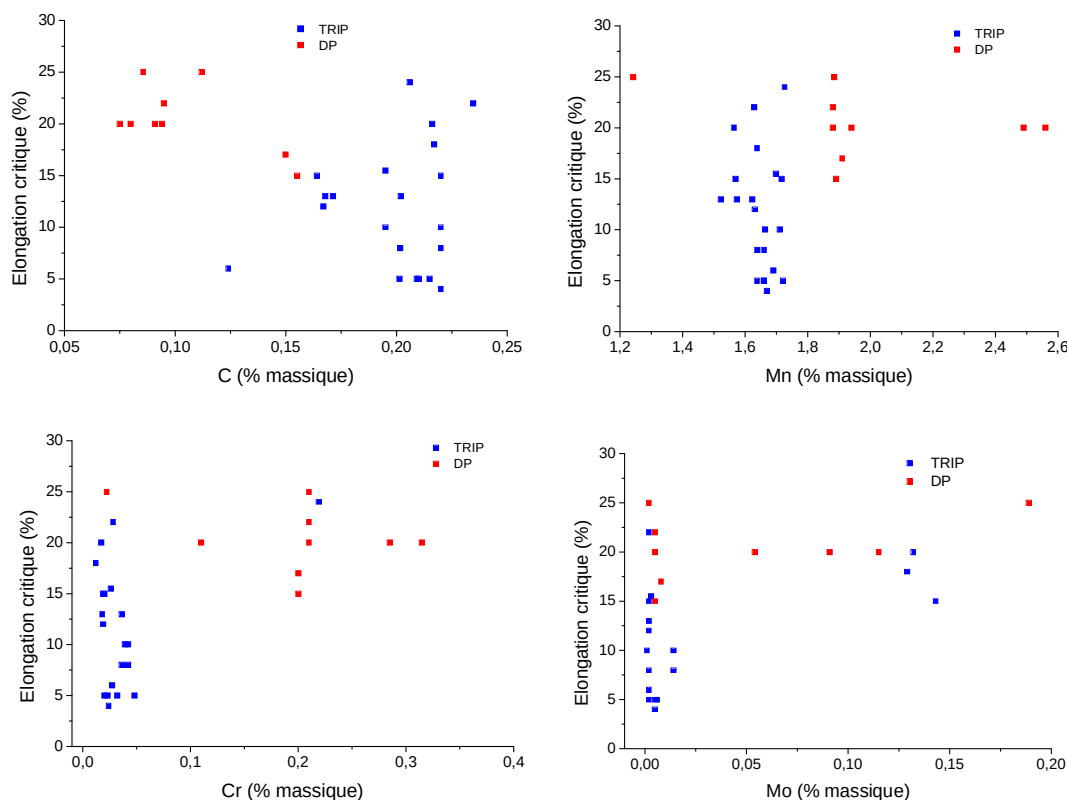


figure 178: Influence des éléments d'alliage sur l'élongation critique. Aucune corrélation claire ne peut être décrite

2.3.2. Etude par régression linéaire multiple

Méthode

La régression linéaire multiple est une méthode très utilisée pour l'analyse d'une série de données. Le détail de cette méthode peut être trouvé dans plusieurs ouvrages de références. Les méthodes décrites dans plusieurs cours universitaires en accès libre en ligne ont été suivis. Le logiciel libre *Regress* éditée par l'Université de Lyon 2 pour l'économétrie a été utilisé [REG1]. Les n variables d'entrée sont les compositions chimiques des m éléments d'alliages. La variable de sortie est l'élongation critique de l'essai de Maizières. Après régression linéaire multiple, un coefficient pour chacun des éléments d'alliage et une incertitude sur ce coefficient sont obtenus. La « qualité » de la régression est définie par le coefficient R^2 corrigé. La pertinence de la régression doit aussi être discutée par l'analyse de la normalité des résidus (droite de Henry). Le détail de la méthode et des moyens d'analyse de la qualité de la régression sont donnés dans [REG1][WIK3][AND1974]. L'application de ces méthodes en totalité pourrait probablement permettre d'aller plus loin que les résultats donnés dans les paragraphes suivants.

Régression sur les principaux éléments d'alliages

Les régressions linéaires ont été effectuées en considérant les principaux éléments d'addition, ou seulement certains d'entre eux. Dans les tableaux de ce paragraphe, les paramètres pour lesquelles l'incertitude relative inférieure à 50 % sont surlignés en jaune. Ceux-ci sont considérés comme significatifs.

Ceux pour lesquelles l'incertitude est supérieure à 100 % sont écrits en rouge. Ceux-ci sont considérés comme non significatifs.

La table 22 présente les résultats de la régression en considérant seulement Si. Ceci revient à faire une interpolation linéaire sur la figure 176. Le modèle linéaire prédit ici un coefficient de – 10 pour faire passer l'élongation à rupture de 20,5 % pour une concentration nulle en Si à 0,5 % pour une concentration en Si de 2 %m. Vu les incertitudes sur les paramètres, ces résultats sont considérés comme significatifs. La valeur de R^2 est assez faible ce qui dénote la difficulté de décrire les points expérimentaux. L'incertitude supposée grande sur les résultats de l'essai explique pour partie la faible valeur de R^2 .

table 22: Résultats de la régression pour Si

Paramètre	Coefficient	Incrtitude
Si (% massique)	-9,89	1,00
Constante élongation critique (%)	20,5	0,913

R^2 corrigé = 0,745

La table 23 présente les résultats en considérant C en plus de Si. Il semble que C ait aussi un effet négatif significatif sur l'élongation critique. De plus l'augmentation du R^2 montre aussi que l'influence de C est intéressante à prendre en compte.

table 23: Résultats de la régression pour Si et C

Paramètre	Coefficient	Incrtitude
C (% massique)	-38,9	10,8
Si (% massique)	-8,91	0,898
Constante élongation critique (%)	26,5	1,85

R^2 corrigé = 0,814

La table 24 montre les résultats en incluant aussi deux autres éléments d'alliages important : Mn et Al. L'effet de Mn apparait légèrement négatif mais avec une très forte incertitude (presque 100 %). L'effet de Al apparait bénéfique mais avec là aussi une incertitude très forte, supérieure à 50 %. Le résultat pour Al et Mn reste donc incertain. Vu les concentrations en Al, Mn, C et Si et leurs coefficients respectifs, l'influence de Al et Mn est considérée comme secondaire (environ trois fois moins importante) que celle de Si et C.

table 24: Résultats de la régression multiple linéaire pour Mn, Al, Si et C

Paramètre	Coefficient	Incrtitude
C (% massique)	-63,5	15,4
Mn (% massique)	-2,15	2,04
Si (% massique)	-7,12	1,28
Al (% massique)	2,58	1,50
Constante élongation critique (%)	32,0	4,8

R^2 corrigé = 0,829

La table 25 donne les résultats en incluant aussi les éléments Cr et Mo. Les résultats de la régression ne sont pas significatifs pour ces deux éléments. Leurs influence est donc négligeable. La même tendance que dans le tableau précédent est observée pour les autres éléments.

table 25: Résultats pour Mn, Al, Si, Cr, Mo et C

Paramètre	Coefficient	Incertitude
C (% massique)	-65,4	16,9
Mn (% massique)	-3,45	2,99
Si (% massique)	-6,65	1,52
Al (% massique)	3,05	1,87
Cr (% massique)	5,03	8,29
Mo (% massique)	2,08	11,8
Constante élongation critique (%)	21,0	5,71

R^2 corrigé = 0,819

Régression sur tous les éléments présents dans la composition

Des régressions multiples sur tous les éléments présents dans la composition chimique, soient sur 18 éléments, ont été réalisées. Le protocole itératif suivant (de type « backward ») a été suivi. Une itération consiste à effectuer une régression sur les tous les éléments chimiques, à analyser les résultats et à supprimer les éléments pour lesquelles l'incertitude dépasse la valeur de leur coefficient. Ces itérations sont répétées sur les éléments restants.

La table 26 présente les résultats obtenus après la troisième itération. Tous les éléments apparaissent significatifs selon nos critères. C et Al n'y figurent pas, alors que Cr est encore présent. Néanmoins, là aussi, la contribution de chacun de ces éléments peut être discutée. Par exemple la concentration maximal en Ni est de 0.038 % ce qui fait que sa contribution est d'un ordre de grandeurs inférieures à celle de Si. La même analyse peut être réalisée pour Ti et Cr. La teneur en B est de 0.002 %m, ce qui fait que sa contribution est de deux ou trois ordres de grandeurs inférieures à celle de Si. La même analyse peut être réalisée avec les éléments suivants : P, As, Zr, Nb.

En résumé, avec ce tableau, l'influence de Si est trouvée comme étant de premier ordre comme pour les résultats du paragraphe précédent, celle de Mn de second ordre. Les autres sont négligeables.

table 26: Résultats de la régression après trois itérations

Paramètre	Coefficient	Incertitude	Contribution relative (Coefficient x (Compo max – Compo min))
Si (% massique)	-9,48	0,59	15
Ni (% massique)	500	60	15
Cr (% massique)	38,6	5,5	10
Nb (% massique)	293	62	8
Mn (% massique)	-14,6	2,2	7

Ti (% massique)	-185	45	6
P (% massique)	-82,2	26,7	6
B (% massique)	-1270	300	5
As (% massique)	853	440	3
Zr (% massique)	734	380	2
Constante élongation critique (%)	32,5	3,1	-

R^2 corrigé = 0,945

2.3.3. Résumé et approfondissement

Les résultats des paragraphes précédents ont montré que l'influence de la plupart des éléments d'alliages est négligeable (dans les gammes de concentration étudiées). L'étude est poursuivie pour les éléments ayant une influence significative.

Influence de Si

A la vue des résultats des régressions, Si semble le principal élément à avoir une influence sur l'élongation critique. Sa contribution apparaît comme la plus grande et la plus significative quelque soit la méthode utilisée. Si réduit fortement l'élongation critique. La figure 176 montrée plus haut constitue donc le résultat principal pour l'influence de la composition chimique sur l'élongation critique.

Influence de C

Les régressions ont montré que le carbone pouvait avoir une influence secondaire lorsqu'on considérait seulement l'influence des principaux éléments d'alliage. Son influence apparaissait significative. L'augmentation du taux de C diminue aussi l'élongation à rupture.

Pour les taux de Si inférieur à 0.4% massique, la teneur en carbone est indiquée sur le graph Elongation critique-Teneur en Si de la figure 179. Pour ce groupe de points, les plus faibles teneurs en C montrent de plus grandes élongations critiques. Les points qui ne respectent pas cette tendance sont entourés en rouge. La même procédure a été appliquée pour les deux autres groupes de points, pour des taux de Si entre 0,7 %m et 0,8 %m sur la figure 180, et pour des taux de Si entre 1,55 %m et 1,8 %m sur la figure 181 .

La figure 182 présente l'évolution de l'élongation critique en fonction du taux de carbone pour plusieurs intervalles de teneur en Si. Grâce à une interpolation linéaire pour chaque groupe de points, il apparaît que le taux de C diminue l'élongation critique. C'est probablement cette tendance qui a été détectée lors de la régression multiple linéaire.

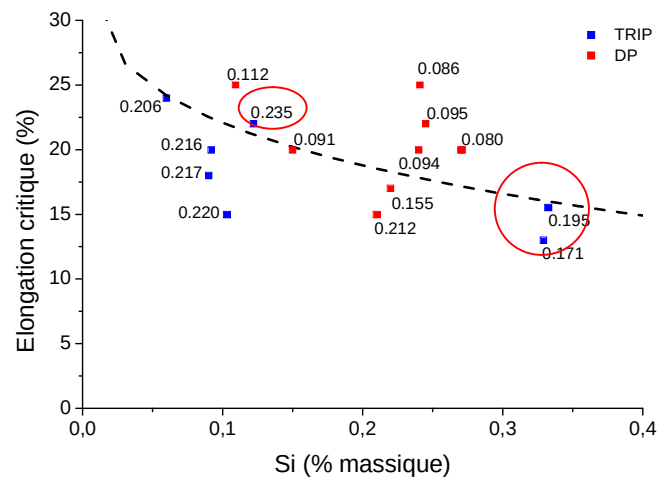


figure 179: Taux de carbone sur le graph Elongation critique-Taux de Si pour $Si < 0,4$

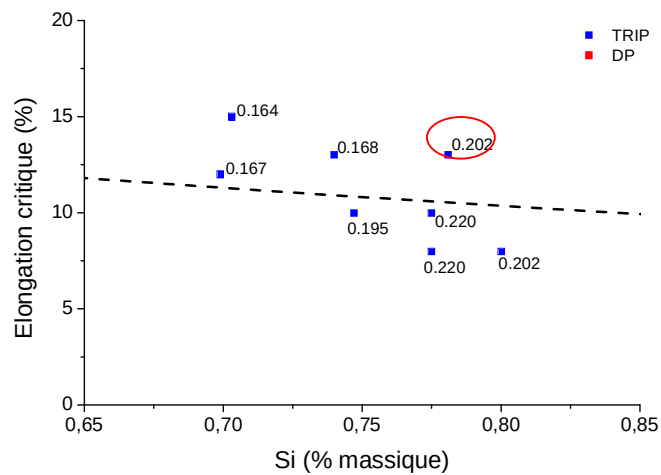


figure 180: Taux de carbone sur le graph Elongation critique-Taux de Si pour $0,7 < Si < 0,8$

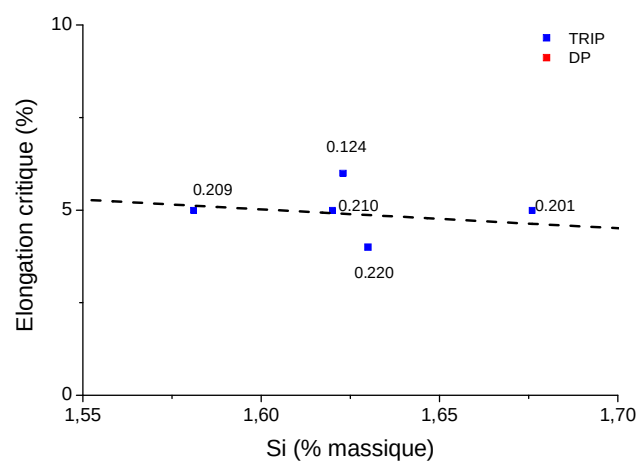


figure 181: Indication du taux de carbone sur le graph Elongation critique-Taux de Si pour $1,55 < Si < 1,7$

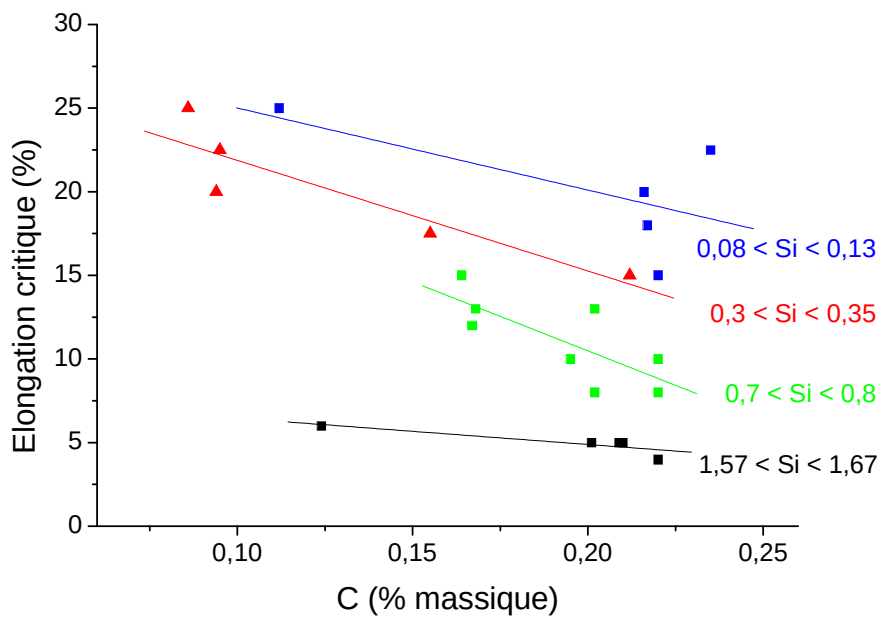


figure 182: Influence du taux de carbone sur l'élongation critique pour différents taux de Si

Influence de Mn et Al

Les résultats des régressions (table 24 et table 25) ont montré une influence de Mn et Al, secondaire et peu significative au vu des incertitudes. La même analyse que celle faite pour le carbone ne montre aucune tendance. L'influence de Al et Mn est aussi supposée négligeable dans la suite de l'étude. Seule l'influence de Si et de C est retenue par la suite.

2.4. Discussion

Il a été rappelé dans le paragraphe 1.2 de ce chapitre que le fond du puits de ductilité caractérise en fait la facilité de la propagation d'une fissure, c'est-à-dire la vitesse de fissuration lorsque le système est au dessus de la température de transition de mouillage.

Deux facteurs ont été identifiés comme ayant le potentiel pour augmenter la sensibilité à la fissuration : la diminution de la solubilité de Zn dans l'acier, et l'augmentation de la dureté à chaud de l'acier. Dans ce paragraphe l'influence de Si et C sur ces deux critères est discutée et comparée avec celle possible de Al et Mn. Solubilité et résistance à chaud sont alors corrélées de manière quantitative avec l'élongation critique.

2.4.1. Solubilité

Influence de Si et C sur la solubilité de Zn dans l'acier

Le système Fe-Si-Zn a été étudié thermodynamiquement. Des diagrammes ternaires sont disponibles dans la littérature [PER1988][SU2005][RAG2007]. Ces études montrent que l'augmentation de la teneur en Si diminue fortement la solubilité de Zn dans Fe-Si. A 750 °C, la figure 183 montre que la solubilité de Zn passe de 35 %m pour 0 %m de Si à 18 %m pour 2 %m de Si. L'effet de Si vis-à-vis de Zn dans le système Fe-Si-Zn peut être expliqué en observant le diagramme d'équilibre du système binaire Si-Zn présenté sur la

figure 184. La solubilité en phase solide de Zn dans Si est négligeable. La revue bibliographique (Chapitre I) a aussi montré que le système Fe-5%Si possède une solubilité très réduite pour le Zn (figure 26), ce qui est en accord avec le calcul thermodynamique (figure 183). De ce fait, il est possible d'affirmer que Si a un effet de réduction de la solubilité de Zn dans l'acier.

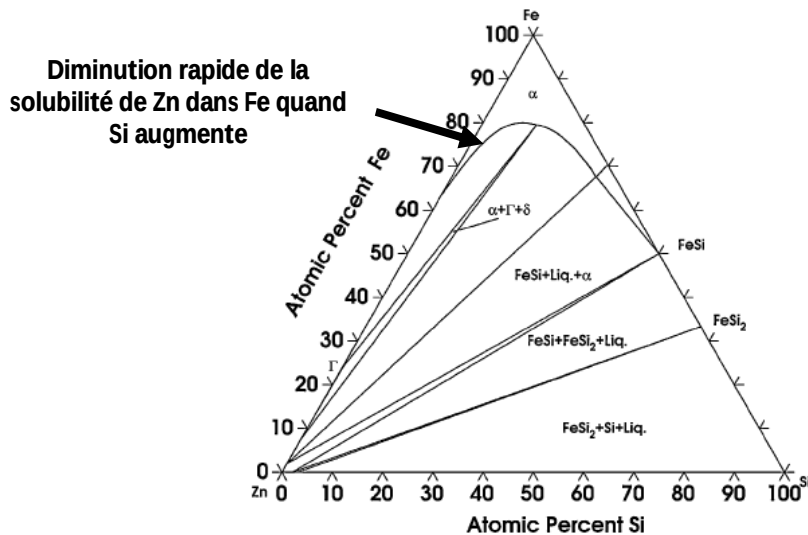


figure 183: Diagramme de phase ternaire Fe-Si-Zn calculé à 750 °C. Reproduit après [SU2005]

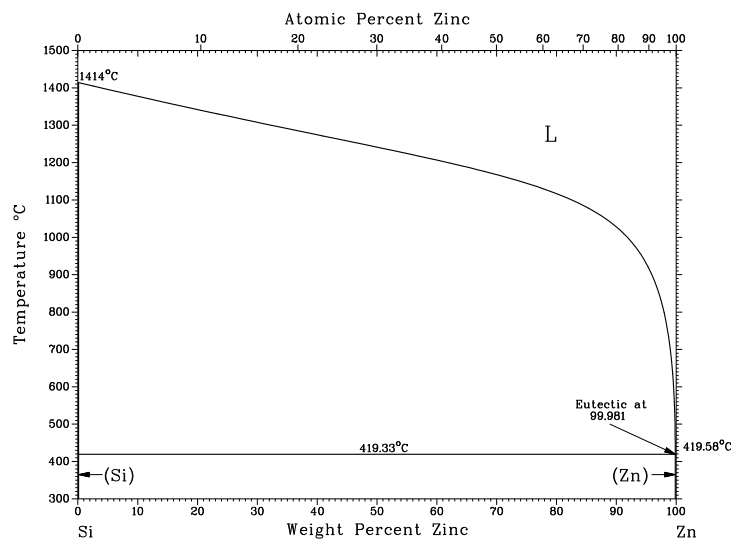


figure 184: Diagramme de phase Si-Zn. Reproduit après [OLE1985]

Peu d'information sont disponible sur l'effet de C sur la solubilité de Zn dans l'acier. Aucune étude du système Fe-C-Zn n'a été trouvée pour alimenter la discussion. Par ailleurs le diagramme de phase binaire C-Zn a les mêmes caractéristiques que celui du système Si-Zn [FRA2007]. Dans ces diagrammes, la solubilité

en phase solide est négligeable. Il est possible de supposer que C aura, comme Si, un effet de réduction de la solubilité de Zn dans l'acier.

La figure 185 montre la corrélation entre la solubilité et l'élongation critique. Chaque point représente en fait un des groupes de nuances d'aciers caractérisées précédemment (figure 176). Les élongations de 5 %, 11 % et 20 % sont respectivement reliées aux teneurs en silicium de 1,6 %m, 0,75 %m, et 0,2%_m. Pour chacune de ces compositions, la solubilité à 750 °C en fonction de la teneur en Si a été déterminée graphiquement (figure 183). La dépendance est apparemment linéaire dans cette gamme de solubilité.

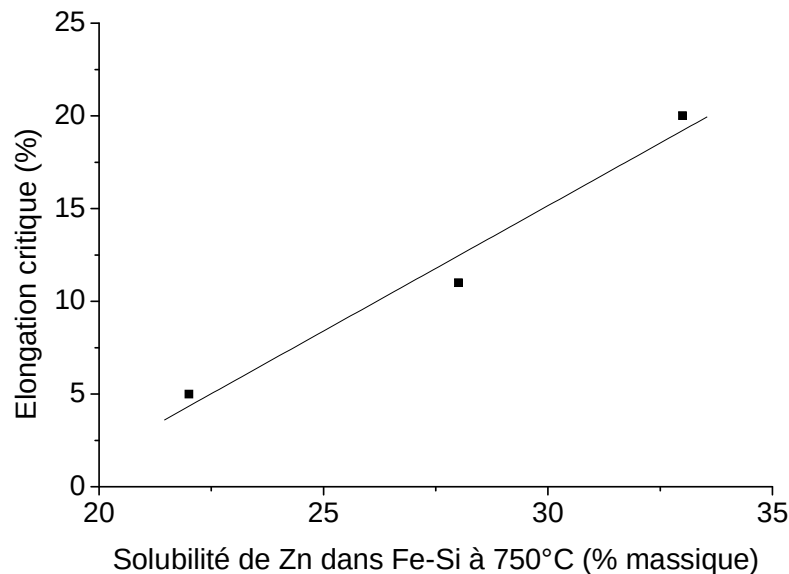


figure 185: Corrélation schématisée entre la solubilité à chaud de Zn dans Fe-Si à 750°C et l'élongation critique moyenne. Points calculés à partir de la figure 176 et de la lecture graphique de la figure 183

Comparaison qualitative avec l'influence de Mn et Al sur la solubilité

L'influence de Si et C peut être interprétée en fonction de leur tendance à baisser la solubilité de Zn dans l'acier aux températures de fissuration. Contrairement à Si et C, l'analyse de l'influence des éléments d'alliages avaient montré que l'influence de Mn et Al sur la sensibilité à la fissuration est négligeable.

Sur les diagrammes binaires Mn-Zn et Al-Zn présentés respectivement sur la figure 186 et la figure 187, la solubilité de Zn dans Al et Mn est grande aux températures de fissuration et/ou que de nombreux intermétalliques existent. Ainsi les systèmes Al-Zn et Mn-Zn sont très éloignés des systèmes Si-Zn et C-Zn vus précédemment.

Le diagramme ternaire Fe-Mn Zn présenté sur la figure 188 [BHA1991] montre que l'augmentation du taux de Mn augmente la solubilité de Zn dans Fe-Mn. Aucune étude complète du système ternaire Fe-Al-Mn n'a été trouvée pour alimenter la discussion. En effet, les études sur ce système sont principalement faites pour la portion riche en Zn [RAV2003]. Vu ces éléments de discussion, il est possible de supposer que Al et Mn ne diminue pas la solubilité de Zn dans l'acier. C'est probablement pourquoi ces éléments ont une influence négligeable sur la sensibilité à la fissuration, contrairement à Si et C.

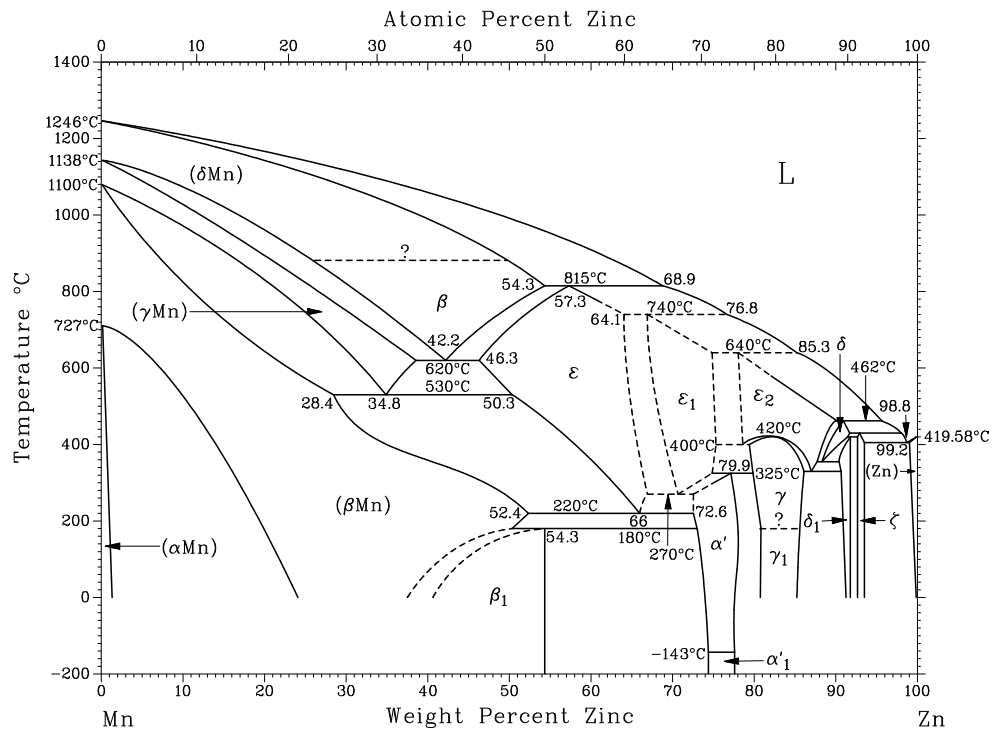


figure 186: Diagramme de phase Mn-Zn

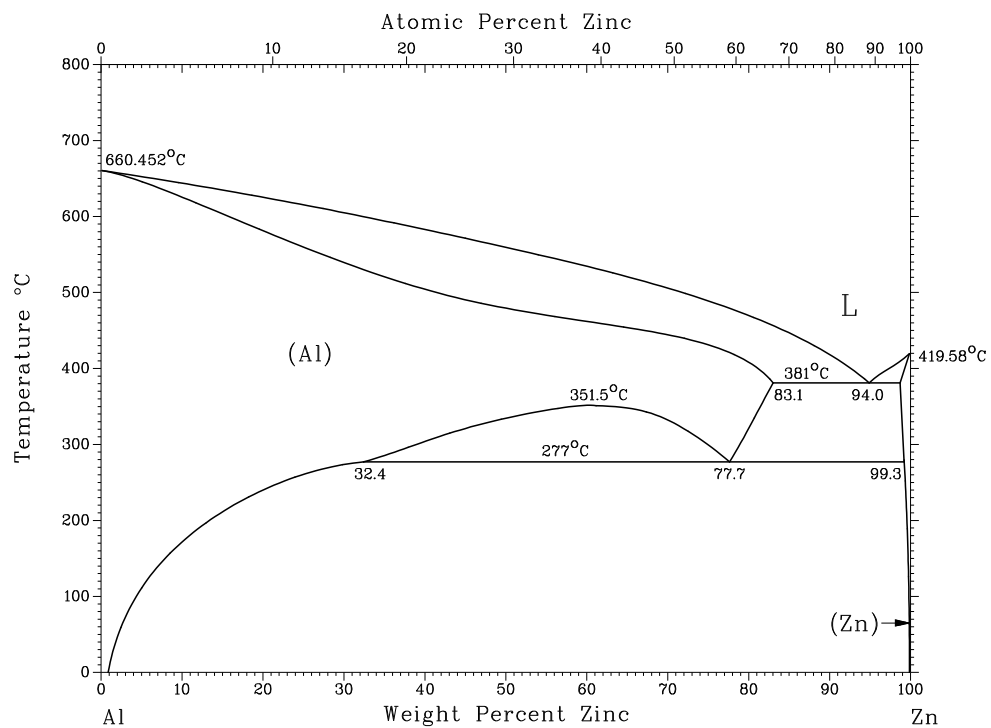


figure 187: Diagramme de phase Al-Zn

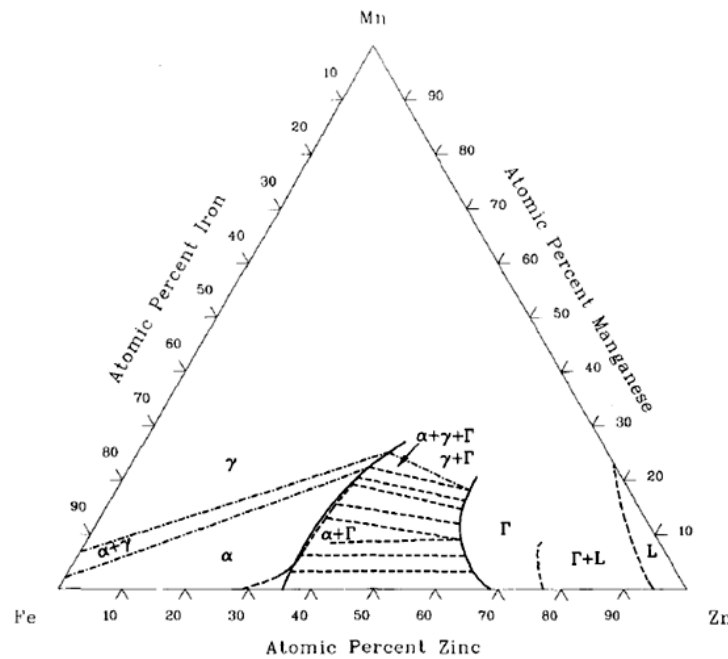


figure 188: Coupe du diagramme ternaire Fe-Mn-Zn à 720 °C. Reproduit après [BHA1991]

2.4.2. Résistance mécanique à chaud

Corrélation entre résistance mécanique à chaud et composition

Le comportement plastique de l'acier à chaud implique des mécanismes de déformation comme la restauration et la recristallisation. Classiquement, la courbe de traction σ - ϵ peut être décrite par le paramètre de Zenner-Hollomon [ZEN1944].

$$\sigma = \sigma(Z, \epsilon)$$

$$Z = \dot{\epsilon} \exp \left(\frac{-Q}{RT} \right)$$

Cette dernière équation montre l'influence de la vitesse de déformation et de la température. L'énergie d'activation apparente Q peut être modélisée en fonction de la composition de l'acier. Le modèle de Medina, et al. pour l'austénite dans les aciers peu alliés est présenté ci-dessous [MED1996]. Les conclusions de cette étude indiquent que l'augmentation de tous les éléments d'alliages sauf C a un effet durcissant. Etant donné les coefficients et les concentrations mis en jeu, Si est décrit comme un élément ayant un fort effet durcissant pour des teneurs de l'ordre de 1,6 %m. L'influence de Al a été calculée à partir des résultats de Poliak et Siciliano [POL2005].

$$Q = 167000 - 2000 C + 1000 Mn + 33000 Si + 36000 Mo + 32000 V + 93000 Ti^{0.5919} + 70000 Nb^{0.5649} + 40000 Al \quad (37)$$

Ces résultats sont valables seulement pour l'austénite. Dans les aciers très peu alliés, la ferrite à 800 °C est moins dure que l'austénite à 900 °C. Dans l'austénite à haute température, c'est le phénomène de

recristallisation dynamique qui est le principal facteur d'adoucissement. Dans la ferrite, c'est la restauration dynamique. Nous n'avons pas trouvé d'étude utilisable sur le lien entre la composition chimique de la ferrite et sa dureté à chaud. Le comportement de l'austénite a été étudié notamment pour la compréhension et la définition des efforts lors du laminage à chaud des aciers (voir ci-dessous).

L'énergie d'activation apparente définie par l'équation (37) est utilisée ici comme critère de dureté à chaud pour différencier les nuances en fonction de leur composition chimique. La figure 189 présente la corrélation entre l'élongation critique et l'énergie d'activation. Dans ce cas l'énergie d'activation discrimine les aciers DP des aciers TRIP. En effet le taux cumulé de Al et Si est beaucoup moins élevé pour les DP que pour les aciers TRIP. En revanche cette énergie d'activation ne décrit pas bien l'évolution de l'élongation critique.

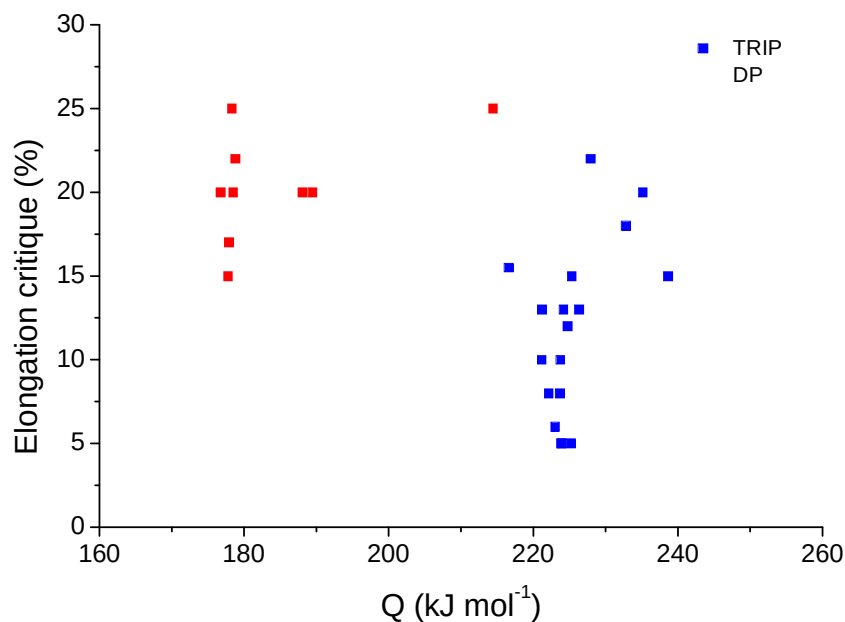


figure 189: Corrélation entre l'élongation critique et l'énergie d'activation apparente

Pour aller plus loin dans la description des propriétés mécaniques à chaud de l'acier, un modèle numérique développé par le centre de recherche ArcelorMittal Maizières pour la prédiction des efforts lors du laminage a été utilisé. Celui-ci permet de trouver les lois de comportement (courbe contrainte déformation) pour l'austénite. Les données d'entrée sont la température, la vitesse de déformation, la taille de grains, et la composition chimique. Ce modèle phénoménologique prédit en fait la densité de dislocations en fonction de la déformation. Les hypothèses de base du modèle peuvent être trouvées dans la littérature scientifique [PER2003][HUA2009]. D'autre part ce modèle a été validé industriellement. Nous ne donnons pas plus de détail dans ce manuscrit. Ce modèle paraît mieux adapté que celui de l'équation (37) pour prédire la dureté à chaud des aciers de l'étude.

Ce modèle n'est pas utilisé pour re-modéliser les courbes de traction et trouver par exemple une contrainte critique pour la fissuration. En effet le Chapitre I a montré que ce type de description pour la rupture de l'éprouvette n'est pas valide. Ce modèle est simplement utilisé pour définir un critère de dureté à

chaud. La contrainte prédite pour 5 % de déformation à la température de 880 °C à la vitesse de 1 s⁻¹, pour une taille de grains de 6 µm et une densité de dislocations initialement nulle, a été choisie comme critère.

La figure 190 montre que la corrélation est relativement bonne entre ce critère et l'élongation critique.

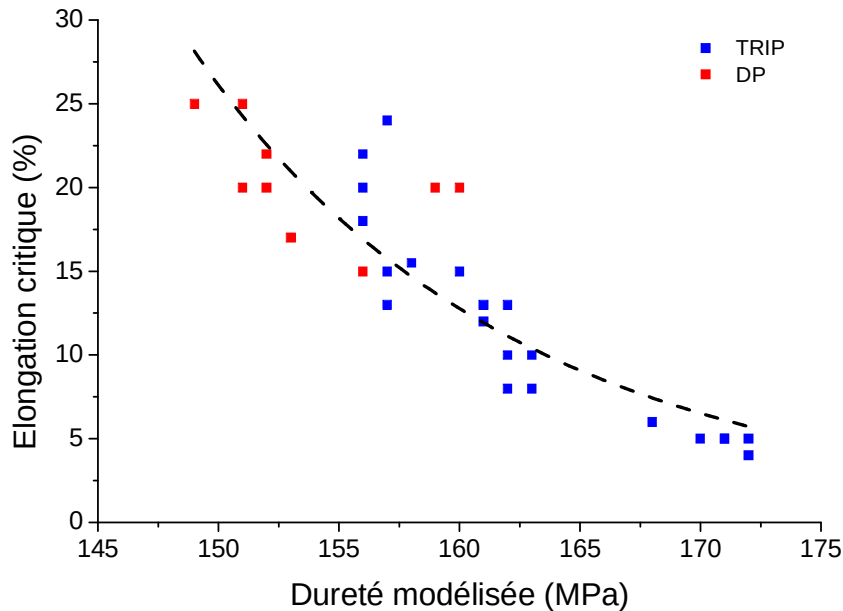


figure 190: Corrélation entre l'élongation critique et la dureté modélisée (à 880 °C, 1s⁻¹, déformation = 5%)

2.4.3. Discussion

L'analyse de l'influence de la composition chimique a montré que l'augmentation du taux de silicium et de carbone augmente la sensibilité de l'acier à la fissuration par le zinc liquide. Deux effets sont possibles : la diminution de la solubilité de Zn dans l'acier ou l'augmentation de la dureté à chaud.

La corrélation avec la solubilité semble très bonne avec le Si et aussi cohérente avec l'effet de C. De plus elle permet d'expliquer que ni Mn ni Al n'aient pas d'effet. La corrélation avec la dureté à chaud semble moins évidente. Par exemple le carbone n'a pas d'effet durcissant sur l'austénite alors qu'on a caractérisé son effet négatif sur l'élongation critique.

Etant donnés les apports de la fin du Chapitre I, une diminution de 50 % de la solubilité est supposé avoir plus d'effet qu'une augmentation de 50 % de la contrainte. Même si la question reste ouverte, l'effet de Si et C sur la solubilité est considéré à ce stade de l'étude le facteur prépondérant pour définir la sensibilité à la fissuration des nuances d'aciers. Les principaux apports de l'étude sont résumés dans la section suivante.

3. Résumé : critères à prendre en compte pour le développement des aciers

Les principaux enseignements de cette étude sont résumés dans cette section sous la forme de pistes de développement formulées en prenant en compte la sensibilité des aciers à la fissuration induite par le zinc liquide. Pour le développement d'aciers – dans lesquelles les principaux éléments d'alliages sont : C, Si, Al, Mn ; et dans une moindre mesure : Cr, Mo, Ni – les lignes suivantes devront être suivies pour diminuer la sensibilité à la fissuration.

Les aciers à haute résistance pour l'automobile (AHSS) sont généralement classés en trois catégories : de 1^{ère}, 2^{ème} et 3^{ème} génération. Les travaux de cette étude montrent que les AHSS de 1^{ère} génération ($Mn < 2\%$, $(Si+Al) < 2\%$) sont sensibles à la fissuration induite par le Zn. Les AHSS de 2^{ème} génération ($Mn > 15\%$, $Si < 3\%$, $Al < 3\%$) ont déjà été caractérisés comme particulièrement sensibles (figure 30) [BEA2011] [BEA2012]. Etant donné que les aciers de 3^{ème} génération vont proposer des compositions intermédiaires entre les deux générations précédentes [MAT2009][GRA2012], il est fort probable qu'ils soient eux aussi particulièrement sensible à la fissuration induite par le Zn liquide si les pistes suivantes ne sont pas prises en compte, ou au moins étudiées.

3.1. Favoriser la présence de joints de grains de basse énergie

3.1.1. Energie et structure des joints de grains.

L'énergie des joints de grains a été identifiée comme un point clé pour définir la gamme de température pour l'apparition de la fissuration. Le développement actuel de l'ingénierie des microstructures et des joints de grains permet pour certains matériaux d'augmenter la proportion de joints de forte cohérence (de faible énergie) [RAN1996]. Les contraintes pour les traitements thermomécaniques industriels des aciers sont fortes. L'ingénierie des microstructures des aciers peut-elle à l'avenir développer des joints de grains de forte cohérence, au moins en surface des tôles? Sur ce point particulier, les apports des travaux de la thèse sont faibles pour fournir des pistes de développement.

3.1.2. Energie et chimie des joints de grains

La chimie des joints de grains joue un rôle sur l'énergie qui lui est associée. Il est possible que le microalliage avec un élément ségrégeant dans les joints de grains et diminuant fortement l'énergie du joint de grain permettent de diminuer drastiquement la sensibilité à la fissuration. Les premières investigations menées sur l'influence du phosphore sont présentées dans la section suivante pour vérifier cette hypothèse. Contrairement aux autres solutions résumées dans cette section, le microalliage avec un élément ségrégeant pourrait permettre de diminuer la sensibilité à la fissuration induite par le Zn liquide sans modifier fortement les autres propriétés d'usage et de mise en forme de l'acier.

3.2. Maintenir ou augmenter la solubilité de Zn dans l'acier

La solubilité de Zn dans l'acier semble être un paramètre clé pour définir la sensibilité de l'acier. L'augmentation du taux de carbone et de silicium réduit la solubilité et par conséquent augmente la sensibilité à la fissuration. Il est clair que maintenir de bas taux de carbone et surtout de silicium semble nécessaire pour ne pas exacerber la sensibilité vis-à-vis de la fragilisation par le zinc. Le remplacement de Si par Al est souhaitable. Celui-ci a déjà été identifié comme une possibilité dans le développement des AHSS notamment pour améliorer leur revêtabilité ou leur soudabilité [LI2007]. Al permet par exemple de maintenir l'effet TRIP initialement identifié dans les aciers au Si [LI2004].

D'autres moyens non identifiés dans ce manuscrit sont probablement envisageables pour augmenter la solubilité de Zn dans les aciers.

3.3. Commentaires

Les apports des travaux de la thèse ont été succinctement résumés sous la forme de lignes générales pour la description de la sensibilité des nuances d'aciers. La plupart de celles-ci restent néanmoins très abstraites. Dans la section suivante (et la dernière du manuscrit de thèse) deux solutions concrètes conçues pour supprimer la fissuration sont décrites. La première veut tester une des hypothèses citées plus haut : celle de l'influence d'un élément de microalliage ségrégeant aux joints de grains. La deuxième se veut une solution process innovante pour supprimer la fissuration de surface au cours du soudage.

4. Conception de solutions pratiques pour supprimer la fissuration

4.1. Une solution « produit »

4.1.1. Motivations

L'énergie du joint de grain a été décrite comme un facteur clé de la fissuration. L'utilisation d'un élément de microalliage qui pourrait ségréger aux joints de grains de l'acier et abaisser en conséquence son énergie est proposée. Le décalage de transition de mouillage vers les hautes températures est attendu, comme le présente la figure 191. La diminution drastique des vitesses de fissuration jusqu'à des valeurs négligeables peut aussi être attendue, ce qui fera aussi disparaître le puits de ductilité.

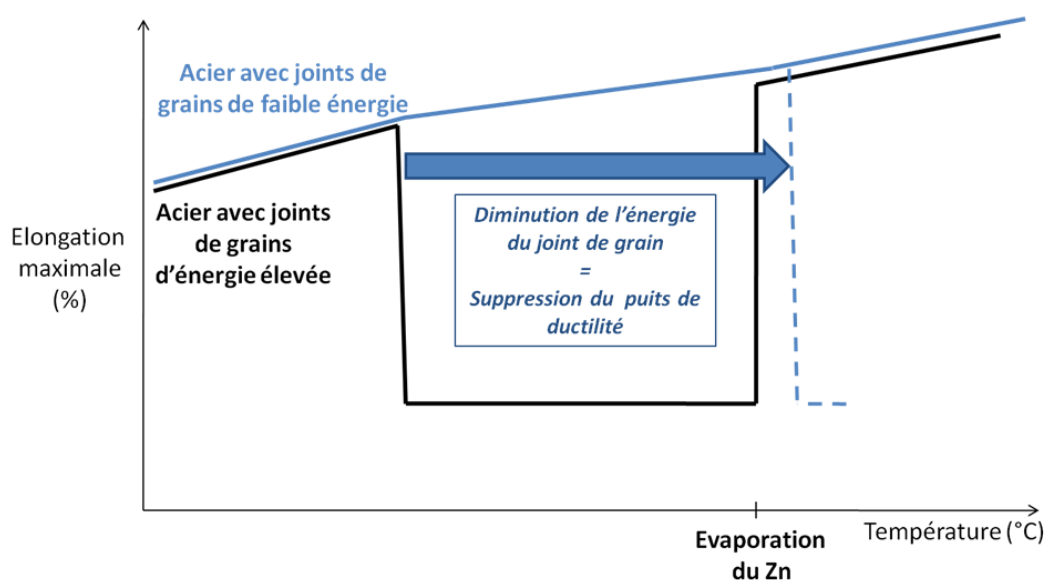


figure 191: Le puits de ductilité disparaît si la température de transition de mouillage est supérieure à la température d'ébullition de Zn

4.1.2. Définition

Une concentration de phosphore de l'ordre de 0.04 %m. à 0.08 % dans l'acier est proposée pour diminuer la sensibilité de l'acier à la fissuration par le Zn liquide. Les indices qui indiquent que ce microalliage est une solution intéressante sont résumés ci-dessous.

Tout d'abord, la diminution de l'énergie intergranulaire induite par la ségrégation de P aux joints de grains est bien connue. Par exemple, l'augmentation de la concentration volumique de P dans un alliage Fe-P de 0.002 %at. à 0.6 %at. permet de diminuer l'énergie des joints de grains de 800 mJ m^{-2} à 400 mJ m^{-2} [HON1965].

D'autre part, l'effet bénéfique du phosphore a déjà plusieurs fois été caractérisé. La ségrégation du phosphore a été identifiée comme un facteur diminuant la fragilisation d'aciers 0,4C 3,5Ni 1,3Cr par le plomb et l'étain dans « the effect of grain boundary segregation on liquid metal induced embrittlement of steels » [DIN1976]. Le phosphore permet de supprimer la pénétration de Zn par diffusion dans un acier comme le montre l'étude « Intergranular Zinc embrittlement and its inhibition by Phosphorus in 55 pct-Al-Zn coated sheet steel » [ALL1983]. Plusieurs indices non publiés chez ArcelorMittal montrent qu'une nuance à 0,6% haut phosphore montre beaucoup moins de fissuration de surface au cours du soudage que les aciers étudiés au Chapitre II. Néanmoins, l'effet bénéfique peut aussi venir du faible taux de Si dans cette nuance. Pour finir, dans le cas de la galvanisation, la ségrégation de phosphore diminue la réactivité du joint de grains avec Zn [JOR1997].

4.1.3. Validation expérimentale en cours

En 2013, une coulée de laboratoire a été réalisée au centre de recherche ArcelorMittal Maizières avec 4 taux de phosphore différents dans une chimie de base similaire à celle du TRIP Si étudié au Chapitre I et Chapitre II. Les taux de phosphore sont :

- 0,014 %m
- 0,022 %m
- 0,044 %m
- 0,069 %m

Les échantillons sont en cours de préparation (laminage, galvanisation). La caractérisation par essais de traction (conformément au Chapitre I) et de soudage (conformément au Chapitre II) devra être menée pour identifier et quantifier l'effet du phosphore sur la fissuration. Les résultats ne sont donc pas contenus dans ce manuscrit.

4.2. Une solution « process »

4.2.1. Motivations

Le Chapitre II a notamment montré que la fissuration de surface apparaissait pour une indentation supérieure à 130 μm . La discussion a montré qu'on pouvait mettre en cause les déformations de surface dans la gamme de température de fragilisation caractérisée au Chapitre I. Une solution process innovante pour contrôler l'indentation et la limiter à une valeur inférieure à 130 μm est décrite dans ce paragraphe. Même sans s'intéresser spécifiquement à la fissuration de surface, le contrôle de l'indentation est un point clé pour le soudage. En effet, il est possible que la limitation de l'indentation permette de supprimer l'expulsion de métal fondue en cas de surintensité de soudage.

4.2.2. Définition

Il s'agit ici de travailler sur la géométrie de l'électrode pour contrôler l'indentation au cours du soudage, et pour supprimer les indentations excessives et la fissuration de surface. La figure 192 montre la géométrie de l'électrode utilisée pour les essais de soudage du Chapitre II et la modification de celle-ci pour obtenir une

électrode « anti-fissuration ». La forme de la face active de l'électrode standard est conservée sur la bosse de l'électrode « anti-LME ». La bosse de l'électrode a une hauteur correspondant à l'indentation maximale d_{max} voulue pendant le soudage. Au cours du soudage, quand l'indentation atteint la valeur d_{max} , la surface plane de l'électrode arrive en contact avec la surface de la tôle en périphérie du point soudé. Tout d'abord une action mécanique qui va bloquer la course de l'électrode et ainsi limiter l'indentation est attendue. D'autre part un effet électrique doit aussi être considéré : le courant va être distribué sur une surface beaucoup plus grande, ce qui va en pratique arrêter le soudage (la croissance du noyau).

Vu que les caractéristiques de la face active sont conservées, le début du cycle de soudage et donc les étapes importantes de la croissance du noyau ne sont pas modifiées. Les domaines de soudabilité standard sont toujours valides. Une augmentation apparente de la largeur du domaine de soudabilité vers les hauts courants peut être probablement attendue s'il est confirmé que la limitation de l'indentation diminue l'expulsion. D'un point de vue pratique, cette électrode n'est pas plus encombrante que l'électrode standard. Le principal défaut de ce type d'électrode est la nécessité d'un très bon alignement (parallélisme) des électrodes. Ceci n'est pas toujours le cas dans le cadre industriel. Par exemple, si l'électrode n'est pas « parfaitement » perpendiculaire à la tôle, le coin de l'électrode touchera la surface de la tôle, ce qui empêchera le bon contact de la face active et le soudage dans de bonnes conditions.

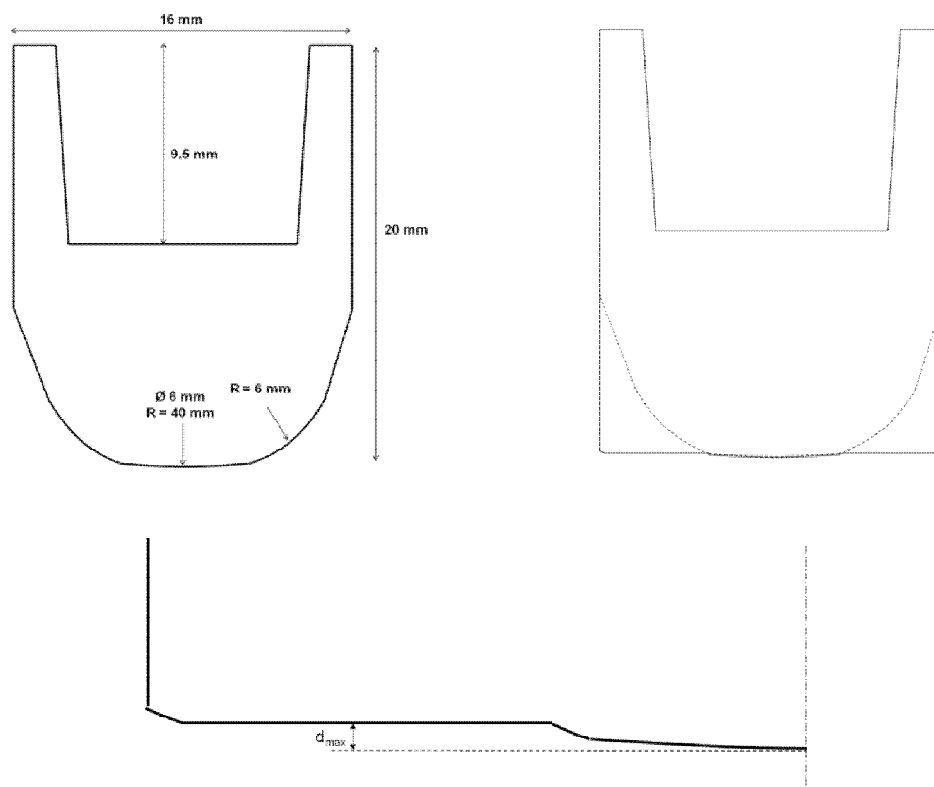


figure 192: Géométrie de l'électrode anti-LME

4.2.3. Validation expérimentale en cours

Deux paires d'électrode avec $d_{max} = 100 \mu\text{m}$ et $d_{max} = 200 \mu\text{m}$ ont été usinées. Des essais de soudage sont actuellement en cours sur les nuances étudiées au Chapitre II. Les électrodes avec $d_{max} = 100 \mu\text{m}$ sont donc supposée supprimer la fissuration. Les résultats de ces essais ne sont pas encore disponibles et donc pas présents dans ce manuscrit.

Conclusion

Résumé de l'argumentation

Tout d'abord, cette étude a permis de préciser l'occurrence et les mécanismes de la fragilisation par le zinc liquide pour trois aciers HR. Il a été montré que le système acier/Zn est sujet à la FML avec les caractéristiques suivantes.

- Une perte très importante de ductilité est observée entre 700 °C et 950 °C (figure 41). Un puits de ductilité pour l'élongation à rupture est visible sur le graphique Elongation-Température. Par comparaison avec le métal nu, le comportement mécanique apparaît inchangé entre le point de fusion du zinc et le début du puits de ductilité et à très haute température.
- L'élongation à rupture, de l'ordre de 40 % à 50 % pour le métal nu, est réduite entre 5 % et 10 % pour les éprouvettes revêtues. Cette ductilité résiduelle apparaît relativement constante (reste très faible devant la ductilité du métal nu) dans la gamme de température de fragilisation. La ductilité résiduelle peut varier d'une nuance à l'autre.
- La température de fin du puits de ductilité correspond à la disparition de la couche de Zn en surface de la tôle d'acier due à l'évaporation du Zn.
- La température de début du puits de ductilité a été décrite comme une température de transition de mouillage. Elle peut varier d'une nuance à l'autre.

D'un point de vue mécanique plus précis, l'exploitation des résultats de traction a permis de préciser le caractère cinétique « lent » (par rapport à la rupture des matériaux fragiles) de la fissuration associée à la FML.

- La rupture n'est pas liée à une contrainte critique ou une déformation critique.
- Le temps d'incubation avant rupture (*life-time*) diminue avec contrainte appliquée.
- Les vitesses de fissuration associées à la rupture de l'éprouvette sont mesurées entre 10^{-2} et 10^{-1} m s^{-1} . L'influence de la température n'a pas été déterminée.

Ces résultats indiquent que la fissuration a un caractère comparable à la corrosion sous contraintes. Le facteur d'intensité de contraintes a donc été estimé en fonction de la profondeur des fissures et des contraintes appliqués par deux méthodes. Suivant une approche non-conventionnelle pour l'exploitation des essais à 850 °C, les vitesses de croissance des fissures pendant le temps d'incubation ont été estimées. La courbe caractéristique obtenue (figure 97), reliant vitesse de fissuration et facteur d'intensité de contrainte en fond de fissure, semble être un moyen pertinent de décrire la fissuration des aciers induite par le zinc liquide.

L'étude a montré que la température de début du puits de ductilité, à (690 ± 20) °C pour les aciers TRIP, n'est ni corrélée à la fusion du zinc, ni à la fusion des intermétalliques zinc-fer. La pénétration (mouillage) des joints de grains de l'acier en contact avec le zinc liquide est observée à partir de (700 ± 50) °C pour la nuance TRIP Si. La corrélation entre les deux phénomènes apparaît forte. La revue bibliographique indique que la pénétration intergranulaire rapide d'un métal liquide se produit au dessus de la température de transition de mouillage du système considéré. C'est pourquoi la température du début de la perte de ductilité a été décrite comme une température de transition de mouillage. La transition de mouillage est décrite par la comparaison entre l'énergie interfaciale acier/zinc et l'énergie du joint de grain.

Ceci montre que les mécanismes de base de la fragilisation et de la pénétration sont les mêmes. Pour dégager une description du mécanisme local de propagation, les hypothèses suivantes ont été faites.

- Au dessus de la température de transition de mouillage, la structure du joint de grain change lorsque que la concentration en Zn, qui augmente par diffusion intergranulaire, atteint la limite de solubilité du joint de grain.
- La pénétration rapide de métal liquide aux joints de grains d'un métal solide est expliquée par la grande diffusivité après transition, de plusieurs ordres de grandeur plus grande que celle du joint de grain solide.
- Après transition, le joint de grain a une résistance mécanique faible.

Le calcul a montré que les cinétiques de diffusion indiquent qu'un profil de diffusion non négligeable existe en avant de la fissure lorsque celle-ci propage à forte vitesse. En avant de la fissure, la limite de solubilité du joint de grain est atteinte sur une profondeur de l'ordre de 100 nm. La zone fragilisée en avant de la fissure abaisse la ténacité du matériau et permet la propagation lors de la déformation macroscopique. La différence entre pénétration (sans contrainte appliquée) et la fissuration (avec contrainte) réside dans le fait que l'ouverture mécanique de la fissure supprime la limitation induite par le transport du zinc par diffusion sur de longue distance (depuis la surface jusqu'au front de pénétration). Cette description montre néanmoins que les cinétiques de diffusion et la transition de mouillage du joint de grain permettent de proposer un modèle qualitatif cohérent pour la propagation des fissures.

Cette étude a permis de préciser les conséquences de la FLM pour le soudage par résistance par point des tôles galvanisées pour les trois nuances. Tout d'abord une caractérisation précise du soudage a été menée, notamment en appliquant des techniques innovantes : la caractérisation des températures de surface par thermographie infrarouge et le mesure du déplacement des électrodes par caméra haute vitesse. Les résultats suivants ont été trouvés pour les trois nuances.

- L'augmentation du courant entraîne :
 - l'augmentation du diamètre du noyau, entre 4 mm et 6,5 mm ;
 - l'augmentation des températures de surface, entre 550 °C et 900 °C ;
 - l'augmentation de la profondeur d'indentation (enfoncement de l'électrode dans le point soudé), entre 80 µm et 300 µm par face,
- Ces paramètres, basiques pour la caractérisation du soudage, sont inter-corrélés.

Pour des courants supérieurs au domaine de soudabilité, l'expulsion, diminution du volume de métal, est associée à l'augmentation abrupte de l'indentation. L'indentation totale peut apparaître en 10 ms pendant le temps de soudage, avant les derniers instants du soudage (typiquement à partir de la moitié du temps de soudage).

Les fissures, identiques à celle observée dans les éprouvettes de traction, apparaissent à partir de la surface, à la fois au centre du point soudé et sur les bords de l'indentation due à l'électrode. L'apparition de la fissuration a été quantifiée en faisant une mesure de la profondeur cumulée des fissures observées sur la vue en coupe du point soudé.

Pour de bas courant, la profondeur cumulée de fissures est nulle. La fissuration apparait en haut du domaine de soudabilité. La profondeur augmente avec l'augmentation du courant de soudage. Au delà du domaine de soudabilité, lorsque l'expulsion est observée, la fissuration devient très importante.

L'augmentation de la profondeur cumulée de fissures peut être corrélée

- à l'augmentation de la profondeur d'indentation ;
- aux températures de surface.

L'étude a montré que l'indentation entraîne des déformations de surface de l'ordre de 1% à 10% à des vitesses de déformation de $0,5 \text{ s}^{-1}$ à 10 s^{-1} . Ces déformations sont particulièrement importantes au bord de l'indentation. A propos des températures, il a été montré que les températures des surfaces pendant la déformation sont comprises entre 650 °C et 1000 °C pour les points soudés sujets à la fissuration. Ces valeurs de température et de déformation en surface sont en très bon accord avec les conditions imposées dans les essais de traction. Il est donc clair que les mécanismes et cinétiques caractérisée ci-avant permettent d'expliquer la fissuration de surface pendant le soudage. Celle-ci apparait donc au moment de l'indentation, pendant les temps de soudage et avant le refroidissement du point. Ceci semble suffisant pour expliquer totalement la longueur des fissures aux congés, mais seulement partiellement pour certaines fissures au centre. En effet la présence de fissures très profondes au centre du point soudé (où les déformations de surface sont les plus faibles), parfois se propageant dans la zone fondue après sa solidification a été observée. Ceci indique clairement que les contraintes internes dues à la contraction du point soudé doivent être mises en jeu dans le cas de ces fissures, qui apparaissent différentes puisqu'elles se propagent dans la microstructure de solidification à gros grains.

Cette étude a aussi mis en évidence les différences de sensibilité des nuances vis-à-vis de la FML. Au soudage, la profondeur des fissures est plus grande pour les TRIP que pour le DP à indentation et température équivalentes. De la même manière, la surface du puits de ductilité est plus grande pour les deux aciers TRIP que pour le DP.

En fait la température de transition de mouillage semble supérieure pour le DP que pour les TRIP. Ceci peut s'expliquer qualitativement en faisant les remarques suivantes.

- L'énergie des joints de grains de l'acier TRIP, interface ferrite/austénite, est plus grande que pour ceux de l'acier DP, interface ferrite/martensite.
- L'énergie de l'interface austénite/Zn est plus faible que celle de l'interface martensite/zinc.
- L'énergie de l'interface ferrite/Zn est plus faible dans le cas des TRIP que dans le cas du DP.

L'explication de la différence de sensibilité peut aussi venir du fait que les vitesses de fissuration, au-delà de la température de transition de mouillage, sont plus faibles pour le DP que pour les TRIP. Vu les mécanismes décrits, ceci peut venir des deux paramètres suivants.

- La limite de solubilité du joint de grain, ou concentration à atteindre localement pour la transition de mouillage, est plus faible dans le cas des TRIP que du DP. Ceci est très probable car la solubilité en volume diminue, par exemple, quand la teneur en silicium augmente. Or les TRIP sont plus alliés que le DP.

- A déformation égale, les contraintes en fond de fissure sont plus grandes pour les TRIP que pour le DP, ceci venant de manière présumée du fait que les propriétés mécaniques (dureté) à ces températures est plus grande pour les TRIP que pour les DP.

Pour mettre en perspective et confirmer certaines de ces hypothèses, l'étude de l'influence de la composition chimique a été effectuée sur une base de données portant sur 30 nuances d'aciers TRIP et DP de compositions variables (essais non réalisés pendant la thèse) et présentant la ductilité résiduelle (élongation critique) dans la gamme de température pour la fragilisation, c'est-à-dire le niveau du fond du puits de ductilité. Cette base de données a été analysée en faisant des régressions simples sur la corrélation entre la valeur de l'élongation critique et la teneur en chacun des principaux éléments d'alliages pris séparément. Des régressions linéaires multiples prenant en compte tous les éléments d'alliages ont aussi été effectuées. Les résultats pour l'influence de la composition chimique, en considérant de manière indifférenciée les aciers TRIP et DP, sont les suivants.

- Le silicium a une influence de premier ordre. L'augmentation du taux de silicium augmente la sensibilité à la FML des aciers, en faisant passer l'élongation critique de 20 % pour 0,1 %m à 5 % pour 1,6 %m.
- Le carbone semble avoir une influence de second ordre. Pour une teneur en Si comparable, l'augmentation du taux de carbone augmente la sensibilité à la FML.
- L'influence des autres éléments, et notamment celle des éléments d'alliages importants Mn et Al, est considérée comme négligeable dans les gammes de concentration étudiées pour chacun d'eux.

Pour expliquer l'influence de ces deux éléments, deux interprétations peuvent être faite.

- Des données quantitatives ont montré que la teneur en silicium diminue la limite de solubilité du zinc dans le fer. La limite de solubilité peut être reliée directement à l'élongation critique. Des indices qualitatifs tendent à montrer que le carbone a un effet similaire sur la solubilité du zinc.
- Des modèles permettent de calculer que la résistance mécanique à chaud augmente avec la teneur en silicium. L'élongation critique peut être reliée à un critère de dureté à chaud.

De manière qualitative, la « non-influence » de Al semble être mieux expliquée avec la limite de solubilité (diagrammes de phases Al-Zn) qu'avec la dureté à chaud (Al augmente autant que Si la dureté à chaud dans les modèles considérés). Des lignes directrices générales pour le développement des microstructures et des compositions chimiques vis-à-vis de la FML ont été proposées.

Points faibles et limites

Plusieurs limites à cette argumentation peuvent être mentionnées. Ceci est notamment dû à la complexité des matériaux et du procédé de soudage étudiés.

Les aciers industriels étudiés sont très complexes à la fois du point de vue de la microstructure (multiples phases cristallographiques et taille de grains), des transformations de phases, et des compositions chimiques : fer, carbone, trois éléments d'alliages principaux (Mn, Si, Al), des éléments d'alliages secondaires et des résiduels.

- L'influence des éléments d'alliages sur le diagramme Fe-Zn n'a pas été prise en compte dans la définition des mécanismes.

- La dissolution et les réactions en volume ont été négligées.
- Les interfaces interphases austénite/ferrite ont été assimilées à des joints de grains (ferrite-ferrite) pour se ramener à une situation symétrique.

D'autres points sont aussi discutables et mériteraient plus d'attention.

- Le facteur d'intensité de contraintes n'est pas applicable ici dans le cas d'une plasticité généralisée du matériau. C'est pourquoi les valeurs de K_I doivent être considérées comme apparentes. Une définition plus rigoureuse de l'intensité des contraintes serait nécessaire.
- L'existence d'une transition de mouillage a été établie par une construction logique mais l'observation expérimentale très locale (par exemple au microscope électronique à transmission à haute résolution) n'a pas été effectuée.

L'interprétation des essais de soudage est effectuée avec quelques approximations (estimation géométrique manuelle de la déformation de surface), ou avec des données de simulations issues de la bibliographie. Des simulations FE dédiées sont nécessaires pour mieux soutenir l'argumentation.

Même si l'analyse sur la base de 30 nuances a permis de mettre en perspective les résultats obtenus sur les trois nuances principales de l'étude, il est clair que les hypothèses émises sont à valider par l'étude de nouvelles nuances.

- L'étude n'a pas permis de montrer définitivement que la solubilité est un paramètre plus pertinent que la dureté pour expliquer l'influence de la composition chimique.
- Les hypothèses pour les énergies acier/zinc et pour les énergies des différents types de joints de grains restent qualitatives.

Perspectives

Deux solutions technologiques ont été proposées. La première consiste à étudier l'influence du phosphore sur la sensibilité, en s'attendant à ce que l'augmentation de la teneur et la ségrégation intergranulaire du phosphore entraîne la diminution de l'énergie des joints de grains et des vitesses de fissuration. D'autre part, une solution « process » a été proposée. Elle consiste en une géométrie d'électrode de soudage permettant de limiter l'indentation à des niveaux qui éviteront la fissuration. La validation expérimentale de ces deux propositions constitue déjà une perspective directe.

Les enseignements et limites de l'étude montrent que de nombreuses autres perspectives sont ouvertes. A propos des essais de traction, il semble que le maintien à contrainte constante au lieu d'un essai à vitesse de déformation constante soit plus pertinent. A température et contrainte constantes, l'observation d'éprouvettes sur des essais interrompus à différents temps permettrait de connaître précisément la vitesse de croissance de la fissure en fonction du temps.

La formulation du mécanisme de fissuration, basé sur le triptyque: diffusion/transition de mouillage/ouverture de la fissure, doit être précisée.

- Quelle est l'influence de la taille de la zone fragilisée en avant de la fissure? Existe-t-il une taille limite pour cette zone liée à un paramètre microstructurale?

- Peut-on trouver une équation liant vitesse de propagation, coefficients de diffusion (intergranulaire et en volume), limite de solubilité du joint de grain et facteur d'intensité de contraintes?

Pour valider le mécanisme de diffusion/transition de mouillage, il est souhaitable que l'étude avec un matériau modèle soit être conduite, par exemple sur Fe-Zn, ou bien sur les alliages Fe-5%Si (étudié par Rabkin, Straumal et co-auteurs) dont le diagramme de phase, les cinétiques de diffusion, les transitions de mouillage sont déjà précisées. La méthode consistant à systématiquement comparer le mouillage et la pénétration dans une situation sans contraintes d'une part, et la perte de ductilité et traction d'autre part, semble être pertinente. Une revue bibliographique pour faire ce lien (entre pénétration et fissuration) dans des couples modèles est peut-être nécessaire, notamment pour des couples où la fragilisation n'apparaît pas à la température de fusion.

L'étude d'alliages modèles Fe-C-Si permettrait aussi de valider l'hypothèse de l'influence de la composition chimique sur la sensibilité des aciers.

D'un point de vue pratique pour la caractérisation de la sensibilité des alliages, il semble très difficile de trouver un essai simple et/ou rapide, au regard la complexité du phénomène et de l'influence de nombreux paramètres.

Pour valider le scénario d'apparition des fissures pendant le soudage par point, le moyen idéal serait de pouvoir combiner la cinétique de fissuration caractérisée de manière précise (après essai de traction interrompu à contrainte et température constante), avec une simulation FE rigoureuse du procédé qui donnerait en tout point de la soudure et à tout moment les contraintes et les températures atteintes. Cette combinaison d'outils permettrait d'aller vers un modèle prédictif de l'importance de la fissuration pendant les procédés de mise en forme.

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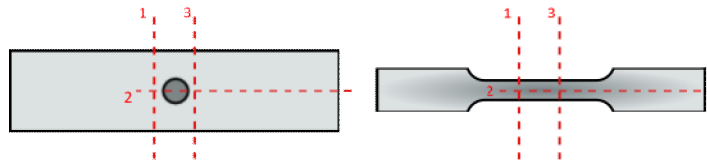
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Appendix 1. Microscopic investigation methods

Sample preparation

Steel samples are extracted from tensile specimens or spot welds by cutting machine with Al_2O_3 cutting disks.

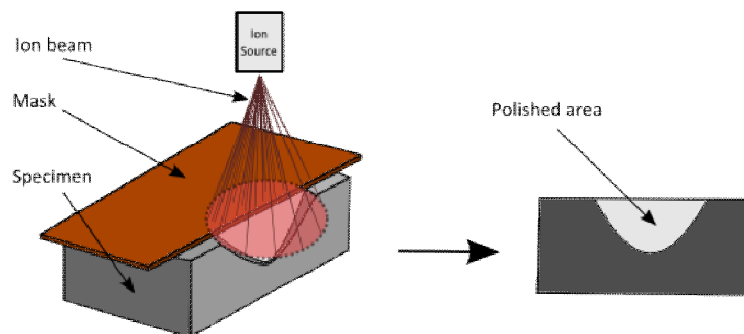


Cutting schedule for spot welds (left) and tensile samples (right)

There are mounted in resin after 5 min at 180 °C. First polishing is made automatically from rough to fine SiC papers, and then with 3 μm diamond particles suspension. Final polishing is carried out manually with a 1 μm diamond particles suspension during 3 min.

If acid etching is chosen, it is performed by immersing the polished surface into a 5 volume percent of nitric acid in EtOH solution during 4 s.

Instead of mechanical, polishing ion-beam cross section polishing is also used. It results in better surface state if readily carried out, but white vertical line may appear in images prepared according to this method because of unwanted space between the mask and the upper specimen surface.



Schematic description of ion-beam cross section polishing

Scanning electron microscopy

Scanning electron microscopy (SEM) is carried out in a “Merlin” Field-emission gun (FEG) microscope from Carl Zeiss, Inc. Imaging is made with 20 kV accelerating voltage, and with current varying from 150 pA nm to 2 nA. In-lens secondary electron (se2) and backscattered electron (bse) detectors are used. Energy

dispersive spectroscopy (EDS) and Wavelength dispersive spectroscopy (WDS) of X-rays was carried out using the INCA system from Oxford Instruments, Inc.

Grain boundary thickness analysis

The analysis of the grain boundary thickness of Zn in steel grain boundaries is performed by making a concentration profile on the cross section across the grain boundary. If the grain boundary is considered to be perpendicular to the surface, and if the quantity of Zn is negligible compared to Fe, the thickness t_{Zn} of the GB channel is described by

$$t_{Zn} = \frac{\rho_{Fe}}{\rho_{Zn}} \frac{A_{Peak}}{100}.$$

The mathematical demonstration can be found in [CHR2012][FER2012].

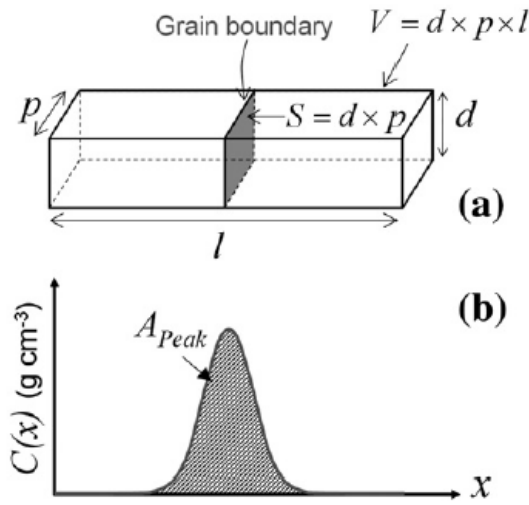


figure 193: Schematic representation of the volume analyzed by WDS when making a profile across the grain boundary (top) and corresponding concentration profile of Zn. V : analyzed volume, p : lateral probe size ($\approx 1 \mu\text{m}$), d : depth of analysis ($\approx 1 \mu\text{m}$), l : length of the beam travel, S : analyzed surface of the GB.

Appendix 2. Crack velocity

To make comparison with crack velocity predicted by models found in the literature, numerical values shown in the table below are considered.

table 27: Materials parameters used for kinetic calculations using the GALOP and RG models

Parameter name	Symbol	Value at T = 700°C	Value at T = 900°C	Units
Fe atomic volume	Ω	1.2×10^{-29}	idem	m^3
Liquid diffusion coefficient	D_L	5×10^{-9}	1×10^{-8}	$\text{m}^2 \text{s}^{-1}$
Solubility	C_L	0.02	0.1	-
Solid-liquid interfacial energy	γ_{SL}	0.3	0.1	J m^{-2}
Boltzmann constant	k	1.38×10^{-23}	idem	J K^{-1}
Dynamic angle	θ	45	idem	deg
Young modulus	E	60×10^3	20×10^3	MPa
Yield strength	σ_Y	130	100	MPa
$C = D_L C_L \gamma_{SL} \Omega_{Fe} / kT$ (GALOP model)	C	2.68×10^{-19}	7.4×10^{-20}	$\text{m}^3 \text{s}^{-1}$
Numerical constant (GALOP model)	φ	40	Idem	-
Elementary step (GALOP model)	ΔL^*	1	idem	nm
Channel width (RG model)	a	1×10^{-8}	idem	m
Thermal kinks (RG model)	$C_J = \exp(-2\gamma_{SL}\Omega^{2/3}/kT)$	9.6×10^{-2}	5.2×10^{-1}	-

The results for crack velocity calculations are shown below. Glickman's model [GLI2003] gives underestimated but interesting values.

Crack velocity predicted by literature models. At 850 °C for TRIP Si steel, experimental results show V in the range $0.1 - 0.01 \text{ mm s}^{-1}$ for K in the range $0.5 - 1.5 \text{ MPa m}^{1/2}$

Model	V at T = 700°C (m s^{-1})	V at T = 900°C (m s^{-1})	K_{th} at T = 700°C ($\text{MPa m}^{1/2}$)	K_{th} at T = 900°C ($\text{MPa m}^{1/2}$)
RG model [JOS1999]	0.0001	0.03	-	-
Glickman's GALOP [GLI2003]	0.002	0.005	1×10^{-1}	3×10^{-2}
Brechet [BRE2002]	1×10^{-6}	2×10^{-6}	-	-

Appendix 3. Modeling K_I with COMSOL

Geometry

A 2D plane strain analysis is conducted with the Comsol Multiphysics v3.5 software. Geometry and boundary conditions are described below. Integration contours for the calculation of the J-integral and the triangular mesh are displayed below.

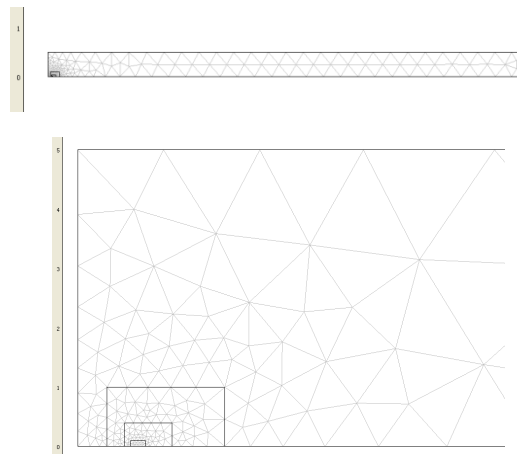
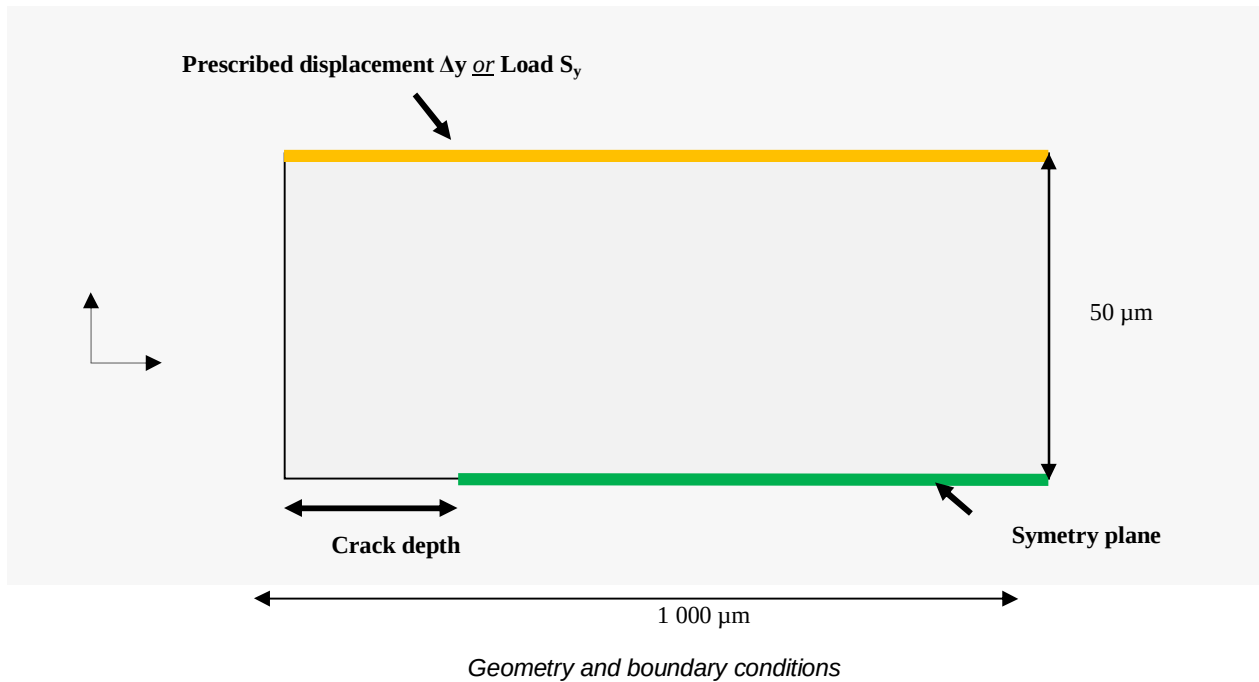
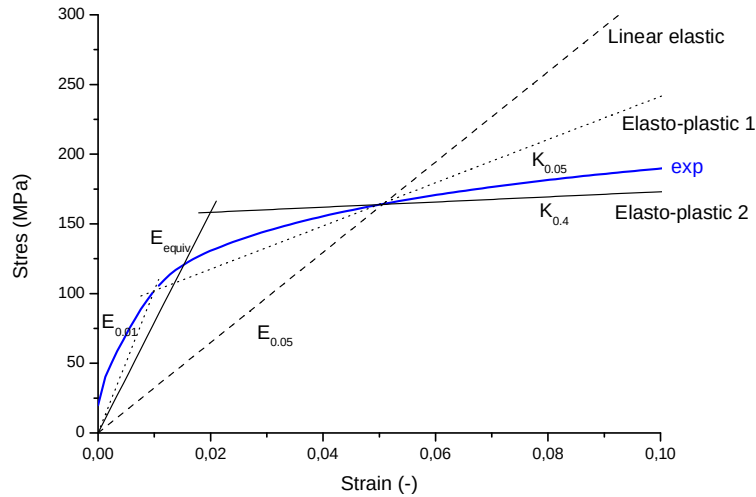


Figure 4: Triangular mesh and integration contours. a) Enlarge view. b) Zoom at the crack tip

Material models

5% strain is the “reference” loading since it corresponds to the maximal elongation in the temperature range of embrittlement. So a prescribed displacement of 25 μm is applied to achieve a 5% macroscopic strain. The bulk mechanical properties are modeled by fitting « real » stress-strain curve. Rough linear or elasto-plastic behaviors with linear hardening are modeled. « Real » means a calculated curve at 850 °C from the model introduced in paragraph 2.4.2 in Chapter III. Parameters are summarized in the table below.



Adjustment of mechanical parameters on the strain-stress curve

Mechanical properties determined from strain-stress curves

Grade	Pure elastic behavior	Elasto-plastic behavior 1	Elasto-plastic behavior 2
TRIP780 MnSi	$E_{0.05} = 3,44 \text{ GPa}$	$E_{0.01} = 10,8 \text{ GPa}$ $YS = 108 \text{ MPa}$ $K_{0.05} = 1,63 \text{ GPa}$	$E_{\text{equiv}} = 8,38 \text{ GPa}$ $YS = 167,6 \text{ MPa}$ $K_{0.4} = 0,191 \text{ GPa}$

K_I calculation method

In this model, the stress intensity factor K_I is determined using the so-called J-integral. Please note that the method has been adapted from the model library of the Comsol software (model also available on the Comsol website). The J-integral is defined as:

$$J = \int_{\Gamma} W dy - T_i \frac{\partial u_i}{\partial x} ds = \int_{\Gamma} \left(W n_x - T_i \frac{\partial u_i}{\partial x} \right) ds$$

where W is the strain energy density:

$$W = \frac{1}{2} (\sigma_x \cdot \varepsilon_x + \sigma_y \cdot \varepsilon_y + \sigma_{xy} \cdot 2 \cdot \varepsilon_{xy})$$

and $\mathbf{T}$ is the traction vector:

$$\mathbf{T} = [\sigma_x \cdot n_x + \sigma_{xy} \cdot n_y, \sigma_{xy} \cdot n_x + \sigma_y \cdot n_y]$$

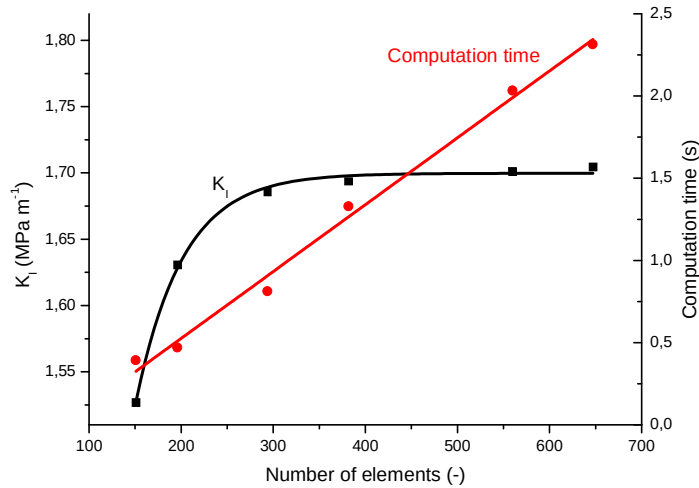
where σ_{ij} denotes the stress components, ε_{ij} denotes the strain components, and n_i the normal vector components. The stress intensity factor can be evaluated for a plane strain case, and for either elastic or elasto-plastic materials:

$$J = \frac{K_I^2}{E}$$

where E is the Young modulus.

Effect of mesh and integration contours

The figure below shows the variation of the result for K_I and the computation time for several mesh refinement. The model shows a good convergence for a relative low number of elements. Computation time increases linearly with the number of elements. For the study a mesh of 300 elements has been chosen. This corresponds to a minimum element size of $0.5 \mu\text{m}$ at the crack tip.



Effect of mesh refinement. Crack length = $10 \mu\text{m}$. Linear elastic model

In the analysis of the J-integral, the choice of the integration contour can have an influence, especially if not in the case of localized plasticity at the crack tip. For examples, the figure below shows the result for K_I for the four contours at different imposed displacement corresponding to 0.1 %, 1 % and 5 % of macroscopic strain, in the case of an elasto-plastic analysis. For 1 % and 5 %, *i.e.* when the material is plasticized, the wide contours 1 and 2 tend to minimize the result for K_I . For practical reasons, the contour 1 is nevertheless chosen for the rest of the study. Absolute value for K_I can be underestimated approximately by 20 % by comparison with other contours.

Furthermore the analysis of the so-called J-integral is rigorously possible only for localized plasticity. Relative results for this parameter would give interesting material for discussion.

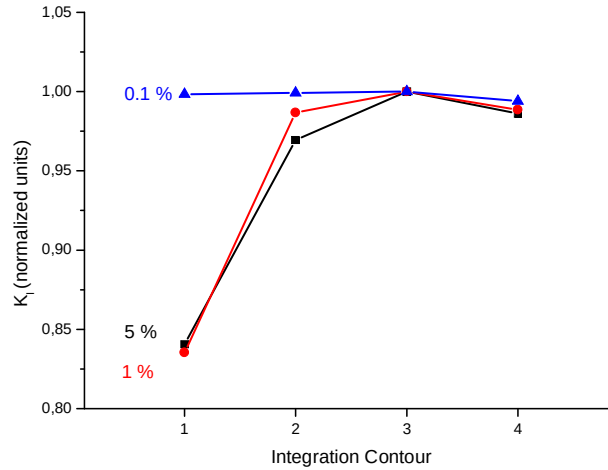
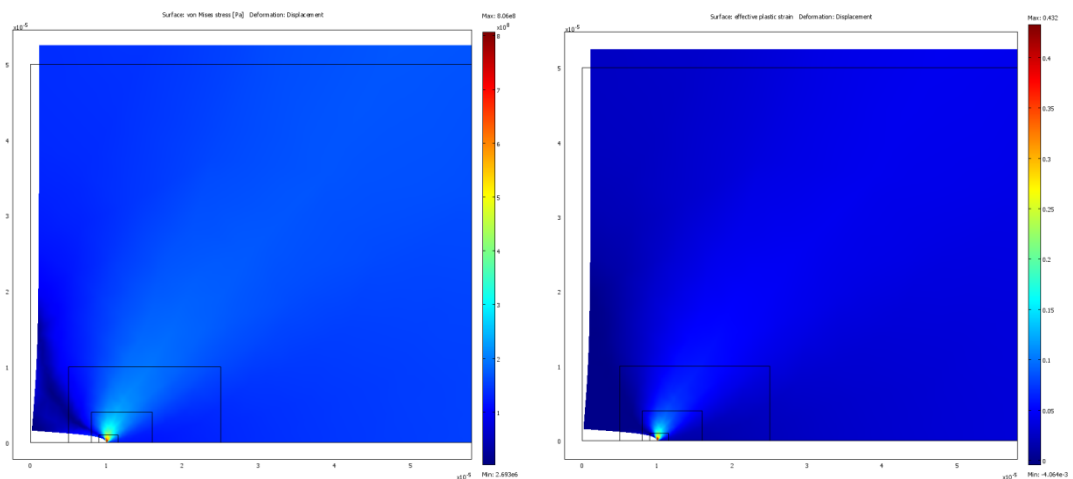


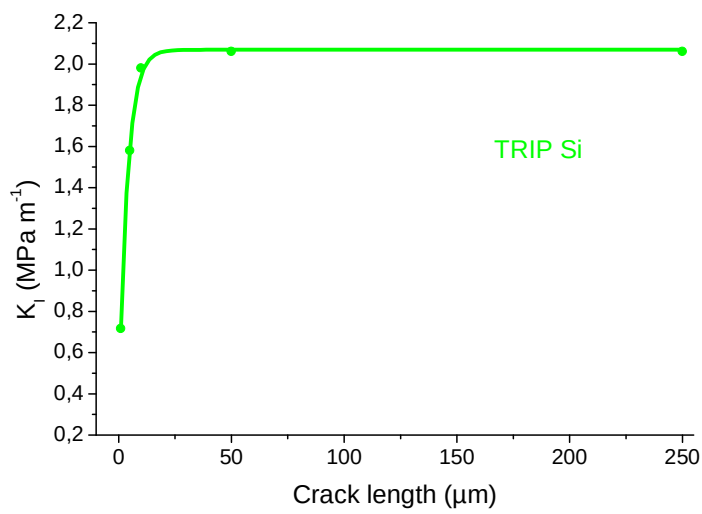
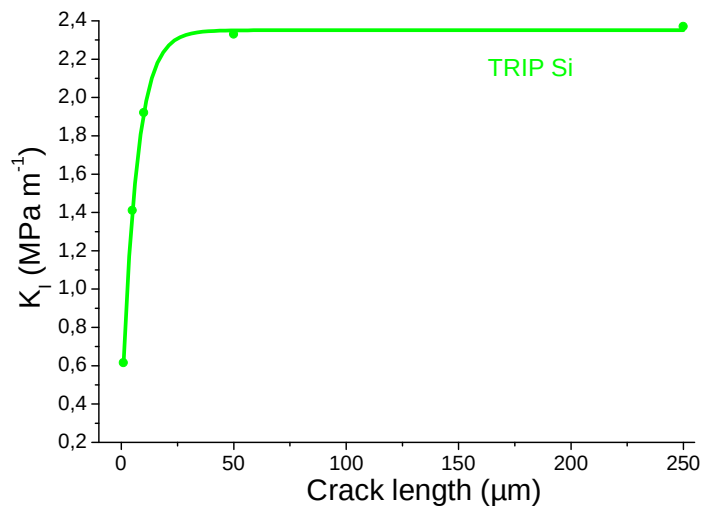
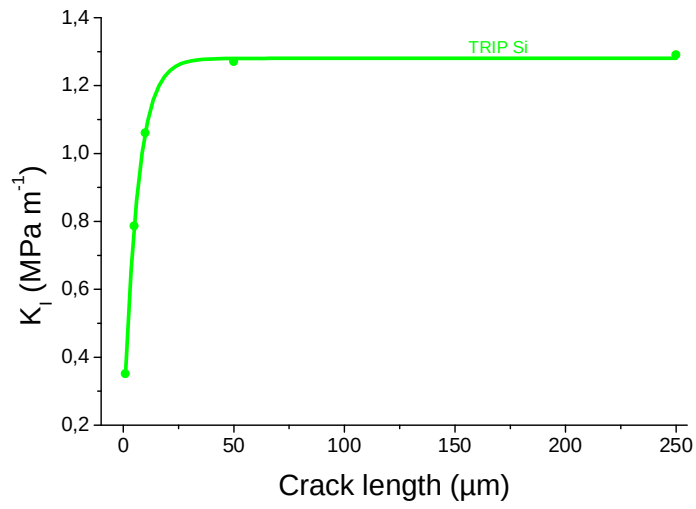
Figure 7: Effect of the integration path. Crack depth = 10 μm . Linear elastic model

Evaluation of K_I

The distribution of Von Mises stress and plastic strain at the crack tip is shown below. The concentration of stress and strain at the crack tip is visible. Figures below also show the results for K_I as a function of the crack depth for the different material behaviors. **K_I increases with the modeled crack length between 1 μm and 30 μm and then is constant for crack length $> 50 \mu\text{m}$.** K_I is lower with the linear elastic model ($K_I \approx 1.3 \text{ MPa m}^{-1/2}$) than for the elasto-plastic 1 model ($K_I \approx 2.3 \text{ MPa m}^{-1/2}$) and elasto-plastic 2 model ($K_I \approx 2.1 \text{ MPa m}^{-1/2}$).



Von Mises stress (left) and effective plastic strain (right). Elasto-plastic 1 behavior. 5 % macroscopic strain. 10 μm crack depth. TRIP Si.



K_I vs. crack depth at 5 % macroscopic strain. Linear elastic behavior (top). Elasto-plastic behavior 1 (middle). Elasto-plastic behavior 2 (down)

Résumé du Chapitre I: Occurrence et mécanismes de la fragilisation

Tout d'abord, cette étude a permis de préciser l'occurrence et les mécanismes de la fragilisation par le zinc liquide pour trois aciers HR. Il a été montré que le système acier/Zn est sujet à la FML avec les caractéristiques suivantes.

- Une perte très importante de ductilité est observée entre 700 °C et 950 °C (figure 41). On observe un puits de ductilité pour l'élongation à rupture sur le graphique Elongation-Température. Par comparaison avec le métal nu, le comportement mécanique apparaît inchangé, ni entre le point de fusion du zinc et le début du puits de ductilité, ni à très haute température.
- L'élongation à rupture, de l'ordre de 40 % à 50 % pour le métal nu, est réduite entre 5 % et 10 % pour les éprouvettes revêtues. Cette ductilité résiduelle apparaît relativement constante (reste très faible devant la ductilité du métal nu) dans la gamme de température de fragilisation. La ductilité résiduelle peut varier d'une nuance à l'autre.
- La température de fin du puits de ductilité correspond à la disparition de la couche de Zn en surface de la tôle d'acier due à l'évaporation du Zn.
- La température de début du puits de ductilité a été décrite comme une température de transition de mouillage. Elle peut varier d'une nuance à l'autre.

D'un point de vue mécanique plus précis, l'exploitation des résultats de traction a permis de préciser le caractère cinétique « lent » (par rapport à la rupture des matériaux fragiles) de la fissuration associée à la FML.

- La rupture n'est pas liée à une contrainte critique ou une déformation critique.
- Le temps d'incubation avant rupture (*life-time*) diminue avec contrainte appliquée.
- Les vitesses de fissuration associées à la rupture de l'éprouvette sont mesurées entre 10^{-2} et 10^{-1} m s⁻¹. L'influence de la température n'a pas été déterminée.

Ces caractéristiques indiquent que la fissuration a un caractère du type corrosion sous contraintes. Le facteur d'intensité de contraintes a donc été estimé en fonction de la profondeur des fissures et des contraintes appliqués par deux méthodes. Suivant une approche non-conventionnelle pour l'exploitation des essais à 850 °C, les vitesses de croissance des fissures pendant le temps d'incubation ont été estimées. La courbe caractéristique obtenue (figure 97), reliant vitesse de fissuration et facteur d'intensité de contrainte en fond de fissure, semble être le meilleur moyen de décrire la fissuration des aciers induite par le zinc liquide.

L'étude a montré que la température de début du puits de ductilité, à (690 ± 20) °C pour les aciers TRIP, n'est ni corrélée à la fusion du zinc, ni à la fusion des intermétalliques zinc-fer. La pénétration (mouillage) des joints de grains de l'acier en contact avec le zinc liquide est observée à partir de (700 ± 50) °C pour la nuance TRIP Si. La corrélation entre les deux phénomènes apparaît forte. La revue bibliographique indique que la pénétration intergranulaire rapide d'un métal liquide se produit au dessus de la température de transition de mouillage du système considéré. C'est pourquoi la température du début de la perte de ductilité

a été décrite comme une température de transition de mouillage. La transition de mouillage est décrite par la comparaison entre l'énergie interfaciale acier/zinc et l'énergie du joint de grain.

Ceci montre que les mécanismes de base de la fragilisation et de la pénétration sont les mêmes. Pour dégager une description du mécanisme local de propagation, les hypothèses suivantes ont été faites.

- Au dessus de la température de transition de mouillage, la structure du joint de grain change lorsque que la concentration en Zn, qui augmente par diffusion intergranulaire, atteint la limite de solubilité du joint de grain.
- La pénétration rapide de métal liquide aux joints de grains d'un métal solide est expliquée par la grande diffusivité après transition, de plusieurs ordres de grandeur plus grande que celle du joint de grain solide.
- Après transition, le joint de grain à une résistance mécanique faible.

Le calcul a montré que les cinétiques de diffusion indiquent qu'un profile de diffusion non négligeable existent en avant de la fissure lorsque celle-ci propage à forte vitesse. Avec les hypothèses ci-dessus, on montre, qu'en avant de la fissure, la limite de solubilité du joint de grain est atteinte sur une profondeur de l'ordre de 100 nm. La zone fragilisée en avant de la fissure abaisse la ténacité du matériau et permet la propagation lors de la déformation macroscopique. La différence entre pénétration (sans contrainte appliquée) et la fissuration (avec contrainte) réside dans le fait que l'ouverture mécanique de la fissure supprime la limitation induite par le transport du zinc par diffusion sur de longue distance (depuis la surface jusqu'au front de pénétration). Alors que la pénétration suit des cinétiques paraboliques, la vitesse de fissuration est linéaire. Cette description montre néanmoins que les cinétiques de diffusion et la transition de mouillage du joint de grain permettent de proposer un modèle qualitatif cohérent pour la propagation des fissures.

Résumé du Chapitre II: Fissuration pendant le soudage

Cette étude a permis de préciser les conséquences de la FLM pour le soudage par résistance par point des tôles galvanisées pour les trois nuances. Tout d'abord une caractérisation précise du soudage a été menée, notamment en appliquant des techniques innovantes : la caractérisation des températures de surface par thermographie infrarouge et la mesure du déplacement des électrodes par caméra haute vitesse. Les résultats suivants ont été trouvés pour les trois nuances.

- L'augmentation du courant entraîne :
- l'augmentation du diamètre du noyau, entre 4 mm et 6,5 mm ;
- des températures de surface, entre 550 °C et 900 °C ;
- de la profondeur d'indentation (enfoncement de l'électrode dans le point soudé), entre 80 µm et 300 µm par face,
- ces paramètres, basiques pour la caractérisation du soudage, sont inter-corrélés.

Pour des courants supérieurs au domaine de soudabilité, l'expulsion, diminution du volume de métal, est associée à l'augmentation abrupte de l'indentation. L'indentation totale peut apparaître en 10 ms pendant le temps de soudage, avant les derniers instants du soudage (typiquement à partir de la moitié du temps de soudage).

Les fissures, identiques à celle observée dans les éprouvettes de traction, apparaissent à partir de la surface, à la fois au centre du point soudé et sur les bords de l'indentation due à l'électrode. L'apparition de la fissuration a été quantifiée en faisant une mesure de la profondeur cumulée des fissures observées sur la vue en coupe du point soudé.

- Pour de bas courant, la profondeur cumulée de fissures est nulle. La fissuration apparaît en haut de domaine de soudabilité. La profondeur augmente avec l'augmentation du courant de soudage. Au delà du domaine de soudabilité, lorsque l'expulsion est observée, la fissuration devient très importante.

L'augmentation de la profondeur cumulée de fissures peut être corrélée

- à l'augmentation de la profondeur d'indentation ;
- aux températures de surface.

L'étude a montré que l'indentation entraîne des déformations de surface de l'ordre de 1% à 10% à des vitesses de déformation de $0,5 \text{ s}^{-1}$ à 10 s^{-1} . Ces déformations sont particulièrement importantes au bord de l'indentation. A propos des températures, il a été montré que les températures des surfaces pendant la déformation sont comprises entre 650 °C et 1000 °C pour les points soudés sujets à la fissuration. Ces valeurs de température et de déformation en surface sont en très bonne accord avec les conditions imposées dans les essais de traction. Il est donc clair que les mécanismes et cinétiques caractérisée ci-avant permettent d'expliquer la fissuration de surface pendant le soudage. Celle-ci apparaît donc au moment de l'indentation, pendant les temps de soudage et avant le refroidissement du point. Ceci semble suffisant pour expliquer

totale de la longueur des fissures aux congés, mais seulement partiellement pour certaines fissures au centre. En effet la présence de fissures très profondes au centre du point soudé (où les déformations de surface sont les plus faibles), parfois propageant dans la zone fondue après sa solidification a été observée. Ceci indique clairement que les contraintes internes dues à la contraction du point soudé doivent être mises en jeu dans le cas de ces fissures-ci, qui apparaissent différentes puisqu'elles propagent dans la microstructure de solidification à gros grains.

FRAGILISATION PAR LE ZINC LIQUIDE DES ACIERS A HAUTE TEMPERATURE ET CONSEQUENCES

La fragilisation induite par le zinc liquide d'aciers haute résistance et les conséquences pour le soudage par résistance par point des tôles galvanisées est étudié. Les essais de traction à haute température montrent une perte de ductilité importante des éprouvettes revêtues de Zn, par comparaison avec les éprouvettes nues, typiquement entre 700 °C et 950 °C. Des fissures intergranulaires sont observées avec la présence de films nanométriques de Zn. La gamme de température pour la fragilisation (au-delà du point de fusion du zinc, env. 420 °C) est corrélée à celle du mouillage des joints de grains de l'acier par le Zn. Les vitesses de propagation de fissures sont reliées au facteur d'intensité de contraintes estimé en fond de fissures. Le phénomène est discuté en fonction de la transition de mouillage des joints de grains, la diffusion intergranulaire et les aspects mécaniques en fond de fissure. Le soudage par résistance par points de ces aciers est caractérisé grâce à des méthodes innovantes : la mesure de température par thermographie infrarouge, et la caractérisation des déformations au cours du soudage par caméra haute vitesse. L'apparition des fissures est quantifiée en mesurant une profondeur de fissures cumulée dans le point soudé en fonction du courant de soudage, des températures et des déformations de surface. Les différences de sensibilité entre les nuances étudiées sont discutées en fonction de la microstructure et de la composition chimique. L'analyse d'une base de données portant sur 30 nuances d'aciers permet aussi de dégager des tendances pour l'influence des principaux éléments d'alliage, et d'envisager des solutions pour supprimer le phénomène.

Mots-clés: Fragilisation par les métaux liquides, Fissuration, Pénétration, intergranulaire Acier, Zinc, Mise en forme

LIQUID ZINC EMBRITTLEMENT OF STEELS AT HIGH TEMPERATURE AND CONSEQUENCES

Liquid-Zn induced embrittlement of advanced high strength steels and the consequences for resistance spot welding of galvanized sheets are studied. High temperature tensile tests show that Zn-coated steels loss its ductility, by comparison with bare steel sheet, for temperature typically between 700 °C and 950 °C. Intergranular cracks are observed with nanometer-thick films of Zn. The temperature range for embrittlement (well above Zn melting point around 420 °C) is correlated to the effective wetting of steel grain boundaries by liquid Zn. Crack velocity is correlated to estimated stress intensity factor at the crack tip. The phenomenon is discussed in terms of grain boundary diffusion of Zn, wetting transition of grain boundary, and simple mechanical features at the crack tip. Resistance spot welding process is characterized by innovative methods: temperature measurement by infrared thermography, and deformation characterization by high speed camera monitoring. Cracking extent for investigated grades is quantified by measuring a cumulated crack depth into the spot as a function of welding current, surface temperature and surface deformation. Differences between investigated steels are analyzed regarding the chemical composition and the microstructure. The analysis of a database of 30 steel grades lead to find tendency for the influence of main alloying elements, and to design tentative solutions to avoid the phenomenon.

Keywords: Liquid metal embrittlement, Cracking, Intergranular penetration, Steels, Zinc, Forming

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