Transgranular Cracking in a Liquid Zn Embrittled High Strength Steel

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Abstract:

Intergranular Zn-assisted liquid metal embrittlement (LME) cracks have been frequently reported in steels, involving austenite grain boundary penetration of liquid Zn at high temperature. In the present study, a Zn-coated high strength steel was deformed at an intercritical temperature, and the characteristics of LME cracking were studied in a mixed microstructure composed of ferrite and austenite. Crack propagation was intergranular in austenite; in contrast, the ferrite exhibited both intergranular LME and *transgranular* LME. Trace analysis of the crack plane orientation was consistent with cracking along {100} cleavage planes in ferrite.



- "Transgranular" LME Cracking

Keywords:

Liquid metal embrittlement; high strength steel; Zn; intercritical temperature; ferrite; transgranular cracking

Liquid metal embrittlement (LME) induced cracking adversely affects the ductility of zinc (Zn)coated steels at elevated temperatures ^[1-5]. LME cracks are usually triggered by the simultaneous presence of liquid Zn and stress ^[1-5]. Previous accounts of Zn-assisted LME in the literature highlighted that the nature of cracking is exclusively "intergranular" in steel substrates ^[4-10]. Phenomenological models interpreted intergranular cracking in steel alloys in the context of liquid Zn penetration along grain boundaries, driven by the reduction of surface energy of boundaries ^[6-12]. In reality, LME cracking is a complicated phenomenon, and the cracking behavior could be potentially influenced by the substrate microstructure. Most reports of LME intergranular cracking in steel are from investigations conducted using fully austenitic substrates; the LME cracking behavior of substrate microstructures containing ferrite is therefore an important missing piece of information; so there is a need for the LME crack propagation path in complex microstructures to be characterized.

The work presented here focusses on the characteristics of LME cracks formed in a Zn-coated high ductility AHSS steel of 1 GPa tensile strength. The Zn-coating was applied through industrial hot-dip galvanizing. The coating thickness was approximately 10 µm. LME cracks were generated through hot deformation of the Zn-coated steel carried out in a Gleeble 3500 thermomechanical process simulator. The dimensions of the uniaxial hot tensile specimen were 145 mm in length (having a reduced section of 25 mm at the center), 25 mm in width, and 1.5 mm in thickness. **Figure 1(a)** schematically presents the thermomechanical cycle imposed on the Zn-coated steel. Hot deformation was conducted at 800 °C, a temperature believed to be relevant to industrial spot welding behavior ^[13]. The specimen was heated to the test temperature at a rate of 1000 °C s⁻¹ and isothermally held for 0.5 s. The specimen was then deformed in tension until failure, using a constant displacement rate of 150 mm s⁻¹. The rapid heating rate, short hold time, and fast displacement rate were targeted to minimize Fe-Zn intermetallic formation during the thermal cycle ^[11-14], and thus maximize the availability of liquid Zn to induce LME. After fracture, the specimen was helium (He)-quenched to room temperature (RT) using a cooling rate of approximately 400 °C s⁻¹. The LME cracks were investigated using scanning electron microscopy (SEM)

imaging, energy dispersive X-ray spectroscopy (EDS), and electron back scatter diffraction (EBSD) in a JEOL JXA-8520F field emission SEM operated at 20 keV using a 80 nA beam current. The EBSD orientation data were post-processed using the TSL-OIM Data Analysis software (version 8.1; EDAX).

Figure 1(b) shows an SEM micrograph of the base microstructure prior to hot tensile testing of the Zn-coated steel. The multiphase microstructure is composed of ferrite (a), bainite (a_B), and martensite- austenite (MA) constituents. The initial microstructure evolved with temperature during the thermal cycle; the high temperature microstructure present at the deformation temperature (*i.e.* at 800 °C) is of specific interest. **Figure 1(c)** shows an SEM image of the substrate microstructure recorded from the as-quenched fractured hot tensile specimen. The final microstructure is composed of ferrite (a) and martensite (M). Based on the final microstructure at RT (**Figure 1(c)**), it is confirmed that the steel was in the inter-critical temperature range at the deformation temperature. That is, the steel microstructure at 800 °C was composed of a mixture of ferrite and austenite, as schematically shown in **Figure 1(d)**. The martensite observed in the final microstructure would have resulted from the transformation of the austenite upon rapid quenching from the test temperature. The ferrite in the RT microstructure was present in the high temperature microstructure.

Figure 2(a) shows a cross-sectional SEM micrograph of a representative LME crack formed on the Zn-coated steel during the hot deformation step. The LME crack initiated at the coating-substrate interface and propagated into the steel substrate in the normal direction (ND) *i.e.* perpendicular to the direction of applied stress (tensile direction was parallel to rolling direction (RD)). The tip of the crack in **Figure 2(a)** was characterized further, to study the characteristics of the crack path. **Figure 2(b)** shows a magnified view of the microstructure in the region surrounding the crack tip (from the region indicated in **Figure 2(a)**). **Figure 2(c)** presents the corresponding EBSD inverse pole figure (IPF) orientation map of the bcc phase in the microstructure. The steel substrate adjoining the LME crack is composed of bcc ferrite (*a*) and bct martensite (*M*) in the after-test RT microstructure (martensite is indexed as bcc). The martensite can be differentiated from the ferrite in **Figure 2(b)** based on its lath morphology in an etched microstructure. The martensitic regions in the RT microstructure correspond to locations that were austenitic at the deformation temperature (800 °C). The prior austenite grain boundaries (PAGBs) are indicated using dashed lines in **Figure 2(b)**. PAGBs were situated at the interfaces of ferrite and martensite in the RT microstructure. In addition, PAGBs were located within some martensitic regions; these PAGBs were identified using the EBSD IPF map as boundaries in the martensite having misorientation angles of $20^{\circ}-46^{\circ}$ ^[15-17]. **Figure 2(d)** shows the corresponding SEM-EDS Zn elemental map, confirming infiltration of Zn along the entire length of the LME crack.

The SEM micrograph and corresponding EBSD map (**Figures 2(b**) and (**c**)) were used conjointly to characterize the propagation path of the LME crack. The SEM micrograph helped identify the microstructural constituent present on adjacent sides of the crack. The EBSD IPF was used to study the crystallographic orientations of the corresponding regions. It is clear that at 800 °C, the crack in the substrate microstructure presented three different paths for liquid Zn penetration, bounded by γ/γ , γ/α , or α/α regions. LME crack propagation was often "intergranular". **Figure 2(e)** overlays red arrows on the SEM micrograph to highlight locations where the crack propagated via separation at prior austenite (γ/γ) grain boundaries. In such locations, martensite is situated on both sides of the crack. Intergranular cracking was noted based on the apparent PAGBs and then confirmed by measuring the crystallographic misorientation between the areas labeled '1' and '2' in **Figure 2(e)** is 37°, indicating that a PAGB (misorientation between 20° to 46° ⁽¹⁵⁻¹⁷⁾) was situated between the corresponding crystals prior to the crack propagation. Also exemplified in **Figure 2(e)** using yellow arrows, are locations, where the crack has ferrite and martensite on adjoining sides in the RT microstructure. At these locations, it is evident that intergranular cracking occurred following the interphase (γ/α) boundaries at high temperature.

LME crack propagation also followed some ferrite (α/α) grain boundaries. Figure 2(f) shows the SEM image labeled with locations of intergranular cracking in ferrite. The corresponding crystals in the EBSD map indicate different crystallographic orientations of the ferrite on adjoining flanks of the crack.

For instance, the misorientation between the ferrite crystals at locations labeled '3' and '4' in **Figure 2(f)** was 57°. A large misorientation between ferrite crystals situated on two sides of the crack confirms intergranular crack propagation.

In several locations, the SEM micrograph and EBSD IPF indicated that the LME crack propagated *within* a ferrite grain. In these instances, the IPF reveals essentially identical ferrite orientations on both sides of the crack. **Figure 2(g)** identifies some of these cracks within ferrite grains. As an example, the crystallographic orientations of the ferrite at sites labelled '5' and '6' are overlaid (using cubes to represent unit cell orientation) on the SEM image in **Figure 2(g)**. The similar crystallographic orientation of the ferrite at sites '5' and '6' (the misorientation was less than 3°) suggests that these sites belonged to the same ferrite grain at the time of cracking. That is, the LME crack propagated in a "transgranular" rather than "intergranular" fashion. The Zn-EDS map (**Figure 2(d)**) showed that Zn was present at all the locations with transgranular cracks highlighted in **Figure 2(g)**. This observation confirms that *transgranular LME* occurred in the ferrite. A trace analysis was also conducted to relate the direction of the transgranular crack surface to the {100} cleavage planes of bcc ferrite. Examples of the traces of {100} planes are presented for a few ferrite grains with transgranular cracks in **Figure 2(g)**. In all cases, the direction of the crack is approximately parallel to one of the {100} plane traces, suggesting the possibility or likelihood of cleavage fracture of ferrite on {100} planes.

To the best of the authors' knowledge, there are no previous reports of transgranular Zn-assisted LME cracking of steels, although transgranular LME has been observed in other solid and liquid metal couples; for example Cd(s)/Ga(1)^[18], Al(s)/Hg(1)^[19], Zn(s)/Hg(1)^[20], Fe-Si(s)/Pb-Bi(1)^[21]. While the mechanism of transgranular LME is not yet clear, one simple hypothesis is presented here to explain the mixed mode of Zn-LME crack propagation in high temperature microstructures containing ferrite. The proposed model first assumes that in a polycrystalline steel substrate, grain boundaries are preferred sites for liquid Zn penetration. However, not every Zn-infiltrated grain boundary is susceptible to cracking, as some boundaries are unfavorably oriented relative to the tensile direction, and may not experience the

critical tensile stress required for cracking. The different cracking susceptibilities of various boundaries present in a microstructure is illustrated using a schematic of an idealized microstructure in **Figure 3(a)**. The microstructure is composed of three grains labelled 'A₁', 'A₂', and 'A₃'. The direction of the applied tensile stress is indicated in **Figure 3(a)**. The A₁/A₂ type boundaries are oriented normal to the tensile direction, thus experiencing a large tensile stress normal to the boundary. In contrast, the A₁/A₃ or A₂/A₃ boundaries in this idealized microstructure are aligned with the tensile direction, thereby having no tensile stress resolved normal to the boundary. Supposing that all boundaries are infiltrated with Zn at high temperatures, only the A₁/A₂ type boundaries are susceptible to intergranular cracking, while the A₁/A₃ or A₂/A₃ boundaries should remain intact and thus resist LME cracking.

The hypothesis is evaluated/illustrated using one representative location with a transgranular crack along the LME crack path. **Figure 3(b)** and **(c)** present an SEM image and corresponding EBSD IPF map from a portion of the investigated LME crack in **Figure 2(a)**. The crack in this region is bounded by ferrite grains (labelled ' α_1 ' and ' α_2 ' in **Figure 3(b)**) and martensite (labelled 'M' in **Figure 3(b)**). ' α_1 ' contained an intergranular crack; we may consider that its cracked boundary plane was oriented nearly normal to the RD (tensile direction). Transgranular cracking occurred in ' α_2 ', situated directly in the path of the intergranular crack along ' α_1 '. In this case, we consider that the boundary presented by ' α_2 ' to the incoming crack was oriented nearly parallel to the tensile axis, indicated in **Figure 3(c)**. These boundaries were prevented from cracking due to a small resolved tensile stress normal to the boundaries.

The formation of a transgranular cleavage crack requires that the tensile stress resolved normal to a cleavage plane exceeds the critical stress for cleavage fracture in the presence of Zn. Ferrite is usually a ductile phase at high temperatures; embrittlement is only expected if there is intimate contact with liquid Zn. The widely accepted 'adsorption-induced cohesion reduction' mechanism proposed by Stoloff-Johnson-Westwood-Kamdar (SJWK)^[18,20-23] is potentially applicable to explain transgranular cleavage cracking of ferrite in a liquid Zn environment. This model suggests that the adsorption of liquid metal species in the vicinity of the crack tip results in localized reduction of atomic bond strength at the crack tip. From this perspective, it is possible that liquid Zn may decrease the critical cleavage stress of ferrite, thereby stimulating its transgranular fracture. For example, electronic structure calculations by Legris *et al.* ^[24] predicted that the absorption of Pb-Bi eutectic liquid could reduce the surface energy of {100} cleavage planes of pure iron by approximately 22 %. Analyses of the surface energy reduction by adsorption of Zn on cleavage planes of ferrite might help to confirm the applicability of the SJWK model to Zn-LME of steels. Transgranular cracking may also be facilitated by bulk diffusion of Zn from liquid infiltrated boundaries, resulting in Zn enrichment of the ferrite in vicinity of the crack tip. Bulk Zn diffusion occurring simultaneously with liquid penetration, has been confirmed by previous Zn LME studies ^[6-8]. The greater Zn diffusivity in ferrite compared to that in austenite might thus help facilitate transgranular cracking in the ferrite. In this regard, the high temperature mechanical behavior of Zn-enriched ferrite would be of particular interest.

Figure 4 (a) through (d) illustrate the proposed sequence of events leading to transgranular LME crack formation in a schematic microstructure composed of three ferrite grains labeled ' α_1 ', ' α_2 ', and ' α_3 '. For simplicity, it is assumed that all crystals in the microstructure are bcc, although the model should also apply in case the ' α_1 ' and/or ' α_2 ' grains were austenitic (fcc). The ' α_3 ' crystal in the schematic microstructure is more specifically ferritic, based on the observation here of transgranular LME cracking in a bcc crystal. The four steps in the sequence are explained as follows:

(a) The α_1/α_2 grain boundary area is infiltrated with liquid Zn at a high temperature. This boundary also experiences high tensile stress due to its orientation normal to the tensile direction. Satisfying the critical conditions for LME, the α_1/α_2 boundary suffers cracking.

(b) Liquid Zn infiltrates the α_1/α_3 and α_2/α_3 boundaries. These boundaries are oriented parallel to the tensile axis, and have no tensile stress normal to the boundaries. Consequently, the α_1/α_3 and α_2/α_3 do not experience LME cracking.

(c) The critical cleavage stress of ' α_3 ' is reduced either by adsorption of Zn atoms onto its cleavage planes, or by its enrichment with Zn beyond a critical limit via bulk Zn diffusion from the liquid.

(d) The stress concentration at the tip of the intergranular crack results in a large resolved normal stress on the cleavage planes of ' α_3 ', initiating a transgranular cleavage crack. Liquid Zn remains available to continue transgranular crack propagation.

In conclusion, it is shown that Zn-assisted LME cracks in steels are not always intergranular in nature; "transgranular" cracking is also found. The present investigation characterized LME crack propagation in high temperature microstructures composed of a mixture of ferrite and austenite. While intergranular cracking markedly affected the austenitic regions in the steel microstructure, the ferrite exhibited susceptibility to both intergranular and transgranular cracking.

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References

- [1] C. Beal, X. Kleber, D. Fabregue, M. Bouzekri, Philos. Mag. Lett. 91(2011) 297-303.
- [2] K.D. Bauer, M. Todorova, K. Hingerl, J. Neugebauer, Acta Mater. 90 (2015) 69-76.
- [3] M. Takahashi, M. Nakata, K. Imai, N. Kojima, N. Otsuka, ISIJ Int. 57 (2017) 1094-1101.
- [4] M.H. Razmpoosh, A. Macwan, E. Biro, D.L. Chen, Y. Peng, F. Goodwin, Y. Zhou, Mater. Des. 155 (2018) 375-383.
- [5] C. Beal, X. Kleber, D. Fabregue, M. Bouzekri, Mater. Sci. Eng. A 543 (2012) 76-83.
- [6] C.W. Lee, W.S. Choi, L. Cho, Y.R. Cho, B.C. De Cooman, ISIJ Int. 55 (2015) 264-271.
- [7] H. Kang, L. Cho, C. Lee, B.C. De Cooman, Metall. Mater. Trans. A Phys. Metall. Mater. Sci. 47 (2016) 2885-2905.
- [8] L. Cho, H. Kang, C. Lee, B.C. De Cooman, Scr. Mater. 90 (2014) 25-28.
- [9] G. Jung, I. S. Woo, D. W. Suh, and S. J. Kim, Met. Mater. Int. 22(2016) 187-195.
- [10] P.J.L. Fernandes, R.E. Clegg, D.R.H. Jones, Eng. Fail. Anal. 1 (1994) 51-63.
- [11] B. Joseph, M. Picat, F. Barbier, Eur. Phys. J. Appl. Phys. 5 (1999) 19-31.
- [12] M.G. Nicholas, C.F. Old, J. Mater. Sci. 14 (1979) 1-18.
- [13] D.Y. Choi, A. Sharma, S.H. Uhm, J.P. Jung, Met. Mater. Int. 25 (2019) 219-228.
- [14] P.J.L. Fernandes, D.R.H. Jones, Int. Mater. Rev. 42 (2014) 251-261.
- [15] J. Han, A.K. da Silva, D. Ponge, D. Raabe, S.M. Lee, Y.K. Lee, S.I. Lee, B. Hwang, Acta Mater. 122 (2017) 199-206.
- [16] J. Hidalgo, M.J. Santofimia, Metall. Mater. Trans. A Phys. Metall. Mater. Sci. 47 (2016) 5288-5301.
- [17] M. Kuzmina, D. Ponge, D. Raabe, Acta Mater. 86 (2015) 182-192.
- [18] M.H. Kamdar, in: Adv. Res. Strength Fract. Mater. (1978) 387-405.
- [19] R.J.H. Wanhill, Corrosion. 10 (1974) 371-380.
- [20] A.R.C. Westwood, M.H. Kamdar, Philos. Mag. 89 (1963) 787-804.
- [21] J. Van Den Bosch, G. Coen, P. Hosemann, S.A. Maloy, J. Nucl. Mater. 429 (2012) 105-112.
- [22] N.S. Stoloff, T.L. Johnston, Acta Metall. 11 (1963) 251-256.
- [23] A.R.C. Westwood, C.M. Preece, M.H. Kamdar, Eng. Fundam. Environ. Eff. (1971) 589-644.
- [24] A. Legris, G. Nicaise, J.B. Vogt, J. Foct, J. Nucl. Mater. 301 (2002) 70-76.



Figure 1- (a) Thermomechanical cycle imposed by the Gleeble 3500 simulator for hot tensile deformation of the Zn-coated steel at 800 °C, (b) SEM micrograph of the base microstructure of the Zn-coated steel prior to the hot tensile test, (c) SEM micrograph of the final microstructure of the steel substrate after hot deformation and subsequent quenching to RT, (d) schematic illustration of the high temperature microstructure of the steel at the 800 °C test temperature. (*ferrite* – ' α ', *austenite* – ' γ ', *bainite* – ' α_B ', *martensite* – *M*, *martensite/austenite* constituent – '*MA*')



Figure 2 - (a) Cross-sectional SEM image of a representative LME crack formed in the Zn-coated steel during hot deformation at 800 °C. The tensile axis is parallel to rolling direction (RD), (b) SEM micrograph of the microstructure surrounding the crack tip (from the region labeled in (a)). *Ferrite* - ' α ' and martensite - 'M'. Dashed lines indicate prior austenite grain boundaries, (c) corresponding EBSD inverse pole figure (IPF) map of bcc phases in the microstructure. Example traces of {100} cleavage planes of bcc are overlaid for three grains, (d) corresponding SEM-EDS Zn elemental map. (e)-(g) highlight the different paths of crack propagation - (e) intergranular LME via prior austenite grain boundaries (red arrows) and ferrite-austenite interphase boundaries (yellow arrows), (f) intergranular LME in ferrite. At the labeled locations, the EBSD IPF map indicates different ferrite orientations on both sides of the LME crack, (g) transgranular LME in ferrite. At the labeled locations on both sides of the LME crack. As an example, the crystallographic orientation of the ferrite at sites '5' and '6' are overlaid (using cubes to represent crystal orientation).



Figure 3 - (a) A simplified schematic of an idealized microstructure illustrating the existence of one type of grain boundary having a large tensile stress (A₁/A₂ type boundaries that are oriented perpendicular to the tensile direction), and another type of boundary having no tensile stress component normal to the boundary (A₁/A₃ or A₂/A₃ type boundaries oriented parallel to the tensile direction). In the event of liquid infiltration, cracking is likely to happen via separation along the A₁/A₂ type boundaries, while the A₁/A₃ or A₂/A₃ type boundaries would remain intact, (b) SEM micrograph and (c) corresponding EBSD IPF map from an actual site of transgranular LME cracking. α_1 and α_2 are ferrite grains (enclosed within blue and black dashed lines, respectively in (b)). *M* is a martensitic (prior austenite) region adjacent to the crack. The α_1 grain was intergranularly cracked; the α_2 grain was transgranularly cracking. The unfavorably oriented boundaries of the α_2 grain (A₁/A₃ or A₂/A₃ type boundaries in (a)) are indicated in (c).



Figure 4 – Schematic illustrating the proposed sequence of events ((a) through (d)) leading to a transgranular Zn-assisted LME crack formation in a microstructure composed of ferrite grains labelled ' α_1 ', ' α_2 ', and ' α_3 '. (a) intergranular LME cracking along the α_1/α_2 boundary, (b) arrest of intergranular crack due to lack of tensile stress normal to α_1/α_3 and α_2/α_3 boundaries, (c) embrittlement of ' α_3 ' upon interaction with the liquid, (d) cleavage cracking of ' α_3 ' and subsequent percolation of liquid to continue the transgranular crack propagation.