4.0 INFLUENCE OF SELECTED ALLOYING ELEMENTS AND STARTING MICROSTRUCTURE ON THE SUSCEPTIBILITY TO LIQUID METAL EMBRITTLEMENT DURING RESISTANCE SPOT WELDING OF Zn-COATED ADVANCED HIGH STRENGTH STEELS

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4.1 Introduction
This project was initiated in September 2017 to fulfill the Doctor of Philosophy requirement for Diptak Bhattacharya in Metallurgical and Materials Engineering at the Colorado School of Mines. The estimated completion date is March 2022. The scope of this project is to investigate the specific influences of starting microstructure and selected alloying elements (C, Mn, and Si) on the sensitivity of advanced high strength steels (AHSS) to Zn-assisted liquid metal embrittlement (LME) during resistance spot welding (RSW). High temperature tensile testing is a useful technique to study the thermomechanical conditions promoting LME crack formation during RSW. The work presented previously in Fall and Spring 2020 characterized the specific influence of starting microstructure (martensitic, quenched and partitioned (Q&P), transformation-induced-plasticity (TRIP) assisted bainitic-ferrite (TBF), and dual phase (DP)) on the Zn-LME susceptibility of a single AHSS alloy. Subsequently, the work presented in Fall and Spring 2021 characterized the specific influence of alloying elements on the Zn-assisted LME susceptibility of AHSS alloys. The Zn-LME behavior of AHSS having different chemical compositions was investigated by performing hot ductility tests at various temperatures above the Zn melting temperature (~ 427 °C) in a Gleeble® 3500 thermomechanical simulator. Additionally, RSW was performed in efforts to compare the extent of LME cracking in spot-welded joints of AHSS sheets with different chemical compositions. From the results of both hot ductility and welding experiments, it became apparent that chemical composition can influence LME susceptibility of AHSS. Specifically, LME sensitivity was strongly correlated with the Si content of an AHSS. A thorough characterization of cracking behavior in relation to the coating and coating-substrate interface microstructure was performed using scanning and transmission electron microscopy techniques to understand the mechanisms by which Si influences LME susceptibility of AHSS.

This current report first summarizes the previous hot ductility experiments that revealed the important influence of Si on Zn-assisted LME susceptibility of AHSS. We then present highlights of results from our microstructural characterization work that clarified the important role played by Si on controlling Fe-Zn alloying (or intermetallic formation) reactions at elevated temperatures. Finally, we present potential mechanisms to explain how Si in the AHSS substrate can influence the interaction between liquid Zn and steel substrate at elevated temperatures, and how these interactions are linked with a greater likelihood of liquid penetration along the grain boundaries of Si-alloyed AHSS.

4.2 Industrial Relevance
The last decade witnessed the development of next generation AHSS for automotive structures to enhance vehicle fuel efficiency and crashworthiness. Zn-coated AHSS are, however, subject to Zn-assisted LME that induces surface cracking during spot welding. AHSS are generally more sensitive to Zn-assisted LME compared to conventional low carbon steels. The difficulty in joining AHSS has impeded the implementation of some new AHSS
into the automotive architecture. The mechanism of embrittlement and controlling factors are still not entirely established. This research aims to establish the specific influence of alloying additions (C, Mn, and Si) and starting microstructure on the critical temperatures (hot ductility trough), and the stresses and strains required to activate LME, which should enhance the understanding of the cracking mechanism. Such understanding is necessary to develop a solution to eliminate cracks and produce defect free spot welds with 3rd Generation AHSS. Welding experiments are generally accompanied by high scatter in the results, making it challenging to fundamentally study the thermomechanical and microstructural influences on crack evolution. Thus, it was proposed to use Gleeble® hot tensile tests as a more quantitative approach to measure critical conditions for LME cracking that also relate to spot welding. SYSWELD® modeling is being employed to understand the evolution of temperature and stress within the spot-welded region, to help relate the hot-ductility test conditions to actual spot welds.

4.3 Summary of Previous Results

In this section of the report, the results of previous hot ductility experiments and microstructural characterization are briefly summarized from the Spring 2021 and Fall 2021 reporting periods to provide context for new results and discussion.

4.3.1 Hot Tension Tests to Investigate Alloying Influences on Zn-LME Susceptibility

For the purpose of investigating the compositional influences on LME sensitivity, AHSS alloys of varying C, Mn, Si, and Al contents (see Table 4.1) were laboratory cast, hot and cold-rolled, followed by continuous annealing to generate a 3rd generation AHSS microstructure via quenching and partitioning. The continuous-annealed panels were electrogalvanized to apply a pure Zn coating on the sheet surface. Hot tension tests were then conducted using bare and Zn-coated AHSS samples of each composition in a Gleeble® 3500 thermomechanical simulator. The hot tension test temperatures were in the range of 600-900 °C. Figure 4.1(a) presents representative hot tension stress-displacement behavior of bare and Zn-coated samples of the different AHSS variants (shown in Table 4.1) for an example temperature of 700 °C. The extent of Zn-associated LME was inferred from the difference in the hot ductility (i.e., total displacement to fracture) of the bare and Zn-coated specimens. Figure 4.1(b) summarizes the extent of Zn-assisted LME as a function of the deformation temperature and alloy chemistry. Note from Figure 4.1(b) that for all temperatures in the tested range (600-900 °C), the Base alloy, Low-C, and Low-Mn AHSS experienced LME and were embrittled to a relatively similar extent. That is, variations in the C or Mn contents relative to the Base AHSS do not remarkably influence LME susceptibility. On the other hand, irrespective of the test temperature, the LME susceptibility of the Low Si AHSS (having 0.5 wt pct Si) was substantially lower compared to each of the 1.5 wt pct Si containing AHSS variants (Base, Low-C, or Low-Mn AHSS). That is, the LME sensitivity is strongly correlated with the Si content of AHSS, and this effect is observed both at lower temperatures where the matrix remains predominantly ferritic, as well as higher temperatures where the steel is predominantly austenitic. Two other AHSS variants (Med-Si and Low-Si High-Al) were included in the test matrix, although the results are not included in this report. Both AHSS exhibited a low to moderate LME susceptibility, i.e., they were significantly less LME sensitive compared to each of the 1.5 wt pct Si-alloyed AHSS variants but slightly more sensitive compared to the Low-Si AHSS. This trend of aggravated LME behavior at high Si levels is consistent with previous research in the Zn-LME literature [4.1-4.4], although the precise mechanism by which Si influences LME sensitivity of AHSS remains unknown.
Table 4.1 – Chemical Composition of Cold Rolled Steel Alloys Used for Hot Tensile Tests (wt pct)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>N</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>0.25</td>
<td>2.7</td>
<td>1.5</td>
<td>0.05</td>
<td>0.004</td>
<td>0.008</td>
<td>0.012</td>
</tr>
<tr>
<td>Low-Mn</td>
<td>0.25</td>
<td>2.0</td>
<td>1.5</td>
<td>0.05</td>
<td>0.004</td>
<td>0.009</td>
<td>0.009</td>
</tr>
<tr>
<td>Low-C</td>
<td>0.15</td>
<td>2.7</td>
<td>1.5</td>
<td>0.05</td>
<td>0.004</td>
<td>0.001</td>
<td>0.010</td>
</tr>
<tr>
<td>*Med Si</td>
<td>0.25</td>
<td>2.7</td>
<td>0.5</td>
<td>0.05</td>
<td>0.004</td>
<td>0.001</td>
<td>0.011</td>
</tr>
<tr>
<td>Low-Si</td>
<td>0.25</td>
<td>2.7</td>
<td>0.5</td>
<td>0.05</td>
<td>0.004</td>
<td>0.001</td>
<td>0.011</td>
</tr>
<tr>
<td>*Low-Si High-Al</td>
<td>0.25</td>
<td>2.7</td>
<td>0.5</td>
<td>1.3</td>
<td>0.004</td>
<td>0.001</td>
<td>0.011</td>
</tr>
</tbody>
</table>

*results not included in this report

The substantial effect of Si on LME susceptibility manifested by the behavior of the Low-Si AHSS compared to the other AHSS variants (i.e., Base, Low-C, or Low-Mn AHSS) was further evident from the surfaces of the fractured Zn-coated specimens (where LME cracks can be observed) in Figure 4.1 as well as the longitudinal cross-sections in Figure 4.2(a), which presents representative backscatter electron (BSE)-SEM micrographs from the for Zn-coated Base, Low-C, Low-Mn, and Low-Si specimens deformed to fracture at a test temperature of 700 °C. Figure 4.2(b) summarizes the severity of LME cracking (in terms of LME crack lengths) in the different AHSS variants, for the entire test temperature range (600-900 °C). Note from Figure 4.2 that each of the 1.5 wt pct Si containing AHSS variants (Base, Low-C, and Low-Mn AHSS) suffered severe LME cracking, whereas the 0.5 wt pct Si containing AHSS (Low-Si AHSS) was significantly more resistant to cracking. Therefore, based on both hot ductility data and associated characterization of cracking behavior, it is apparent that the Low-Si AHSS was much less LME sensitive than the other AHSS variants.

4.3.2 Characterization of the Coating/Substrate Interface of Zn-Coated AHSS

The increased LME sensitivity of Si-alloyed AHSS can perhaps be understood by considering that the Si concentration in the AHSS substrate might affect alloying reactions between Fe and Zn, which directly influences the interaction between the liquid and the AHSS substrate. Figures 4.3(a)-(h) present representative BSE-SEM micrographs comparing the microstructure of the Zn-coated layer in the 0.5 wt pct Si and 1.5 wt pct Si containing AHSS after hot deformation in the temperature range of 600-900 °C. For the 600 °C and 700 °C deformation conditions, i.e., at temperatures below the peritectic temperature (782 °C) in the Fe-Zn system, the formation of the Γ Fe-Zn intermetallic phase at the steel/coating interface (by reaction between liquid Zn and steel substrate) was greatly suppressed in the Si-alloyed AHSS. On the other hand, at elevated temperatures above the peritectic temperature in the Fe-Zn system (782 °C), the Si concentration in the steel influences the uniformity and thickness of the α-Fe(Zn) interfacial layer at the steel/coating interface. Note that for both 800 °C and 900 °C conditions, a relatively thick and continuous α-Fe(Zn) layer was formed at the steel/coating interface of the Low-Si AHSS; conversely, a discontinuous and non-uniform α-Fe(Zn) layer appears in the reacted coating of the High-Si AHSS. Based on these noteworthy differences between the (reacted) coating microstructure of the Si-alloyed and Si-lean AHSS, it is clear that Si in the steel substrate suppresses Fe-Zn alloying reactions and retards the nucleation and growth of intermetallic phases at the coating-substrate interface in these spot weld simulations.

To understand the precise mechanism by which Si in the AHSS substrate influences Fe-Zn alloying interactions, STEM-EDS was employed to characterize the distribution of Si in the coating and steel/coating interface regions of the high LME-sensitive 1.5 wt pct Si-alloyed AHSS. Figure 4.4 presents an example of
Figure 4.1  
(a) Gleeble® 3500 engineering stress-displacement behavior for bare and Zn-coated Base (0.25C-2.7Mn-1.5Si), Low-C (0.15C-2.7Mn-1.5Si), Low-Mn (0.27C-2.0Mn-1.5Si), and Low-Si (0.25C-2.7Mn-0.5Si) AHSS hot-deformed at 700 °C. Macrophotographs of fractured Zn-coated specimens are also presented to qualitatively compare the LME between the different AHSS variants. (b) Summary comparison of the extent of Zn-assisted LME as a function of hot tension test temperature for the Base, Low-C, Low-Mn, and Low-Si AHSS. 
(color image – See PDF copy)
Figure 4.2
(a) Backscatter electron (BSE)-SEM images showing LME cracks in the longitudinal cross-section of Zn-coated Base, Low-C, Low-Mn, and Low-Si AHSS specimens hot deformed at a temperature of 700 °C. (b) Average lengths of LME cracks as a function of AHSS composition and hot tension test temperature. The crack lengths were measured from BSE-SEM images in a region within 5 mm from the fracture end of the Zn-coated specimens. Error bars in (b) represent standard deviation in crack lengths. (*color image – See PDF copy*)
STEM-EDS characterization results from the 700 °C deformation condition, showing the elemental distribution of Fe, Zn, and Si in the steel/coating interfacial region of the Si-alloyed AHSS. The reacted coating of the Si-alloyed AHSS was composed largely of liquid Zn, as evidenced by the presence of Zn in high concentrations ranging from 86-87 wt pct (or low Fe concentration of 13-14 wt pct) in the majority of the coated region. Note that the Zn-rich regions of the sample (i.e., where liquid Zn existed at 700 °C) have a negligible concentration of Si (less than 0.1 wt pct), relative to the Si content in the steel matrix (1.5 wt pct Si). That is, liquid Zn exhibits extremely low solubility for Si. On the other hand, Si enrichment occurred in particular locations in the substrate and coating
(pointed by arrows in Figure 4.4) as a result of liquid-steel interaction. Note that in these Si enriched locations, the measured Si concentration was significantly greater than in both the liquid and the steel substrate. For instance, Si enrichment up to 3.5 wt pct is evident in a thin region of the ferritic substrate located immediately adjacent to the coating. Similarly, fine particles of Si-enriched α-Fe(Zn) are found dispersed in the liquid Zn near the coating/steel interface. Although not presented here, similar Si enrichment behavior was also prominent in the High-Si AHSS samples deformed at an elevated temperature of 900 °C. In that case, Si enrichment was noted in the thin and non-uniform layer of α-Fe(Zn) crystals that developed at the steel/coating interface by reaction between liquid Zn and the (austenitic) substrate.

This observation of Si enrichment provides valuable insights into the mechanism of suppressed Fe-Zn alloying (and increased Zn-LME susceptibility) at elevated Si levels in a steel. In this report, we will present thermodynamic and kinetic analyses, performed using Thermo-Calc® and DICTRA®, and propose an explanation for the Si enrichment behavior. Subsequently, we show how this Si enrichment behavior can be closely linked with the retarded growth of a protective interfacial layer in the Si-alloyed AHSS, which would increase the likelihood of direct contact between the liquid and Si-alloyed steel substrate for LME to be activated.

4.4 Mechanism of Si enrichment

Figure 4.5 presents a simple schematic diagram showing the sequence of steps involved in alloying interactions between a steel substrate and a Zn layer when a Zn-coated steel is rapidly heated to an elevated temperature above the Zn melting temperature (427 °C). For simplicity, we first consider a scenario where the substrate is (pure) Fe, i.e., there are no alloying elements in the steel. The steps (a) through (d) presented in Figure 4.5 are described as follows:

a) At room temperature, both the steel substrate and Zn-layer exist in the solid state, and limited Fe-Zn exchange (interdiffusion) occurs between the substrate and the coating.

b) Upon (rapidly) heating to a temperature above the Zn-melting point, the Zn layer melts, and liquid Zn comes in direct contact with the substrate. Due to the large difference in chemical potential of Fe between the substrate and the liquid, there would be a driving force for Fe atoms from the surface layers of the substrate to diffuse into the liquid. Similarly, Zn atoms from the liquid would tend to migrate into the substrate driven by the difference in chemical potential of Zn between the liquid and the steel. Note that the diffusion in liquid is generally several orders of magnitude faster than the diffusion in solid. That is, the flux of Fe atoms entering the liquid is expected to be much greater than the flux of Zn atoms migrating into the steel.

c) Due to the rapid migration of Fe atoms from the surface layers of the substrate into the liquid, we can consider that the liquid “dissolves” the surface layers of the substrate. Note that as the substrate is dissolved layer-by-layer into the liquid, the liquid/substrate interface migrates towards the substrate side of the initial interface.

d) Substrate dissolution continues to add more Fe into the liquid and depending upon the temperature and Fe concentration in the liquid, a point is reached where there would be a driving force for intermetallic phases to nucleate at or near the steel/coating interface.
(a) Scanning-TEM (STEM)-EDS elemental maps indicating the distribution of Fe, Zn, and Si in the reacted Zn-coating and substrate layers of the 1.5 wt pct Si-alloyed AHSS hot-tension-tested at 700 °C. (b) STEM-EDS elemental line scan showing the concentration profiles of Fe, Zn, Si, and Mn across the steel/coating interface of the 1.5 wt pct Si-alloyed AHSS hot-tension-tested at 700 °C. White arrows in (a) and black arrows in (b) indicate Si enrichment in the steel substrate and α-Fe(Zn) crystals dispersed in the Zn-coated layer near the steel/coating interface.

(color image – See PDF copy)
When Si is present in the steel substrate as an alloying element, it is expected that both Fe and Si from the substrate will readily migrate into the liquid as the surface layers of the Si-alloyed steel are dissolved by liquid Zn. However, in this instance it is important to recognize that the diffusion of atoms (Fe or any other alloying element) from the substrate into the liquid Zn occurs under a “driving force”, which is essentially the difference in the chemical potential (rather than concentration) of that element between the steel substrate and the liquid. The Fe-Zn-Si ternary phase diagram is helpful to (qualitatively) understand if there would be a substantial driving force for Si to partition into the liquid. Figure 4.6 presents the Fe-Zn side of the 700 °C isothermal section of the Fe-Zn-Si ternary phase diagram. Labelled on the phase diagram (using grey arrows) are the composition limits of the liquid, \( \Gamma \), and \( \alpha \) phases. Single phase fields exist over a range of Fe, Zn, or Si concentrations and are shaded grey in Figure 4.6. Consider the phase field of liquid Zn on the Zn-rich side of the phase diagram. The liquid Zn phase is stable across a range of Zn (or Fe) concentrations, and so liquid Zn is capable of dissolving Fe upon contact with a steel substrate. On the other hand, the ternary phase diagram indicates that the liquid Zn phase field does not exist over an appreciable range of Si concentrations. In other words, liquid Zn is characterized by an extremely low solubility for Si. Based on Thermo-Calc® calculations, the equilibrium solubility for Si in liquid Zn is as low as 10^{-6} wt pct at 700 °C. When the substrate dissolution process initiates, i.e., at a time when there is no Si in the liquid, there is a driving force for Si atoms in the first few atomic layers of the Si-alloyed steel substrate to migrate to the liquid. However, as more substrate layers are dissolved, the solubility limit of Si in the liquid will soon be reached, and there should be no further driving force for Si to continue partitioning into the liquid. Under such a scenario, there remains a driving force for Fe atoms to diffuse into the liquid, and such substrate dissolution would require the Si atoms from newly dissolved substrate layers to backdiffuse into the undissolved layers of the substrate. This mechanism is required because Si is soluble in the steel substrate but not in the liquid. Note from the phase diagram in Figure 4.6 that \( \alpha \)-Fe is the only Zn/Fe phase (shaded grey) in this region of the Fe-Zn-Si ternary system.
that is capable of accommodating Si in meaningful amounts, i.e., Si atoms should be comfortable migrating back to
the substrate where it would be more stable compared to the liquid. We hypothesize that this “backdiffusion”
behavior of Si perhaps explains the occurrence of Si-enrichment in a thin layer of the substrate in the vicinity of the
liquid Zn region (See Figure 4.4).

![Figure 4.6](image)

The qualitative hypothesis presented above was numerically simulated using the DICTRA® software, the
diffusion module of Thermo-Calc®, in an effort to further quantify the expected behavior. DICTRA® allows 1-D
diffusion simulations to be performed using multicomponent alloy systems, with the assumption of local equilibrium
at the moving phase interface. A diffusion simulation model was set up between two regions, shown schematically
in Figure 4.7(a). The region on the left side of the diffusion couple was liquid Zn. The thickness of the liquid Zn
region was 5 µm. The initial composition of the liquid phase was nearly 100 pct Zn with only trace amounts of Fe
(10⁻² wt pct) and Si (10⁻⁸ wt pct). Conversely, the region on the right side of the diffusion couple was ferrite, and the
thickness of the ferrite layer was 10 µm. The ferrite composition was set as 98.49 wt pct Fe with 1.5 wt pct Si and a
trace amount of Zn (10⁻² wt pct). In both regions of the diffusion couple, the grid size was defined to be 0.1 µm.
The simulation temperature was set as 700 °C, and the diffusion simulation was run for a total time of 1 s. Note that the
formation of additional phases such as Fe-Zn intermetallics at the interface was not allowed during the simulation as
DICTRA® databases do not include sufficient information on the chemical activity (and mobility) of Si in Fe-Zn
intermetallic phases.

Figure 4.7(a) presents DICTRA® simulation results showing the Fe concentration profiles developed at
time different times (0.05 s, 0.1 s, and 0.5 s) from the start of interdiffusion. Note that the initial Fe concentration
profile at t = 0 s is represented by the blue dotted line in Figure 4.7(a). After the start of the simulation, as expected,
the Fe concentration profiles indicate that the Fe from the steel substrate diffuses into the liquid Zn region and,
consequently, the Fe content in the liquid Zn increases with the passage of time. Note from the inset plot in
Figure 4.7(a) providing a magnified view of the Fe content profiles near the moving interface, that dissolution of the
substrate results in the migration of the liquid/steel interface towards the steel, as expected. The corresponding Si
ccentration profiles developed at t = 0.05 s, 0.1 s, and 0.5 s are shown in Figure 4.7(b). Again, the initial Si
content profile at $t = 0$ s is represented by the blue dotted line in Figure 4.7(b). Clearly, the Si concentration profiles indicate a spike in Si concentration in the ferritic substrate at the moving liquid/steel interface. As time progresses and the ferritic substrate is dissolved into the liquid, Si atoms from the substrate are forced to enter the liquid, as evidenced by the increasing concentration of Si in the liquid Zn region with time. It is interpreted that Si atoms originating from those dissolved layers partition back or “back-diffuse” into the substrate, thereby leading to Si enrichment of the substrate at the interface. Some Si depletion from the liquid is also shown near the interface at 0.05 and 0.1 s. The higher Si concentration in the ferrite at the interface also increases the Si concentration in the liquid in local equilibrium with the ferrite. As the Si concentration builds up in the liquid, there might eventually be a driving force for the liquid to relieve its Si supersaturation by nucleating Si-rich α-Fe(Zn). That might (partly) explain the observation of Si-rich α particles inside the liquid Zn region in the reacted coating of the Si-alloyed AHSS (Figure 4.4).

4.5 Potential Influences of Si on LME behavior of AHSS

In this section of the report, the negative influence of Si on Zn-LME susceptibility is discussed in the context of the Si behavior near the interface that potentially destabilizes intermetallic phases at the coating/steel interface and reduces the driving force for Fe-Zn alloying.

4.5.1 Destabilizing Effect on Intermetallic Phases

The Fe-Zn-Si ternary phase diagram is useful to understand that Fe-Zn intermetallic formation should generally be suppressed if appreciable Si is present either in the steel or in the liquid Zn. The 700 °C isothermal section of the Fe-Zn-Si ternary phase diagram, determined using Thermo-Calc®, is presented in Figure 4.8(a). A detailed view of the Fe-Zn side of the ternary isotherm is shown in Figure 4.8(b). Consider a binary Fe-Zn alloy “A” having a composition of 15Fe-85Zn-0Si (in wt pct). At equilibrium, the predominant phase present in this alloy is Γ (approximately 87 wt pct), along with a small fraction (approximately 13 wt pct) of Zn-rich liquid (L). Note that if Si is increasingly added to the alloy (maintaining the Fe/Zn ratio), the intermetallic (Γ) phase, having no solubility for Si, will be rapidly destabilized and replaced by the liquid (L) and ferrite (α) phases (follow the red dashed line in Figure 4.8(b)). This behavior is represented in Figure 4.8(c), that plots the equilibrium fractions of the Γ, liquid, and Si-rich α phases as a function of increasing Si concentration (up to 1.5 wt pct Si) in a ternary Fe-Zn-Si alloy having a fixed Fe/Zn ratio of 15:85. This destabilizing effect of Si on the Γ Fe-Zn intermetallic phase explains the significantly smaller fraction of Γ developed in reacted coating of the Si-alloyed AHSS compared to that in the Low-Si AHSS.

4.5.2 Reduced Driving Force for Fe-Zn Alloying

In a recent publication by Hong et al. [4.1], the effect of Si on Fe-Zn alloying behavior is described as follows: “...The retardation of Fe-Zn alloying by Si is attributed to sluggish Fe dissolution into liquid Zn...” A few other publications in the hot dip galvanizing literature also reported similar mechanisms with respect to the Si effect on suppressed Fe-Zn alloying (or galvannealing) reactions [4.5-4.9]. The origin of slower Fe dissolution rates at elevated Si levels was not identified/explained, however. In theory, the migration of Fe into the liquid would occur under a driving force, which is the difference in the chemical potential of Fe between the steel and the liquid. It can be demonstrated that Si enrichment of the substrate, developed through the interaction between liquid and
Figure 4.7  DICTRA® numerical calculations at 700 °C showing (a) Fe and (b) Si concentration profiles developed after various durations (0.05 s, 0.1 s, 0.5 s) for a diffusion couple of 5 µm thick liquid Zn layer plus 10 µm thick 1.5 wt pct Si-alloyed ferrite layer. Inset plots in (a) and (b) show Fe and Si concentration profiles near the moving interface boundary between liquid Zn and ferrite. The position of the liquid/ferrite interface at various times are indicated by arrows on the inset in (a). (color image – See PDF copy)
Figure 4.8  
(a) 700 °C isothermal section of the Fe-Zn-Si ternary phase diagram, calculated using Thermo-Calc®. (b) Fe-Zn side of the 700 °C isothermal section of the Fe-Zn-Si ternary phase diagram, (c) variations in the equilibrium fractions of the gamma (Γ), liquid (L), and ferrite (α) phases as a function of increasing Si concentration (up to 1.5 wt pct Si) in a ternary Fe-Zn-Si alloy at a fixed Fe/Zn ratio of 15:85 (following the red dotted line in (a) and (b)).

*(color image – See PDF copy)*
Si-alloyed steel explained above, should generally reduce the driving forces for both Fe migration into the liquid and Zn diffusion into the substrate. Consider a situation illustrated in the schematic diagram shown in Figure 4.9, where liquid Zn is in contact with ferrite at a temperature of 700 °C. The liquid phase composition was fixed in this illustration at 99 wt pct Zn and 1 wt pct Fe. Using this phase composition, the chemical potentials of Fe in the liquid (\(\mu_{\text{Fe}}^{\text{Liq}}\)) and Zn in the liquid (\(\mu_{\text{Zn}}^{\text{Liq}}\)) were obtained using Thermo-Calc®. The composition of the ferrite was initially set as 99.99Fe-0Si-0.01Zn (in wt pct). Again, the chemical potentials of Fe in ferrite (\(\mu_{\text{Fe}}^a\)) and Zn in ferrite (\(\mu_{\text{Zn}}^a\)) were obtained from Thermo-Calc®. To explore the influence of Si enrichment on the chemical potentials of Fe and Zn in the substrate, the Si concentration in the ferrite was varied from 0 to 12 wt pct while maintaining a fixed Zn concentration. Figure 4.9(a) and Figure 4.9(b) present the variation of \(\mu_{\text{Fe}}^a\) and \(\mu_{\text{Zn}}^a\) as a function of the Si concentration in ferrite as solid lines. The values of \(\mu_{\text{Fe}}^{\text{Liq}}\) and \(\mu_{\text{Zn}}^{\text{Liq}}\) are indicated by dotted lines in Figure 4.9(a) and Figure 4.9(b); note that these values in Thermo-Calc® are independent of the Si concentration in the substrate, because the liquid was assumed to be free of Si for this illustration. Figure 4.9(a) indicates that Si enrichment would result in a reduction in the chemical potential of Fe in the ferrite; thus, as a consequence the driving force, \(\mu_{\text{Fe}}^{\text{Liq}} - \mu_{\text{Fe}}^a\), for Fe migration into the liquid is decreased. Similarly, Figure 4.9(b) indicates that the chemical potential of Zn in the ferrite increases with Si enrichment, which reduces the driving force, \(\mu_{\text{Zn}}^a - \mu_{\text{Zn}}^{\text{Liq}}\), for Zn diffusion into the substrate. It is reasonable that both these effects, i.e., reduced driving forces for Fe dissolution into the liquid and Zn diffusion into the substrate would simultaneously act to slow down the kinetics of Fe-Zn alloying.

![Schematic diagram](image-url)
The enhanced Fe dissolution kinetics in the absence of Si in the steel substrate was confirmed via DICTRA® simulations for a diffusion couple involving liquid and pure Fe, Figure 4.10, at a temperature of 700 °C. Comparing the Fe concentration evolution profiles for the case when liquid Zn interacts with pure Fe (Figure 4.10) as against the Si-alloyed Fe substrate (Figure 4.7(a)), it is apparent that the Fe dissolves into the liquid Zn almost instantaneously, i.e., at a much faster rate, when the liquid is in contact with a pure Fe substrate. For instance, after 0.05 s of contact, the Fe concentration of the liquid Zn was already about 5 wt pct when the substrate was pure Fe. Contrarily, in the case of the Fe-Si substrate, the Fe concentration in the liquid for the same duration of time (0.05 s) was only about 0.15 wt pct, i.e., significantly lower compared to the case of the pure Fe substrate. Note that, at such low Fe concentration in the liquid, conditions are far from enabling the nucleation of any Zn-Fe intermetallic phases. The faster Fe dissolution behavior in the case of the pure Fe substrate is also reflected in the position (or velocity) of the liquid/steel interface. For example, the inset in Figure 4.10 shows that after 0.05 s of contact, the liquid/steel interface has moved by 0.33 µm into the Fe substrate. In contrast, for the Fe-Si substrate, the interface moved by only 0.008 µm. Similar trends are observed at the greater diffusion times of 0.1 s and 0.5 s respectively. For instance, after 0.5 s, the liquid contains approximately 6 wt pct Fe in the case of the Si lean substrate, while the Fe concentration was approximately 4 wt pct in the case of the Fe-Si AHSS. Therefore, in addition to the destabilizing effect of Si on Fe-Zn intermetallic phases, the sluggish Fe dissolution kinetics perhaps also contributes to suppressed intermetallic formation behavior at elevated Si levels.

As indicated clearly in Figure 4.9(b), Si enrichment of the ferrite increases the chemical potential (or activity) of Zn in the ferrite. That is, if Si is present in large concentrations in a ferrite crystal, there is reduced driving force for Zn atoms to diffuse into that crystal. Likewise, if both Zn and Si are hypothetically present in large concentrations in ferrite, Zn (or Si) atoms would tend to migrate out of that ferrite. This characteristic that the maximum accommodation capacity (or solubility) of Zn and Si in ferrite cannot be simultaneously increased at the same time, is easily inferred from the Fe-Zn-Si ternary phase diagram. Consider the Fe-Zn side of the 900 °C isothermal section of the Fe-Zn-Si ternary phase diagram, Figure 4.11. Note the grey shaded ferrite (α) phase field in the ternary phase diagram. If we consider a binary Fe-Zn alloy, the α phase can accommodate up to 35.8 wt pct Zn. If Si is added to the system, the Zn solubility in ferrite is substantially reduced. For instance, when the Si concentration in the alloy is increased to 2.5 wt pct, Zn is soluble only up to 20.3 wt pct in ferrite. Similarly, if the Si concentration in the alloy is 5 wt pct, the Zn solubility in ferrite is as low as 2 wt pct. The same trend of reduced Zn solubility at elevated levels of Si is also applicable at other temperatures (for example, see the 700 °C isothermal section in Figure 4.6). The fact that Si reduces the solubility of Zn in ferrite has an important influence on LME susceptibility. If liquid Zn begins to penetrate along a grain boundary in a Si-containing steel, Zn atoms in the boundary will resist interactions with the bulk of the substrate, so formation of Fe-Zn intermetallics will be suppressed, and diffusion of Zn atoms from the boundary into the steel matrix will be suppressed. The reverse trends apply when it comes to the interaction between Si and Fe, i.e., Si enrichment will reduce the activity of Fe in ferrite. In that case, Fe atoms will tend to remain in the bulk of substrate instead of alloying with the liquid Zn located either in the coating or at the grain boundaries. These effects can perhaps explain the increased propensity of liquid penetration along the grain boundaries of Si bearing steels.
The work reported here was conducted to determine the specific influence of chemical composition on the Zn-assisted LME sensitivity of AHSS. Q&P heat treated panels of five AHSS variants having varying C, Mn, and Si concentrations were subjected to hot tension testing in a Gleeble® 3500 thermomechanical simulator. The LME behavior of each AHSS variant was characterized at 600-900 °C, a temperature range extremely relevant in the

Figure 4.10  DICTRA® calculations at 700 °C showing Fe concentration profiles developed at various times (0.05 s, 0.1 s, 0.5 s) for a diffusion couple of 5 µm thick liquid Zn layer and 10 µm thick pure Fe layer. The inset shows concentration profiles near the moving interface boundary between liquid Zn and Fe. The positions of the Zn/Fe interface at various times are indicated by arrows on the inset. (color image – See PDF copy)

Figure 4.11  Fe-Zn side of the 900 °C isothermal section of the Fe-Zn-Si ternary phase diagram. The grey shaded region is the α phase field. White arrows indicate the maximum solubility limit for Zn in the α phase for three different Si levels in a ternary Fe-Zn-Si alloy (0 wt pct, 2.5 wt pct, 5 wt pct). (color image – See PDF copy)

4.6  Summary

The work reported here was conducted to determine the specific influence of chemical composition on the Zn-assisted LME sensitivity of AHSS. Q&P heat treated panels of five AHSS variants having varying C, Mn, and Si concentrations were subjected to hot tension testing in a Gleeble® 3500 thermomechanical simulator. The LME behavior of each AHSS variant was characterized at 600-900 °C, a temperature range extremely relevant in the
context of spot weld LME behavior. The base, Low-C, and Low-Mn AHSS (all with High-Si) exhibited the highest LME susceptibility among all the investigated AHSS. The Low-Si AHSS was the least LME sensitive of all investigated AHSS, while the Med-Si steel exhibited low to moderate LME susceptibility. Thus, C or Mn variation relative to the base alloy composition did not remarkably influence LME susceptibility. On the other hand, the LME sensitivity correlated strongly with the Si content of the AHSS. A comparison of the microstructure of the Fe/Zn alloyed coating layer in AHSS samples with high and low Si contents, revealed that Si in the steel substrate suppresses Fe-Zn alloying reactions and retards the nucleation and growth of intermetallic phases at the coating-substrate interface. In the context of Zn-assisted LME, therefore, Si is hypothesized to influence Zn-LME susceptibility by increasing the liquid Zn availability for LME and the likelihood of direct contact between liquid Zn and the steel substrate; this hypothesis is supported by analyses of the phase equilibria and diffusion kinetics using Thermo-Calc® and DICTRA®.

4.7 References


