Liquid Metal Corrosion of 316L, Fe₃Al, and FeCrSi in Molten Zn-Al Baths

XINGBO LIU, EVER BARBERO, JING XU, MATTHEW BURRIS, KEH-MINN CHANG, and VINOD SIKKA

Corrosion tests of 316L and two intermetallic compounds Fe₃Al and FeCrSi in industrial Galvanizing (Zn-0.18Al), GALFAN (Zn-5Al), GALVALUME (Zn-55Al), and Aluminizing (Al-8Si) baths and lab-scale static baths were conducted. In on-line tests in industrial hot-dip baths, 316L steel shows better corrosion resistance than Fe₃Al in Galvanizing, GALFAN, and GALVALUME baths. The corrosion resistance of 316L and Fe₃Al is similar in Aluminizing bath. In static tests, FeCrSi shows the best corrosion resistance in pure Zn, Zn-55Al, and Al-8Si baths. The corrosion resistance of 316L is better than that of Fe₃Al. In Zn-5Al bath, 316L shows no thickness loss after the test. For the same bath composition, the corrosion rates of the alloys in industrial baths are higher than those in static baths. Bath temperature and chemical composition play important roles in corrosion and intermetallic layer formation. Increasing bath temperature accelerates the corrosion process and changes the nature of intermetallic layers. A small amount of aluminum reduces the corrosion process by reducing the activity of Zn and forming inhibition layer. However, after aluminum content reaches the critical point, the dominant corrosion process changes from Zn-Fe reaction to Al-Fe reaction, and, consequently, the corrosion process accelerates by increasing aluminum content in the bath.

I. INTRODUCTION

THE coating of steel sheet by continuous hot dipping in a molten metal bath of zinc or in a Zn/Al melt is the most efficient and economical method of providing corrosion protection to most steel sheet compositions. Reliable performance of galvanizing pot hardware is essential to the productivity of a hot dip galvanizing line and the quality of coatings produced. As shown in Figure 1, the pot hardware in galvanizing bath includes the snout, sink roll, stabilizing rolls, and the bearings supporting them. The most frequent cause of galvanizing line stoppage is pot hardware problems that are related to one or more of the following three issues: (1) wear of bearings supporting the stabilizer roll and sink roll; (2) corrosion of the pot hardware in molten Zn/Al bath; and (3) the nucleation and growth of dross (intermetallic compound) on roll surfaces.^[1]

Corrosion of the hardware by molten Zn/Al alloys is one of the most important reasons to cause the downtime of production lines; thus, the corrosion resistance becomes the primary criterion for the selection of pot hardware materials. Besides corrosion resistance, there are other properties requirements for pot hardware materials, among which the resistance to intermetallic dross buildup on the surface for roll materials, wear resistance for bearing materials, and ductility are the most important ones. Since corrosion resistance is the primary criterion for the pot-hardware materials

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and each candidate material needs to show good corrosion resistance before other properties being investigated, other properties of the intermetallic materials were not investigated in this article. Corrosion behavior of the pot-hardware materials and coating have been studied;^[2-5] however, many investigators show contrasting liquid zinc immersion results for the same alloys.^[3,4,5] For instance, literature^[3] concluded that aluminum in the molten zinc bath did not diffuse into the WC-Co coating layer. However, the results in the literature^[4] showed that aluminum diffused as much as zinc diffused into the coating. The authors of the literature^[4] proposed two possible reasons to explain the difference: (1) the study in literature^[3] was carried out in high aluminum contents bath, *i.e.*, 0.3 and 3.0 wt pct of aluminum; and (2) the sample in the literature^[4] were immersed in zinc baths containing iron.

316L stainless steel is the most popular material for stabilizer and sink rolls in the industry and STELLITE* 6, a

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Co-based superalloy, is the most popular material for bearings supporting the sink and stabilizer rolls in hot-dipping bath. In recent years, improvement of pot-hardware materials is receiving significant attention and is largely focused on practical bases. Various types of Fe- and Co-based superalloys, ceramics, as well as WC coatings, have been developed for this application.

Intermetallic compounds, for their relatively low material cost, excellent corrosion resistance in some oxidation environments, and lower density, have also been extensively studied in the past decades.^[6–9] The purpose of the present work is to investigate, by means of corrosion testing and microscopic examination, the effectiveness of Fe₃Al-type intermetallic alloys as materials of construction for bath hardware in continuous lines. The corrosion behaviors of 316L

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stainless steel and two types of intermetallic compounds, Fe₃Al and FeCrSi, in Galvanizing (Zn-0.18 pct Al), GALFAN* (Zn-5 pct Al), GALVALUME** (Zn-55 pct Al),

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**GALVALUME is a trademark of BIEC Inc., Vancouver, WA.

and Aluminizing (Al-8 pct Si) baths, were studied and the mechanisms of corrosion and intermetallic compound formation are discussed.

II. EXPERIMENTAL PROCEDURE

A. Material

Both Fe₃Al and FeCrSi alloys used throughout the course of this research were prepared at Oak Ridge National Laboratory (Oak Ridge, TN). The induction melting was performed using high-purity, raw materials. Ingots were cast from the alloy melt and hot rolled to the final thickness. Test specimens were then cut from the as-rolled plates in the longitudinal direction. The stainless steel used in the corrosion tests was commercial grade 316L stainless steel plate with a thickness of 3.2 mm. Table I lists the chemical composition of all alloys being evaluated in this work. The Vickers hardness data of these alloys are shown in Table II.

The three different base materials used throughout the course of this corrosion study contained distinctly different microstructures. Optical micrographs of Fe₃Al, 316L, and FeCrSi alloys can be seen in Figure 2. Grain sizing calculations were performed with the aid of SCION*



Fig. 1—Sketch of hot-dip bath.

image software. Grain sizes that were calculated by the use of the SCION image software were compared with grain size measurements taken with the HIROX* optical micro-

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scope to confirm the values. Compared to Fe₃Al (ASTM 5.5), the grain size of the low-carbon stainless steel 316L (ASTM 8.5) was substantially smaller. The grain size of the FeCrSi alloy was extremely large (>400 μ m) when compared to the other two alloys.

B. Test Procedure

The on-line corrosion tests in the industrial Galvanizing (Zn-0.18Al), GALFAN (Zn-5Al), GALVALUME (Zn-55Al), and type 1 aluminizing bath (Al-8Si) were conducted on a commercial production line. The operating temperatures of the various hot-dip coating processes are the following: Zn bath, -460 °C, Zn-5Al bath, -490 °C, Zn-55Al bath, -600 °C; and Al-8Si bath, -660 °C. Five specimen pairs of Fe₃Al and 316L were immersed in the baths for times of 2, 8, 24, 72, and 240 hours. A schematic of the test specimens used in on-line corrosion tests is illustrated in Figure 3. After the tests, the samples were cut at levels 1 and S, and the metallographic samples on the cross section at these two levels were prepared. Then, the thickness of every specimen was measured at multiple locations across the cross section of the specimen. Figure 4 shows the locations and designations of the thickness measurements that were made on each cross section. The corrosion rates were calculated by measuring thickness loss, which equals the thickness at level S (as reference) minus the thickness at level 1 (after immersion).

The static immersion testing was conducted in laboratory furnaces at temperatures of 460 °C, 560 °C, and 660 °C for 24-hour periods in order to investigate the temperature effect of the molten metal corrosion in the specified bath materials. The bath materials used for the static immersion tests were obtained from the molten baths of on-line tests. In addition to the Fe₃Al and 316L, the FeCrSi alloy was also tested for comparison. The matrix of lab-scale static test is shown in Table III.

Samples were cut from the tested specimens in order to quantitatively compare the corrosion rate of the materials in the different testing scenarios. Thickness measurements of the various test specimens were taken with the aid of a Hi-Scope KH-2400R optical microscope by HIROX (River Edge, NJ). The optical microscope was used in conjunction with Vision Gauge version 4.98 imaging software by Vision. The HIROX microscope and Vision Gauge software allowed accurate, reproducible measurements to be made and stored with the aid of a personal computer. The resolution of the measurements taken was 0.006 mm. Scanning electron

Table I. C	Chemical	Composition	of Tested	Alloys	(Weight	Percent)
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Alloy	Fe	Al	Cr	Zr	С	Ni	Мо	Mn	Si	Р	S
Fe ₃ Al	bal	15.83	5.45	0.96	0.01						
316L	bal		17.00		0.03	12.00	2.5	2.00	1.00	0.045	0.030
FeCrSi	bal		35.00			· · · ·		'	2.50		

Table II. Vickers Hardness of Tested Alloys (HV)

Alloy	Maximum	Minimum	Average	
316L	173	170	171	
FeCrSi	374	352	363	
Fe ₃ Al	308	301	304	



(a) Fe3Al



(c) FeCrSi

Fig. 2-Optical microscopy of three materials used in this study.

microscopy and energy-dispersive spectroscopy (SEM/EDS) were used to study the details of corrosion and formation of intermetallic layers. The thickness of the intermetallic layer





Center T10 T1 B1 B10 B10D10 D10 D1



was measured using SEM, and then the "net" thickness of the sample was calculated by subtracting the thickness of the intermetallic layer from the total thickness of the sample measured by the optical microscope.

III. EXPERIMENTAL RESULTS

A. On-Line Corrosion Tests

1. Aluminizing (Al-8Si) bath

Figure 5 illustrates a plot of specimen thickness loss measured at specified locations on the cross section of a test specimen that the thickness losses of the 316L specimens increase with an increase in testing time. An edge effect on corrosion can be noticed in the 72-hour test. The data show greater thickness losses occurring at the end of the specimen, compared to the specimen center. From the thickness loss data in Figure 5, average thickness losses were calculated and these values were plotted vs time.

Figure 6 shows the results of the corrosion testing of the two materials in the Al-8Si bath. From this graph, it can be seen that the two materials perform similarly in the

	316L			Fe ₃ Al			FeCrSi		
Bath (Melting Point)	460 °C	560 °C	660 °C	460 °C	560 °C	660 °C	460 °C	560 °C	660 °C
Al-8Si (605 °C)			×			×			×
Zn-0.18Al (420 °C)	×	×	×	\times	×	×	×	×	X
Zn-5Al (390 °C)	×	×	×	×	×	×	×	×	×
Zn-55Al (570 °C)			×			×			×

Table III. Test Matrix of Static Corrosion Tests



Fig. 5-Thickness loss of 316L specimens in Al-8Si bath at 660 °C.



Fig. 6—Thickness loss of 316L and Fe3Al specimens in Al-8Si bath at 660 $^{\circ}\mathrm{C}.$

type 1 aluminizing bath. The iron aluminide specimen, however, seems to have a slightly lower resistance to corrosion than the stainless steel alloy. The linear nature of the thickness reduction rate (dy/dt), the slope of the fitted line, can also be observed from the presented data. This linear trend seems to hold true for all on-line tests.

2. GALFAN (Zn-5Al) bath

Though both materials seemed to perform similarly in the Aluminizing (Ai-8Si) bath, the 316L specimens appeared to have a better resistance to corrosion than the iron aluminide (Figure 7). Even after 240 hours in the bath, the 316L specimen showed little thickness loss. For the same time of 240 hours, the Fe₃Al specimens showed approximately 0.75 mm of thickness reduction across the specimen cross section. The linear nature of the thickness reduction rate is evident from this graph and the previous graphs. This linearity, however, contradicts the study by Lampe *et al.*^[10] in which it



Fig. 7—Thickness loss of 316L and Fe3Al specimens in GALFAN bath at 490 $^{\circ}\mathrm{C}.$



Fig. 8—Thickness loss of 316L and Fe3Al specimens in Galvanize bath at 460 $^{\circ}\mathrm{C}.$

was stated that, in a zinc melt containing 4 pct aluminum, the time law for the corrosion of steel was found to be parabolic up to 500 °C. Our study indicates a linear time law at 490 °C in a zinc bath containing 5 pct aluminum.

3. Galvanizing (Zn-0.18Al) bath

Figure 8 shows the performance of the two alloys in the Galvanizing (Zn-0.18Al) bath. While 316L shows very little corrosion even after a time of 240 hours, Fe₃Al alloy shows a substantial thickness loss. Considering that the initial iron aluminide specimens had a thickness of approximately 3.2 mm, a thickness loss of close to 2.5 mm demonstrates the severe amount of corrosion that occurred with this material in the zinc bath.

4. GALVALUME (Zn-55Al) bath

Figure 9 illustrates the performance of the stainless steel and iron aluminide alloys in the on-line testing in the GAL-VALUME (Zn-55Al) bath. As in the Galvanizing bath, the 316L stainless steel alloy shows a higher resistance to corrosion than the Fe₃Al alloy. The stainless steel alloy does show slightly more corrosion in the GALVALUME bath, when compared to the GALFAN bath. Iron aluminide specimens have a similar corrosion trend in the GALVALUME bath, to those obtained from on-line testing in the GALFAN bath.

B. Static Immersion Tests

Table IV lists measured thickness loss data from the static immersion tests. All specimens were immerged in the bath at the specific temperatures for 24 hours. Because the melting point of the type 1 aluminizing mixture is approximately 605 °C, the tests could not be run at temperatures of 460 °C and 560 °C.

It should be pointed out that the experimental FeCrSi alloy seems to outperform both 316L and Fe₃Al in the Zn-0.18Al, Zn-55Al, and Al-8Si bath. This fact can be observed from the corrosion rates listed in Table IV. Within the Al-8Si bath, the 316L alloy showed the highest corrosion rate during the static immersion tests. Though the corrosion rate of the FeCrSi alloy was lower than the 316L and Fe₃Al alloys, the performance of all three materials tested was very similar in the aluminizing bath.



Fig. 9—Thickness loss of 316L and Fe3Al specimens in GALVALUME bath at 600 $^\circ\text{C}.$

C. Intermetallic Layer Formation

Analysis of the interface layers formed during the corrosion testing was conducted with the aid of a scanning electron microscope and the EDS capability of the microscope. Table V summarizes the phases identified upon the examination of the corrosion specimens with SEM. Figure 10 shows the backscattered electron image (BSI) of the interface layers formed by the immersion of 316L, Fe₃Al, and FeCrSi specimens in the laboratory aluminizing bath at 660 °C for a period of 24 hours. As seen in Figure 9(a), the bright area on the left of the micrograph is the 316L base material. To the right of the matrix, a relatively thin alloy layer was observed. This alloy layer was approximately 20 μ m in thickness and had a uniform, continuous structure. From the EDS characterization of this thin alloy layer, the chemical composition was determined to be the n-Fe₂Al₅ phase. This alloy layer is noted to form on the surface of steels that have been hot-dip coated in type 1 aluminizing baths and was mentioned in various literature sources.^[11] A small amount of chromium that diffused from the matrix material can also be seen in the EDS spectrum for the first alloy layer. The next alloy layer contained less iron than the η -Fe₂Al₅ phase, and was identified as θ -FeAl₃. Within this second alloy layer, a crack can be seen that propagates within the brittle alloy layer, parallel to the edge of the original specimen. This second layer is much thicker than the η -Fe₂Al₅ layer, which formed adjacent to the 316L matrix. The cracks are believed to form during the cooling process, when the samples were taken out of the baths. The different coefficients of thermal expansion among various intermetallic layers lead to internal stress. It is interesting that the cracks formed within one thick intermetallic layer instead of along with the phase interfaces, which means that the bonding between different layers is strong.

Figure 10(b) reveals the interface layers formed by the corrosion of the Fe₃Al specimen in the Al-8Si bath. The first alloy layer formed on the Fe₃Al specimen had the same chemical composition as the first alloy layer formed on the 316L specimen in this bath, and was therefore identified as the η -Fe₂Al₅ phase. Instead of forming a thin layer of the η -Fe₂Al₅ phase, the iron aluminide specimen formed a thick layer of this phase. In Figure 10(b), a crack can be seen in this alloy layer that propagates parallel to the specimen surface. The second alloy layer to form was identified as the θ -FeAl₃ phase, which is the same as the second alloy layer formed on the 316L sample. However, instead of form-

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Bath (Melting		316L			Fe ₃ Al				
Point)	460 °C	560 °C	660 °C	460 °C	560 °C	660 °C	460 °C	560 °C	660 °C
Al-8Si (605 °C)	NA	NA	3.02×10^{-1}	NA	NA	2.41×10^{-1}	NA	NΔ	1.51×10^{-1}
Zn-0.18Al			5.02 / 10	1121	147 \$	2.41 × 10	142 4		1.51 × 10
(420 °C)	2.30×10^{-1}	2.99×10^{-1}	1.04×10^{0}	3.61×10^{-1}	5.06×10^{-1}	2.54×10^{0}	6.80×10^{-2}	2.25×10^{-1}	1.00×10^{0}
Zn-5Al									
(390 °C)	$0.00 imes 10^{0}$	3.00×10^{-3}	1.90×10^{-2}	4.00×10^{-3}	1.64×10^{0}	2.55×10^{0}	1.13×10^{-1}	1.17×10^{-1}	6.02×10^{0}
Zn-55Al									
(570 °C)	NA	NA	3.94×10^{-1}	NA	NA	2.54×10^{0}	NA	NA	1.57×10^{-1}

METALLURGICAL AND MATERIALS TRANSACTIONS A

Table V.Phase Identified from Corrosion Testing in Zn-Al
Hot-Dip Coating Baths for 24 Hours

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	Bath Alloy	Test Types	Temperature	Phase Identified
316L	Al-8Si	static	660°C	η -Fe ₂ Al ₅ ,
	Zn-0.18A1	on-line	460 °C	Fe-Al-Zn phase
	Zn-5Al	on-line	490 °C	η -Fe ₂ Al ₅ , θ -FeAl ₂
	Zn-55Al	on-line	600 °C	η -Fe ₂ Al ₅ , θ -FeAl ₂
Fe3A1	Al-8Si	static	660 °C	η -Fe ₂ Al ₅ , θ -Fe Al ₅
	Zn-0.18Al Zn-5Al	on-line on-line	460 °C 490 °C	θ -FeAl ₃ η -Fe ₂ Al ₅ ,
	Zn-55Al	on-line	600 °C	θ -FeAl ₃ η -Fe ₂ Al ₅ , θ -FeAl ₂
FeCrSi	Al-8Si	static	660 °C	Fe-Al-Cr phase (one layer)
	Zn-0.18Al	on-line	460 °C	no phase formation
	Zn-5Al	static	490 °C	Fe-Al-Cr phases (two layers)
	Zn-55Al	static	600 °C	Fe-Al-Cr phases (two layers)

ing a thick alloy layer as with the stainless steel sample, the Fe_3Al formed a relatively thin alloy layer of $FeAl_3$.

One distinct alloy layer was formed on the FeCrSi specimen (Figure 10(c)). The alloy layer that formed consisted of a ternary phase of aluminum, iron, and chromium. The exact phase that composed this alloy layer requires further identification. This layer contained a relatively high amount of aluminum, compared to the amounts of chromium and iron.

The 316L and Fe₃Al alloys formed similar Fe-Al phases upon corrosion in Zn-55Al and Al-8Si baths. In both baths, the materials formed alloy layers consisting of η -Fe₂Al₅ and θ -FeAl₃. The formation of these alloy layers may have contributed to the fact that during the on-line corrosion tests in the Al-8Si and Zn-55Al, the 316L and Fe₃Al alloys demonstrated similar corrosion rates.

In the galvanizing (Zn-0.18Al) bath, the 316L alloy formed a ternary alloy phase consisting of aluminum, iron, and zinc. The iron aluminide formed a single alloy layer consisting of θ -FeAl₃, and the FeCrSi specimen formed no observable alloy layers.

IV. DISCUSSION

A. On-Line Corrosion vs Static Corrosion

Tables VI and VII show the corrosion rates of the alloys for on-line corrosion and static corrosion tests. It can be seen that the corrosion rate of the 316L specimen from on-line dynamic testing was found to be nearly 3 times higher than the value received in the static Al-8Si bath (Figure 6). The static corrosion rate of Fe₃Al also shows a considerable reduction when compared to the corrosion rate received from the dynamic tests. The reasons for the reduction are illustrated as follows.

At first, the small volume of the static corrosion test bath becomes saturated with dissolved elements from the specimen



(c) - FeCrSi

Fig. 10—Interface layers formed from the static testing of the alloys in an Al-8Si at 660 °C for 24 h (BSI).

 Table VI.
 Corrosion Rates for On-Line Corrosion

 Tests (cm/h)
 Tests (cm/h)

Bath	Bath Temperature (°C)	316L	Fe3A1		
Al-8Si	690	1.78×10^{-3}	2.25×10^{-3}		
Zn-55Al	600	3.00×10^{-5}	1.65×10^{-4}		
Zn-5Al	490	2.00×10^{-6}	1.55×10^{-4}		
Zn-0.18Al	460	4.51×10^{-6}	4.96×10^{-4}		

Table VII. Corrosion Rates for Static Immersion Tests (cm/h)

Bath (Melting Point)		316L			Fe ₃ Al		FeCrSi		
	460 °C	560 °C	660 °C	460 °C	560 °C	660 °C	460 °C	560 °C	660 °C
Al-8Si (605 °C)	NA	NA	6.33×10^{-4}	NA	NA	5.06×10^{-4}	NA	NA	3.09×10^{-4}
Zn-55Al (570 °C)	NA	NA	8.23×10^{-4}	NA	NA	5.30×10^{-3}	NA	NA	3.22×10^{-4}
Zn-5Al (390 °C)	0	0	3.8×10^{-5}	1.49×10^{-5}	3.41×10^{-3}	5.33×10^{-3}	2.42×10^{-4}	2.42×10^{-4}	1.29×10^{-2}
Pure Zn (420 °C)	4.81×10^{-4}	6.2×10^{-4}	2.17×10^{-3}	7.59×10^{-4}	1.06×10^{-3}	5.30×10^{-3}	1.48×10^{-4}	4.7×10^{-4}	2.09×10^{-3}

and this may have slowed the specimen's corrosion. The dissolution of a solid metal in molten metal is described by the Nernst–Shchukarev equation,^[12] or Berthoud equation.^[13] It may be written as

$$dC/dt = K \cdot A/V \cdot (Cs - C)$$
[1]

where C is the instantaneous concentration of the dissolved metal in the melt, Cs is the saturation concentration, K is the dissolution rate constant, A is the surface area of the solid metal, and V is the volume of the melt. In the integrated form, Eq. [1] becomes (initial conditions: C = 0, t = 0)

$$C = Cs[1 - \exp(-K \cdot A \cdot t/V)]$$
 [2]

It is indicated from Eqs. [1] and [2] that if the volume of molten metal is small, the dissolution of solid metal will increase C, and then the dissolution rate dC/dt will decrease. On the contrary, if the volume of molten metal is large, as in industrial hot-dip baths, the dissolution of solid metal will have a minor effect on C; then, the dissolution rate dC/dt will be constant. Tunca *et al.*'s investigation^[14] on corrosion of Mo, Nb, Cr, and Y in molten aluminum confirmed that in small volume of molten aluminum, dC/dt decreases with time.

Second, brittle intermetallic layers that form on the outside of a corroded specimen would be more likely to spall off into the melt in the moving industrial bath. The breaking off of these alloy layers would facilitate new growth and faster corrosion in on-line testing.

Finally, the flowing molten metal in the industrial bath has a strong acceleration effect on the corrosion of the alloys. As a matter of fact, during the past decades, the dynamic corrosion behavior of the stainless steel in the molten lead-lithium alloy system in the nuclear industry has been widely studied.^[15–20] It is generally concluded that (1) the corrosion behavior is velocity dependent; (2) the flow pattern at various speeds, *i.e.*, laminar or turbulent flow, has a strong effect on the corrosion rate; and (3) the mechanisms of flow-induced corrosion may be different at various flow speeds. It can be mass-transport controlled, phase-transport controlled, erosion corrosion, or cavitation corrosion, according to the flow speed. These concepts can be applied to molten metal corrosion in the hot-dip industry to explain faster corrosion rates in moving industrial baths when compared to static lab-scale baths.

B. Aluminum Effect on Corrosion and Intermetallic Layer Formation

During the galvanizing process, the steel tends to react with molten zinc and form a series of Fe-Zn intermetallic compounds layers, including γ -Fe₃Zn₁₀, δ -FeZn₁₀, ξ -FeZn₁₃, *etc.*^[21,22,23] The morphology and thickness of each individual layer are different, depending upon bath temperature and processing time. However, the bonding between Fe-Zn intermetallic layers and steel substrate was not satisfactory. Aluminum is always added to the molten zinc bath to form the η -Fe₂Al₅ inhibition layer, which can prevent diffusion or reaction between Fe and Zn and improve the bonding between the steel substrate and coating layer.^[24]

The presence of aluminum in the bath changes the chemical environment and introduces new aluminum-content phases into the Fe-Zn alloy system. Therefore, in essence, bath chemistry management is the control of aluminum content. Aluminum also plays an important role in the corrosion of pot hardware in molten hot-dipping baths. In pure Zn bath, the dominant corrosion reaction between the molten metal and the alloys is Fe from the alloys reacting with Zn to form a series Fe-Zn intermetallic compounds. Onishi et al.^[25] showed that the growth of the Fe-Zn phase in solid Fe-Zn diffusion couples (annealed at 410 °C for up to 100 hours) was controlled by the dominant one-sided diffusion of Zn through the phase layers toward the substrate Fe. When a small amount of aluminum was added into the Zn bath, the concentration and activity of Zn was reduced; therefore, both the reaction rates between Fe and Zn and the diffusion of Zn in the phase layers were reduced. Yamaguchi and Hisamatsu^[26,27] studied the reaction between molten Zn and steel substrate as a function of dipping time, bath temperature, and aluminum content in the Zn alloy. They found that the amount of Fe dissolved from the strip substantially decreased with increasing aluminum content, when the Al content was no more than 0.2 wt pct. Tang^[28] analyzed Fe dissolution in molten Zn-Al alloys and found that the transient Fe solubility in the vicinity of the substrate/melt interface is much higher than the equilibrium value. He also concluded that aluminum atoms would segregate to the substrate surface and form complexes, or so-called inhibition layer, with Fe atoms because of their high affinity for Fe. This results in a decreasing Fe dissolution rate with increasing bath Al content. The study by Tani et al.^[3] showed that as aluminum content increased in a molten zinc bath, the diffusion depth of zinc into the WC-Co coating layer decreased. It is certain that aluminum in a zinc bath suppresses zinc diffusion into the WC-Co coating layer.^[4]

A small amount of Al can reduce the activity of Zn and form an inhibition layer, therefore reducing the corrosion rates of the steel substrate or pot-hardware materials. However, the Fe-Zn reaction is still the dominant process in the bath. After Al content reaches a critical value, the dominant process in the molten bath is changed from Fe-Zn reaction to Fe-Al reaction. Therefore, increasing aluminum content will increase the aluminum activity and accelerate the corrosion reaction. This can be confirmed by comparing the corrosion data in the Galvanizing (Zn-0.18A1), GALFAN (Zn-5A1), and GALVALUME (Zn-55A1) baths in Tables V and VI. As a matter of fact, in recent years, thermodynamics and kinetics in the Fe-Zn-Al system have been extensively studied.^[28-33] In Figure 11, a phase diagram of Zn-Fe-Al at 460 °C is presented and the chemical ranges of molten zinc baths for GA and GI are marked.^[33] Under Galvanneal (0.12 to 0.14 wt pct Al) conditions, if the iron content is higher than 0.03 wt pct, FeZn₇ (δ) or Fe₂Al₅ (η) phase can be formed according to the aluminum content in a zinc bath. Under Galvanize (0.16 to 0.22 wt pct Al) conditions, Fe₂Al₅ (η) is more stable in the range of lower iron content than in GA conditions.^[31]

The corrosion rates of the alloys as a function of aluminum contents were proposed as Figure 12. A small amount of aluminum reduced the activity of zinc and slowed the corrosion rates. However, there is a "valley" in the curve where the corrosion rate can reach the lowest point. The aluminum content at this point will be in the range of GA/GI (0.12 to 0.22 wt pct Al) and will coincide with, or close to, the "knee point"^(28,33) in the Zn-Fe-Al ternary phase diagram. Above that point, Fe-Al reaction dominates the chemical process and the corrosion rates increase with increasing of Al content.



Fig. 11—Equilibrium phase diagram of Zn-Fe-Al at 460 °C.^[32]





Fig. 12—Sketch of corrosion rate as a function of effective Al contents at Zn-rich corner.

Similar transition effects of Al happened in other alloy systems. Zhang's investigations^[34,35] on the corrosive wear of Co-base superalloys in hot-dip baths show that the Co-Zn reaction is the dominant process in pure Zn bath, while a small amount of Al in molten Zn bath changes the dominant process to Co-Al reaction. It should be pointed out that the activity coefficient of Al drops dramatically when Al content is above 0.3 pct.^[30] Therefore, the preceding discussion could not be extended to the system with high Al contents (>0.3 pct wt).

C. Temperature Effect

Figure 13 shows the corrosion rates of the 316L, Fe₃Al, and FeCrSi alloys after static testing in the zinc bath for a period of 24 hours. Though an increase in testing temperature from 460 °C to 560 °C slightly increases the corrosion rate in all three materials, an increase from 560 °C to 660 °C has a drastic effect on the corrosion rates. In this range, iron aluminide shows the most prominent increase in corrosion rate. At the final testing temperature, the corrosion rate of Fe₃Al was more than twice that of the other two materials. The effects of temperature on the corrosion and intermetallic compound formation can be discussed in the following aspects.

(1) Corrosion is a thermal-activated process, which can be generally illustrated by the Boltzmann equation:

$$C = C_0 \times \exp\left(\frac{-Q}{kT}\right)$$
[3]

where C is the controlling factor of the process, such as diffusion coefficient and reaction rate, C₀ is a constant, Q is the activation energy, k is the Boltzmann constant, and T is temperature. From Eq. [3], it is clear that increasing temperature can accelerate the thermal-activated process.
(2) During the Galvanizing process, if the Al content is higher than the knee point (around 0.13 wt pct effective Al at 460 °C), the dominant chemical reaction in the bath is 2Fe + 5Al ↔ Fe2Al5. In the study of Fe solubility in molten Zn alloy as a function of Al contents and bath temperature, it has been established that^[36]

$$\ln [\text{Fe}]^2 [\text{Al}]^5 = 28.1 - \frac{33,070}{T}$$
[4]



Fig. 13—Temperature effects on corrosion rates for static immersion tests in zinc bath Galvanized Steel Sheet Forum-Automotive (London), 2000, pp. 143-51.

where [Fe] and [Al] are the Fe and Al solubility in the melt in weight percentage, and *T* is the absolute temperature. Therefore, changing temperature can change the solubility of Fe and Al in the molten Zn bath. For example, if temperature is changed from 460 °C to 500 °C, the equilibrium solubility product $[Fe]^2[Al]^5$ increases from 4.06×10^{-8} to 4.20×10^{-7} . It should be pointed out that the increase of equilibrium solubility product with temperature means the thermodynamic driving force of corrosion increases with temperature. However, the corrosion tests in this investigation were stopped before the system reached equilibrium. Therefore, the increase of corrosion rates with temperature, than the increase of thermodynamic driving force.

(3) Changing the temperature can change the Gibbs free energy of the phases and change the equilibrium phase transformation in the alloy system. Verma's study^[21,22] in pure Zn bath showed that at 455 °C, the well-known three-phase structure, *i.e.*, δ-FeZn₁₀, ξ-FeZn₁₃, and η, was formed. The thin innermost γ-Fe₃Zn₁₀ layer did not form. In the temperature range 520 °C to 550 °C, it was found that coatings at the lower end of the temperature range had a well-defined ξ-FeZn₁₃ layer on the top of a δ-FeZn₁₀ layer. When the temperature was 560 °C, there was a thin layer of γ-Fe₃Zn₁₀ between δ and the steel substrate.

Similar to that of the Zn bath, changing temperature also changes the nature of phase equilibrium in aluminizing bath. Fotouchi found that at temperatures below 750 °C, there were two distinct intermetallic strata.^[11] The outer thicker layer was identified as α -Fe₂SiAl₈, while the inner, much thinner layer consisted of θ -FeAl₃. At temperatures higher than approximately 750 °C, the thinner FeAl₃ was not identified, and the alloy layer consisted entirely of α -Fe₂SiAl₈.^[22]

V. CONCLUSIONS

Liquid metal corrosion of 316L stainless steel and two intermetallic compounds, Fe_3Al and FeCrSi, were studied by on-line and static corrosion tests in various Zn-Al baths. Several conclusions were drawn from this investigation and are as follows.

- 1. In on-line tests in industrial hot-dip baths, 316L steel shows better corrosion resistance than Fe₃Al in Galvanizing (Zn-0.18Al), GALFAN (Zn-5Al), and GAL-VALUME (Zn-55Al) baths. The corrosion resistance of 316L and Fe₃Al are similar in type I aluminizing (Al-8Si) bath.
- 2. In static tests, FeCrSi shows the best corrosion resistance in pure Zn, Zn-55Al, and Al-8Si baths. The corrosion resistance of 316L is better than that of Fe₃Al. In Zn-5Al bath, 316L shows no thickness loss after the test.
- 3. For the same bath composition, the corrosion rates of the alloys in industrial baths are higher than those in static baths. The small scale of the static test bath is one of the reasons because the small volume of the static corrosion test bath becomes saturated with dissolved elements and slows the corrosion process. Another reason is that the hydraulic flow in industrial baths accelerates the erosion-corrosion process

- 4. Bath temperature and chemical composition play an important role in corrosion and intermetallic layer formation. Increasing bath temperature accelerates the corrosion process and changes the nature of intermetallic layers.
- 5. Aluminum content in the molten Zn bath plays a complex role in the corrosion process. A small amount of aluminum reduces the corrosion process by reducing the activity of Zn and by forming an inhibition layer. However, after aluminum content reaches the critical point, the dominant corrosion process changes from Zn-Fe reaction to Al-Fe reaction, and therefore, the corrosion process is accelerated by increasing aluminum content in the bath.

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REFERENCES

- 1. F. Goodwin, K.-M. Chang, and V. Sikka: 94th Annual Meeting, Galvanizer Association, Algona, MI, 2002.
- M. Brunnock, R Jones, G. Jenkins, and D. Llewellyn: Zinc-Based Steel Coating Systems, TMS, Warrendale, PA, 1998, pp. 51-62.
- K. Tani and T. Tomita: Iron Steel Inst. Jpn., 1994, vol. 34, pp. 822-28.
 B. Seong, S. Hwang, M.C. Kim, and K.Y. Kim: Surface Coating
- Technol., 2001, vol. 138, pp. 101-10.
 M. Brunnock, R Jones, G. Jenkins, and D. Llewellyn: Ironmaking and Steelmaking, 1997, vol. 24, pp. 40-46.
- A. Mignote, S. Frangini, A. La Barbera, and O. Tassa: Corr. Sci., 1998, vol. 40, pp. 1331-47.
- 7. V.K. Sikka: Processing, Properties, and Applications of Iron Aluminides, TMS, Warrendale, PA, 1994, pp. 3-18.
- C.G. McKamey, J.H. DeVan, P.F. Tortorelli, and V.K. Sikka: J. Mater. Res., 1991, vol. 6, pp. 1779-1805.
- C.T. Liu, C.G. McKamey, and E.H. Lee: *Scripta Metall. Mater.*, 1990, vol. 24, pp. 385-89.
- 10. V. Lampe, H. Roos, and M. Svensson: Werkstoffe Korr., 1977, vol. 28, pp. 226-32.
- R.W. Richards, R.D. Jones, P.D. Clements, and H. Clarke: *Metallurgy* of Continuous Hot-Dip Aluminizing, M. Yan, Z. Fan: J. Mater. Sci., 2001, vol. 36, pp. 285-95.
- 12. V.I. Dybkov: J. Mater. Sci., 1990, vol. 25, pp. 3615-33.
- 13. J.R. Weeks and D.H. Gurinsky: *Liquid Metals and Solidification*, ASM, Materials Park, OH, 1958, pp. 106-61.
- 14. N. Tunca, G.W. Delamore, and R.W. Smith: *Metall. Trans. A*, 1990, vol. 21A, pp. 2919-28.
- J.J. Park, D.P. Butt, and C.A. Beard: Nucl. Eng. Des., 2000, vol. 196, pp. 315-25.
- F. Balbaud-Celerier and F. Barbier: J. Nucl. Mater., 2001, vol. 289, pp. 227-42.
- 17. E. Heitz: Corr. Eng., 1991, vol. 47, pp. 135-45.
- 18. J. Weber: Br. Corr. J., 1992, vol. 27, pp. 193-99.
- H.U. Borgstedt and H. Feurstein: J. Nucl. Mater., 1992, vols. 191–194, pp. 988-91.
- M.G. Baker, D.J. Siddons, and F. Barbier: J. Nucl. Mater., 1996, vols. 233-237, pp. 1436-40.
- 21. A.R.B. Verma and W.J. van Ooij: Surf. Coating Technol., 1997, vol. 89, pp. 132-42.
- A.R.B. Verma and W.J. van Ooij: Surf. Coating Technol., 1997, vol. 89, pp. 143-50.
- 23. C.E. Jordan and A.R. Marder: *Metall. Mater. Trans. A*, 1997, vol. 28A, pp. 2683-94.
- 24. M.L. Hughes: J. Iron Steel Inst., 1950, Sept. p. 77.
- 25. M. Onishi, Y. Wakamatsu, and H. Miura: *Trans. JIM*, 1974, vol. 15, p. 331.

- 26. H. Yamaguchi and Y. Hisamaysu: Tetsu-to-Hagané, 1973, vol. 59, pp. S553-54. 27. H. Yamaguchi and Y. Hisamaysu: Tetsu-to-Hagané, 1974, vol. 60,
- pp. 96-103.
- N.-Y. Tang: *Metall. Mater. Trans. B*, 1999, vol. 30B, pp. 144-48.
 S. Chen and Y. Chang: *CALPHAD*, 1993, vol. 17, pp. 113-24.
 A. Costa e Silva *et al.*: *Z. Metallkd.*, 1999, vol. 90, pp. 38-43.
 N.Y. Tanga *et al.*: *Del articles 2000*, pp. 38-43.

- 31. N.-Y. Tang: J. Phase Equilibria, 2000, vol. 21, pp. 70-77.
- 32. S. Yamaguchi and N. Fukatsu: Galvatech '95 Conf., ISS-AIME, Warrendale, PA, 1995, pp. 647-55.
- N.-Y. Yang: *Metall. Mater. Trans. A*, 1995, vol. 26A, pp. 1699-74.
 K. Zhang: *Wear*, 2003, vol. 255, pp. 545-55.
- 35. K. Zhang and N.-Y. Tang: Metall. Mater. Trans. A, 2003, vol. 34A, pp. 2387-96.
- 36. N.-Y. Tang: Galvanised Steel Sheet Forum-Automotive, London, UK, 2000, pp. 143-51.