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**Special Issue on “Fundamentals and Application Technologies for High-performance Hot-dip Galvanized Coatings”**

Preface to the Special Issue “Fundamentals and Application Technologies for High-performance Hot-dip Galvanized Coatings” (Preface)  

Influence of Annealing Temperature and Dew Point on Kinetics of Mn External Oxidation  
Yusuke Okumura, Minoru Tanaka, Yusuke Fushiwaki and Yasunobu Nagataki (JFE Steel Corp.)  
In the process of hot-dip galvanizing of steel, alloying elements such as Si and Mn are easily oxidized by H2O in the annealing atmosphere, causing coating defects. Because this selective oxidation depends on the annealing heat pattern, i.e., the soaking temperature and time, basic research on the kinetics of selective oxidation is important for clarifying the phenomenon of selective oxidation. In this study, the effects of the annealing temperature and dew point on the kinetics and compounds of Mn external oxidation were investigated experimentally, and the Mn external oxidation rate was estimated based on a diffusion equation and thermodynamic equilibrium, considering the diffusion coefficient and the activity coefficient of Mn in steel. The amount of Mn oxide increased in proportion to the square root of the soaking time. This result suggests that Mn oxidation is a diffusion limited process. The Mn oxidation rate increased with increasing temperature and reached a peak value, and at higher temperatures, the Mn oxidation rate became dramatically slower. The peak value also depended on the dew point. To clarify the reason for this slowdown of Mn oxidation, the Mn oxidation rate was estimated. Considering the activity coefficient and the diffusion coefficient of Mn in steel, the calculated Mn oxidation rate was consistent with the measured value. It is thought that the Mn oxidation rate slows at high temperature because the gradient of the Mn concentration around the steel surface becomes small at high temperatures near the equilibrium temperature of Mn/MnO.  
KEY WORDS: galvanizing; diffusion; dew point. (cf. *Tetsu-to-Hagané*, 105 (2019), 676)

Effect of Si/Mn Ratio on Galvannealing Behavior of Si-added Steel  
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The influence of the Si/Mn ratio on the galvannealing behavior of 1.5 wt% Si -1.5-2.5 wt% Mn-added steel in the Fe oxidation-reduction process was investigated. The Si/Mn ratio of the steel affected the formation of Si-containing oxides during the annealing process. The amount of SiO2 formed on the steel surface decreased with as the Si/Mn ratio decreased, while the amount of MnSiO4 increased. In addition, the internal oxide formed in a relatively narrow area near the surface in the lower Si/Mn ratio sample, which indicated that the content of solute Si near the surface was lower in the lower Si/Mn ratio sample. The galvannealing reaction was accelerated by decreasing the Si/Mn ratio of the steel. The species and morphology of the Si-containing oxides determined the galvannealing behavior of the Si-added steel. The Si-containing selective surface oxide affected the formation of the initial Fe-Zn intermetallic compounds (IMC) during hot-dipping in molten Zn. The formation of SiO2 was suppressed in the sample with the lower Si/Mn ratio, which resulted in accelerated Fe-Zn IMC formation. On the other hand, solute Si in the steel affected the growth of the Fe-Zn IMC during heating in the galvannealing process. The content of solute Si was assumed to be lower in the lower Si/Mn ratio sample, which resulted in acceleration of Fe-Zn IMC growth.  
KEY WORDS: Si-added steel; hot-dip galvanizing; galvannealing behavior; Si-containing oxide. (cf. *Tetsu-to-Hagané*, 105 (2019), 683)

Enhanced Interfacial Reaction of Fe-Si Alloy Sheets Hot-Dipped in Zn melt at 460ºC  
Naoki Takata, Kunihisa Hayano, Asuka Suzuki and Makoto Kobashi (Nagoya Univ.)  
In order to understand the effect of solute Si (in the steel sheet) on the interfacial reaction between liquid Zn and solid Fe (α-Fe phase) during the hot-dip galvanizing process, a change in the interfacial microstructure between Zn coating and Fe substrate in Fe-Si alloy sheets hot-dipped in Zn melt with dipping time at 460ºC was examined. In pure Fe sheet, the Fe-Zn intermetallic layers form at the interface between solid Fe and liquid Zn at an early stage of dipping and subsequently grow to approximately 60 μm in thickness after 600 s. In Fe-1Si (wt%) alloy, the thickness of Zn coating substantially increases to beyond 500 μm after 600 s and the coarse ζ-FeZn13 phase with several facet planes was often observed in the Zn coating. The thickness of the Fe-1Si alloy sheets continuously decreases till 60 s and then is reduced significantly after 600 s. The thickness loss in the later stage of dipping is more significant in the Fe-Si alloy with higher Si content. These results indicate a significant Fe dissolution into liquid Zn could occur at the later stage of dipping the Fe-1Si alloy in Zn melt, which is distinguished from the interfacial reaction between pure Fe and liquid Zn. The enhanced interfacial reaction would be responsible for the decomposition of the initially formed ζ-FeZn13 phase layer to liquid and FeSi phases, which can be proposed based on thermodynamic calculations of the Fe-Zn ternary system.  
KEY WORDS: galvanized steels; intermetallics; interfacial reaction; thermodynamic calculation; sandelin phenomenon. (cf. *Tetsu-to-Hagané*, 105 (2019), 693)

Formation of Fe3Alη Phase Layer on Fe-Si Alloy Sheets Hot-Dipped in Zn-0.2Al Alloy Melt  
Naoki Takata, Kunihisa Hayano, Asuka Suzuki and Makoto Kobashi (Nagoya Univ.)  
We have characterized η-Fe3Alη phase layers formed on Fe-Si binary alloys (pure Fe, Fe-0.2Si and Fe-1Si (wt%)) hot-dipped in a Zn-0.2Al (wt%) alloy melt at 460ºC for various times ranging from 2 to 3600 s. The Al addition in the Zn melt suppressed the interfacial reaction between liquid Zn and α-Fe phase with Si in solution. At an early stage of dipping (less than 10 s), Fe dissolution into the Zn-0.2Al alloy melt occurs more significantly on the α-Fe phase with higher Si content. The thickness of Fe3Alη phase layer becomes slightly larger on α-Fe phase with higher Si content. These indicates that solute Si in α-Fe phase could enhance the Fe dissolution providing the driving force for the formation of η phase in liquid Zn alloy, resulting in the enhanced formation of η phase layer. The thicker η phase layer formed on Fe-Si alloy sheets would play a role of diffusion barrier, resulting in the suppression of subsequent interfacial reactions even after 3600 s in dipping.  
KEY WORDS: galvanized steels; iron aluminide; interfacial reaction;
thermodynamic calculation.

\[ \text{(cf. Tetsu-to-Hagané, 105 (2019), 701)} \]

In-Situ Observations of Nucleation and Growth Behavior on Fe\textsubscript{2}Al\textsubscript{5} Intermetallic Compound Formed in Molten Zinc Bath
Sho Katsura, Ryo Sasaki, Noriaki Nakatsuka (Kobe Steel, Ltd.) and Hideyuki Yassuda (Kyoto Univ.)

In-situ X-ray transmission imaging experiments were performed to the simulated molten zinc baths of CGL in order to clarify the nucleation and growth behavior of Fe\textsubscript{2}Al\textsubscript{5} solid intermetallic compound called "top dross". Zn alloy samples containing a small amount of Fe and Al were melted in a high vacuum atmosphere and cooled by various rates. The in-situ X-ray transmission observations were performed during the cooling process. The nucleation and growth behavior of Fe\textsubscript{2}Al\textsubscript{5} particles were observed directly. The nucleation behavior is strongly affected by cooling rate, as cooling rate gets faster, the average particle size gets smaller and the number of particles increases. The total volume of crystallized particles is not changed by cooling rate. It is suggested that we have a possibility to control their size or number of dross particles by controlling bath temperature. Their nucleation behavior also suggested that they need a certain amount of Al, Fe supersaturation or supercooling in order to nucleate new dross particles in the bath. The growth speed of the particles in the molten zinc was also analyzed by image analysis. It is suggested that the growth behavior of Fe\textsubscript{2}Al\textsubscript{5} particles is restricted by the diffusion of Fe, Al components. In-situ X-ray imaging method can be a promising technique to understand the nucleation or growth behavior of dross particles generated in CGL baths.

KEY WORDS: X-ray imaging; nucleation; crystallization; dross; continuous galvanizing line; CGL; Fe\textsubscript{2}Al\textsubscript{5}.

\[ \text{(cf. Tetsu-to-Hagané, 105 (2019), 709)} \]

Structural and Mechanical Characterizations of Top Dross in a Molten Zinc Bath
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In a molten zinc bath in a continuous galvanizing line (CGL), top dross particles crystallize as Fe-Al-Zn intermetallic compounds. These particles easily adhere to the steel sheets causing surface defects. Therefore, controlling the top dross particles is a key issue. The present study focused on the structural and mechanical characterizations of top dross particles using an electron probe micro analyzer, X-ray diffraction, electron back scattering diffraction, Vickers hardness measurement and nano-indentation measurement. The following results were obtained: (1) The crystal structure of top dross particles Fe\textsubscript{2}Al\textsubscript{5}Zn, having Fe: 37~38 wt%, Al: 44~45 wt% and Zn: 18~19 wt% belongs to the orthorhombic system with a lattice constant of \( a=7.61 \text{ Å}, \quad b=6.48 \text{ Å} \) and \( c=4.23 \text{ Å} \). The \( a \) axis of Fe\textsubscript{2}Al\textsubscript{5}Zn becomes shorter, while the \( b \) and \( c \) axes become longer compared to those of binary Fe\textsubscript{2}Al\textsubscript{5}. (2) The top dross particles with the facetted interface were postulated to coarsen by the mechanism of the anisotropic interface energy between the top dross particles and molten Zn as a driving force rather than by the aggregation mechanism. (3) The hardness and the elastic modulus of the top dross particles are the lowest in the [001] direction like Fe\textsubscript{2}Al\textsubscript{5}, and are lower than those of Fe\textsubscript{2}Al\textsubscript{5}. (4) The fracture toughness of top dross particles is approximately 1.1 MPa m\textsuperscript{1/2}, which is slightly lower than that of Fe\textsubscript{2}Al\textsubscript{5}.

KEY WORDS: top dross; molten zinc; crystal structure; mechanical property; Fe\textsubscript{2}Al\textsubscript{5}Zn; intermetallic compounds; electron back scattering diffraction.

\[ \text{(cf. Tetsu-to-Hagané, 105 (2019), 716)} \]

Improvement of Powdering Resistance of Zn-Fe Galvannealed Coating by Controlling of Its Composition and Microstructure: Verification with Sputtering Method
Aimi Uchiyama, Kohei Kawasaki, Yui Satou, Daisuke Ando and Junichi Koike (Tohoku Univ.)

Improvement of the powdering resistance of galvannealed (GA) coatings is a key issue in automotive GA steel sheets. To make the relationship between powdering resistance and microstructure of GA layer, sputtering fabrication process was used to prepare Zn-Fe intermetallic films with various composition and microstructure in this study. Zn-Fe films with 1500 nm in thickness were deposited on an iron substrate by RF magnetron sputtering. \( \Gamma+\Gamma' \) two-phase film (17.2~24.4 at.%Fe) was found to show a severe powdering by 3-point bending test, while \( \Gamma_1 (16.2 \text{ at.} % \text{Fe}) \) or \( \Gamma' (34.3 \text{ at.} % \text{Fe}) \) single-phase films showed much better powdering resistance. These results indicate that \( \Gamma+\Gamma' \) interfaces boundaries have a low interfacial strength compared to that of \( \Gamma/\text{iron} \) or \( \Gamma'/\text{iron} \) interfaces. To improve the low powdering resistance of the \( \Gamma+\Gamma' \) two-phase film, we investigated the effect of grain size refinement by B addition on the powdering resistance. It was found that the grain size refinement by B addition drastically improves the powdering resistance of \( \Gamma+\Gamma' \) two-phase film. The decrease in the fracture toughness of \( \Gamma+\Gamma' \) two-phase film by grain refinement was suggested to cause the improvement of its powdering resistance.

KEY WORDS: galvannealed coating; Zn-Fe layer; powdering resistance; grain refinement.

\[ \text{(cf. Tetsu-to-Hagané, 105 (2019), 724)} \]

Effect of Microstructure at Coating Layer on Fatigue Strength in Hot-Dip Galvanized Steel
Kayo Hasegawa, Motoaki Morita and Shinichi Motoda (Tokyo Univ. of Marine Technology)

To understand the fatigue mechanism of hot-dip galvanized steel, the fatigue strength and fracture surface of hot-dip galvanized S45C (carbon steel) specimens were investigated. The galvanized coating layer was composed of \( \delta \)-phase, \( \zeta \)-phase and \( \eta \)-phase, and its thickness was about 100 mm. In low cycle range (10\textsuperscript{4} cycles < \( \Delta N \) < 10\textsuperscript{6} cycles), the fatigue strengths of both the carbon steel and the galvanized steel corresponded to the static strength. The fatigue strength of the galvanized steel was lower than that of the carbon steel. As the number of cycles increased, the difference between fatigue strength of the carbon steel and that of the galvanized steel increased. In addition, the morphologies of the fatigue fracture were also different in low cycle range and high cycle range. In the galvanized steel, the morphology of stage II crack on the fracture surface at low cycle range exhibited crescent shape, and multiple crack initiation sites in low cycle range were observed. On the other hand, the morphology at high cycle region (\( \Delta N > 10^6 \) cycles) exhibited an ellipse shape, and the crack initiation site was single. At both ranges, the crack initiation sites were in the coating layer. The mechanical properties of the microstructure in coating layer affect on the fatigue strength. When \( \eta \)-phase was removed from the galvanized coating layer, the fatigue strength increased only in high cycle range. Therefore, \( \delta \)-phase and/or \( \zeta \)-phase cause the fatigue strength to decrease in low cycle range, and \( \eta \)-phase causes it in high cycle range.

KEY WORDS: galvanized steel; crack initiation site; high cycle fatigue; multiple cracks; plating.

\[ \text{(cf. Tetsu-to-Hagané, 105 (2019), 733)} \]

Effect of Boron Addition on Liquid Zinc Embrittlement of Heat Affected Zone in 490 MPa Grade Steels
Masayuki Yamamoto, Keiji Murayama (Chubu Steel Plate Co., Ltd.), Hongmei Li and Naoki Katata (Nagoya Univ.)

We examined the effect of boron (B) addition (up to 10 ppm) on the liquid zinc (Zn) embrittlement of 490 MPa grade steels (SN490B) containing a trace amount (approximately 70 ppm) of nitrogen (N) via notched-bar tensile (NBT) tests. The studied steels were heat-treated in order to reproduce the microstructure (martensite structure) of the heat-affected zones
Mechanism of Corrosion Protection at Cut Edge of Zn-11%Al-3%Mg-0.2%Si Coated Steel Sheets

Yuki Suzuki, Shinichi Yamaguchi, Masamitsu Matsumoto (Nippon Steel Corp.) and Izumi Muto (Tohoku Univ.)

Zinc and zinc alloy coated steel is widely utilized for home appliance, construction, automobile, and so on for its high corrosion resistance. In this work, corrosion behavior at cut edges of Zn-11%Al-3%Mg-0.2%Si alloy coated steel sheets (SD) was investigated with cyclic wet-dry corrosion test. The result showed that SD have the superior anti-corrosive property to zinc coated steel sheets (GI) at early period of corrosion. GI produced red rust, whereas SD produced no red rust. After the cyclic wet-dry corrosion test, zinc-containing white rust deposited on steel substrate. In the case of SD, magnesium reached the center of cut edge and larger area on the steel was covered with white rust. With polarization measurements of steel substrate on which white rust deposited, it was clarified that white rust of SD reduced both anodic and cathodic current density of steel substrate more largely than that of GI. In the case of SD, galvanic current between steel substrate with white rust and coating layer was small compared with GI. It was suggested this anti-corrosive property of SD is due to magnesium-containing white rust.

KEY WORDS: zinc coated steel; Zn-11%Al-3%Mg-0.2%Si; cut edge; corrosion product; electrochemical property.

Corrosion Behavior of Aluminized Steel Sheets in 50-year Outdoor Exposure Test

Jun Maki (Nippon Steel & Sumitomo Metal Corp.)

Aluminized steel sheets are very resistant to corrosion in the outdoor exposure environment. We evaluated the corrosion behavior of aluminized steel sheets with a Type1 coating containing around 10%Si but also a Type2 coating not containing Si in a 50-year outdoor exposure test. Both specimens had strong perforation resistance, but those with Type2 coating had superior perforation resistance. The Type2 aluminized steel sheets had two sublayers composed of Fe$_2$Al$_5$ and FeAl$_2$ as the intermediate layer between the aluminized layer and the steel substrate. The FeAl$_2$ phase has less noble potential than steel substrate and the Fe$_2$Al$_5$ phase in an artificial rain water environment. As a result, this layer provided sacrificial corrosion protection for the steel substrate. That was why the specimens with the Type2 coating had better perforation resistance than those with Type1 coating.

KEY WORDS: aluminized steel sheets; outdoor exposure test; corrosion resistance; intermetallic compound layer.