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Annealing and Galvanizing Reactions of Hot-Rolled-in Scale on a Mn/Si Steel Sheet

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Various intermetallic compounds and interfacial precipitates play an important role in the galvanizing reactions for advanced high strength Mn/Si steels. The interactions after annealing and galvanizing treatments on a Mn/Si steel surface with hot-rolled-in scale were investigated. Several kinds of Fe, Mn and Si oxides and pure iron were observed at the interface of the simulated galvanized specimens. Furthermore, it was shown that the Fe/Zn alloy was strongly attached to FeO particles from the rolled-in scale, implying that a selective galvanizing reaction took place between the steel and annealed oxide scale. In addition, MnO and SiO_2 particles were also formed at the interface. A significant factor in the galvanizing of these steels has been determined to be the oxidation state of the alloying elements. The reactions taking place at the bath/substrate interface will be discussed.

Keywords: hot-rolled-in scale, annealing, galvanizing, Zn/Fe intermetallic compounds

1. INTRODUCTION

For energy saving, passenger security, and vehicle durability, the demand from the automotive industry for advanced high strength galvanized steel has increased significantly. Adding solid-solution hardening elements into steel, such as Mn, Si, Cr, P, is the most economical and effective manner to increase the strength and toughness of steel sheet(1-4). However, Si-added steel very easily induces some surface defects in the fabrication process of a galvanized steel sheet, such as rolled-in scale in hot-rolling, residual scale in pickling, and bare spots in the continuous galvanizing process(5-13). Some individual studies of these surface defects have been published in recent years. But very few articles have involved a complete series research of the process.

In this study, a special galvanized Mn/Si added steel sheet with hot-rolled-in scale was prepared. The microstructures of the as-cold rolled, annealed, and galvanized samples were observed and analyzed by GDOES, SEM, and TEM. The interactive behaviors of Fe, Mn, Si, O and Zn at the scale/substrate interface during the annealing and galvanizing processes were also discussed.

2. EXPERIMENTAL METHOD

The chemical composition of the experimental steel is shown in Table 1. The Mn/Si added dual-phase (DP) steel sample was cast and then hot-rolled to a thickness of 4 mm at the China Steel 2nd Hot-Rolling Plant. Prior to pickling in the laboratory in a 10% HCl solution with 0.25% inhibitor, a width of 25 mm in the central part was protected by acid-resistant tape. The pickled hot-rolled steel was then cold-rolled to a thickness of approximately 1.0 mm. The hot rolling start, finish, and coiling temperatures were 1250, 890 and 230°C, respectively. This sample was then cut into experimental panels with size 120 mm (w) x 200 mm (l). They were cleaned with a 5% NaOH solution at 80°C for 5 min, followed by rinsing with pure water and acetone. After drying with warm air, they were packed

Table 1 The chemical compositions of hot rolled Mn/Si steel sheet

Alloy	C	Si	Mn	P	S	Al	Fe
Mn/Si (wt%)	0.07	0.78	1.36	0.014	0.002	0.028	Bal.

with anti-corrosion paper, and stored in a dry box. Prior to the galvanizing simulation test, the panel surface was finally cleaned with acetone again.

The panel was annealed and galvanized in an Iwatani-Surtec Type III hot dip process simulator (HDPS) in McMaster University. Figure 1 shows the schematic diagram of the galvanizing simulator. More details concerning the configuration of this simulator have been described elsewhere(14). In the annealing process, the panel was annealed in an atmosphere of N_2-30%H_2 with a dew point of -30°C, heated at 15°C/s to the peak annealing temperature (PAT) of 800°C for 120s, and cooled at -15°C/s to the galvanizing temperature of 460°C. In the galvanizing process, an annealed panel was formed by immersing it for 3s in a Zinc bath containing 0.20 wt% dissolved Al and Fe-saturated, which was held at 460°C.

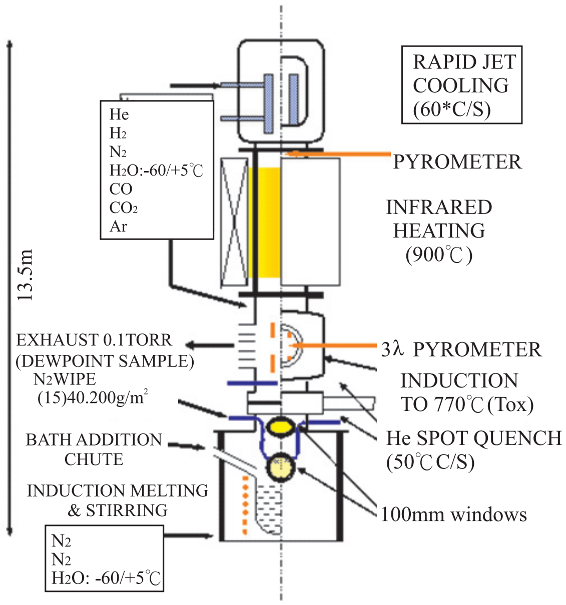


Fig.1. Schematic diagram of the galvanizing simulator.

The as-rolled, annealed and galvanized samples were analyzed by GDOES for an elemental depth profile, by SEM/EDS and TEM/SAED to identify the microstructures of the scale/substrate interface. All cross-sectional specimens were fabricated by the focus ion beam mining technique (FIB).

3. RESULTS AND DISCUSSION

3.1 Rolled-in scale in DP steel

Figure 2 shows the features of the scale on the DP steel after cold rolling, annealing and galvanizing. The central band was the area protected from pickling to retain the original hot-rolled scale which was the rolled-in scale from our cold rolling process. After the subsequent annealing at 800°C for 120s in an H_2-N_2 atmosphere, the scale band was clearly observable. After the final galvanizing for 3s, the scale band was still observable even if it was covered by a zinc layer. As we know, the major phase was composed of iron oxide. However, the GDOES results of the scale in Fig.3(a) show that the thickness of the rolled-in scale was about 2~3 μm according to the depth profile. In addition, Mn and Si elements could also be found in the oxide scale according to Fig.3(b). As a result, the composition of the oxide scale of the DP steel should be further investigated.

Figure 4 shows a series of TEM analyses of the hot-rolled-in scale sample of Fig.2(a). The grains were obviously separated within 2~3 μm of the steel surface depth from the observation of the cross section of the steel/scale boundary shown in Fig.4(a). It implies that the hot-rolling scale at 10~15 μm depth was squashed during the cold rolling process. Based on the EDS results, Si and Mn were found at the interface between the scale and the steel matrix. The SAED patterns shown in Figs.4(d) and 4(e) examined from Figs.4(b) and 4(c) revealed FeO and SiO_2, respectively. In the hot-rolling process, the Fe_2SiO_4 at the interface plays an important role owing to its descalability. However, we found that the scale might undergo decomposition from Fe_2SiO_4 to FeO and SiO_2 at high temperature. According to the nature of the Fe_2SiO_4 studied by Brinkmann(15), the decomposition reaction is dependent on the partial oxygen pressure. In the hot-rolling

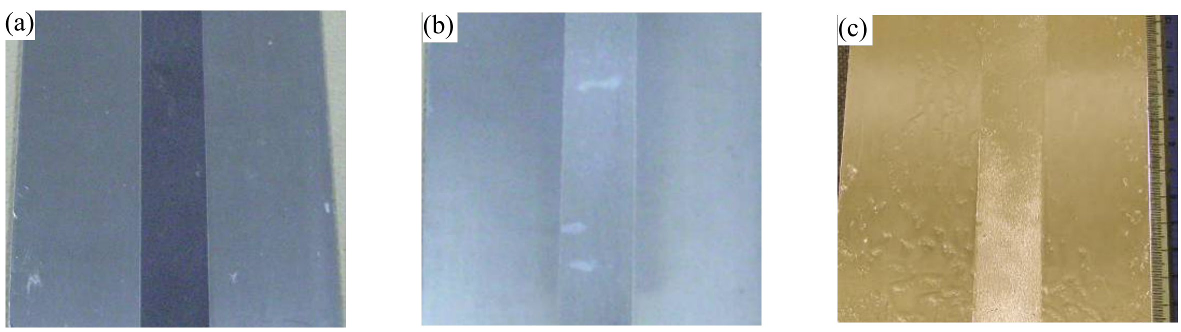


Fig.2. Images of the (a) as-rolled, (b) annealed and (c) galvanized, Mn/Si DP steel samples.

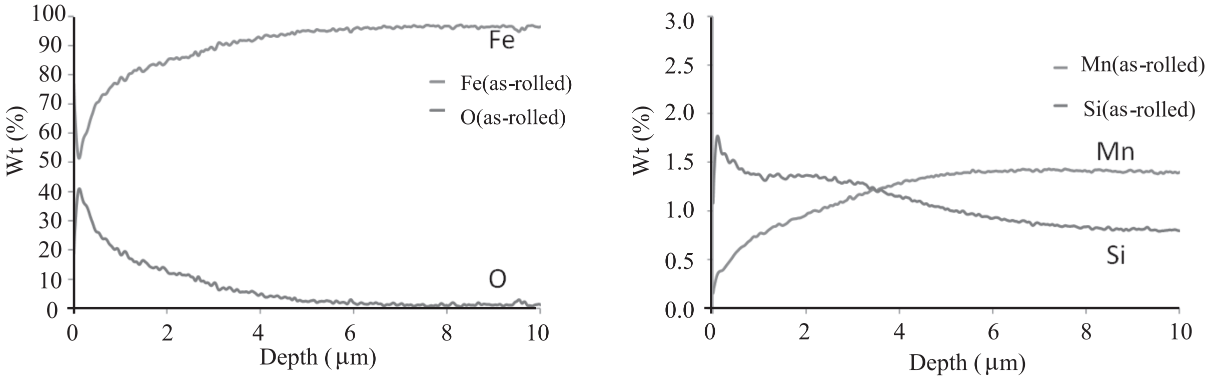
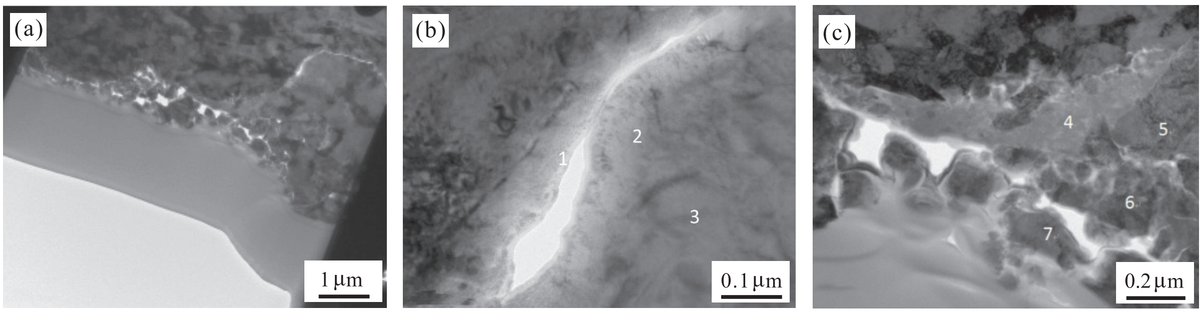
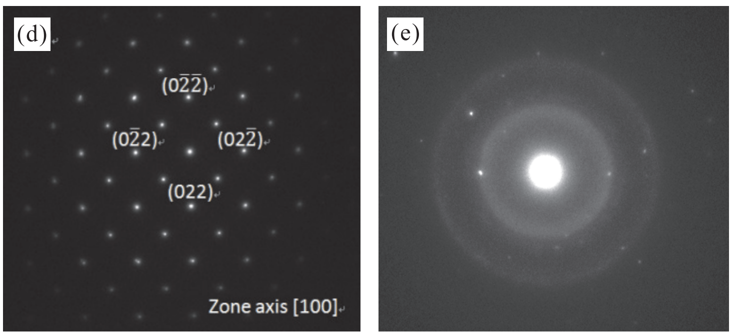


Fig.3. GDOES depth profiles for (a) Fe-O and (b) Si-Mn analyses of the as-rolled sheet containing rolled-in scale.





Spectrum	Fe	Mn	Si	O
1	78.17	1.21	2.29	18.32
2	56.84	0.76	2.35	40.05
3	65.36	0.42	0.35	33.87
4	24.67	2.33	13.28	59.72
5	58.98	0.55	0.56	39.91
6	60.75	0.43	0.43	38.39
7	55.93	0.43	0.76	42.88

Fig.4. A series of TEM analyses of the cross section of the hot-rolled-in scale area.

process, the Fe_2SiO_4 was formed in the reheating furnace and then exposed in air during the rolling process in case rolled-in scale was produced. Hence, FeO and SiO_2 became the major substances on the Si/Mn steel sheet before annealing and galvanizing processes.

3.2 Reducing reactions of oxide scale during annealing

The annealing process is carried out in a galvanizing simulator using a 30%H_2-70%N_2 atmosphere. After annealing at 800°C for 120s, the thickness of the scale is less than 1 μm as shown in the GDOES result in Fig.5. In addition, the Si and Mn are gathered in the area 0.1 μm near the surface. It can be suggested that most oxygen ions in the oxide were removed because of the reducing reaction during annealing.

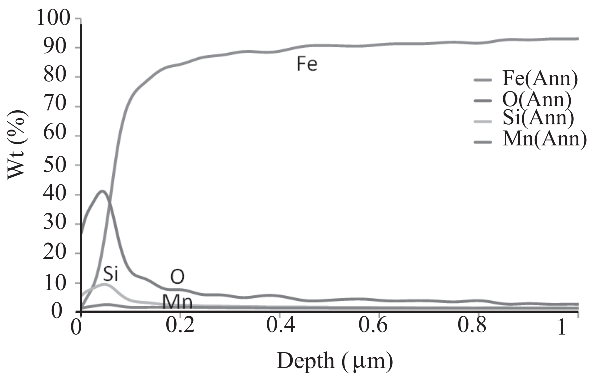
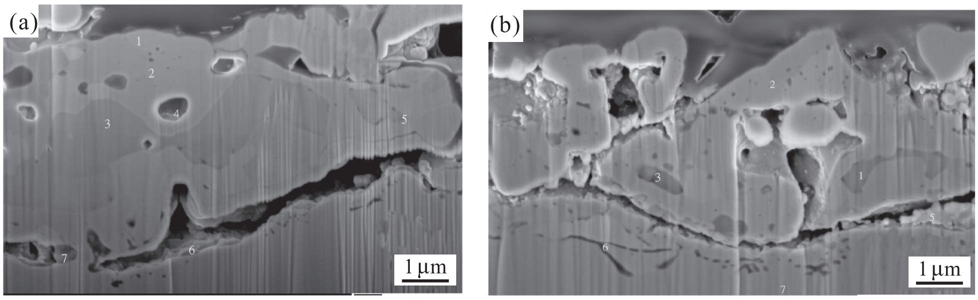


Fig.5. GDOES depth profiles of the annealed sheet containing rolled-in scale.

Figure 6 shows the cross sectional image of the rolled-in scale area. Under a reductive environment, the oxide was reduced to iron and some pores were obviously formed along the steel/scale interface. However, the rolled-in scale grains became larger with Fe, Mn, Si and O inside. EDS analyses revealed that all the alloying elements were distributed over the scale and interface. Based on the well-crystallized morphologies of the scale grains, the appearance of the non-stoichiometric oxide could be suggested. In addition, another image shown in Fig.6(b) also revealed that the substructure in the grains contained Si and Mn. As a result, the fact that Si and Mn were diffused into iron and oxide after annealing process can be confirmed. Nevertheless, the reaction between Mn and Si should be clarified.

Figure 7 shows the microstructure analysis results



spectrum	Fe	Mn	Si	O	C
1	57.23				38.23
2	100				
3	41.43	5.45		49.74	3.38
4	93.32				5.29
5	46.90	7.74		41.74	3.65
6	59.27	14.90	11.95	12.55	
7	66.20		13.01	20.97	

spectrum	Fe	Mn	Si	O	C
1	45.00	27.90		23.92	3.18
2	94.61				5.39
3	36.34	15.25	10.25	35.37	2.79
4	71.79	6.07	5.13	12.33	4.69
5	77.65		3.03	9.12	9.42
6	82.73		8.35		8.92
7	98.59		1.41		

Fig.6. Cross sectional analysis of SEM/EDS in the rolled-in scale area of the annealed sample.

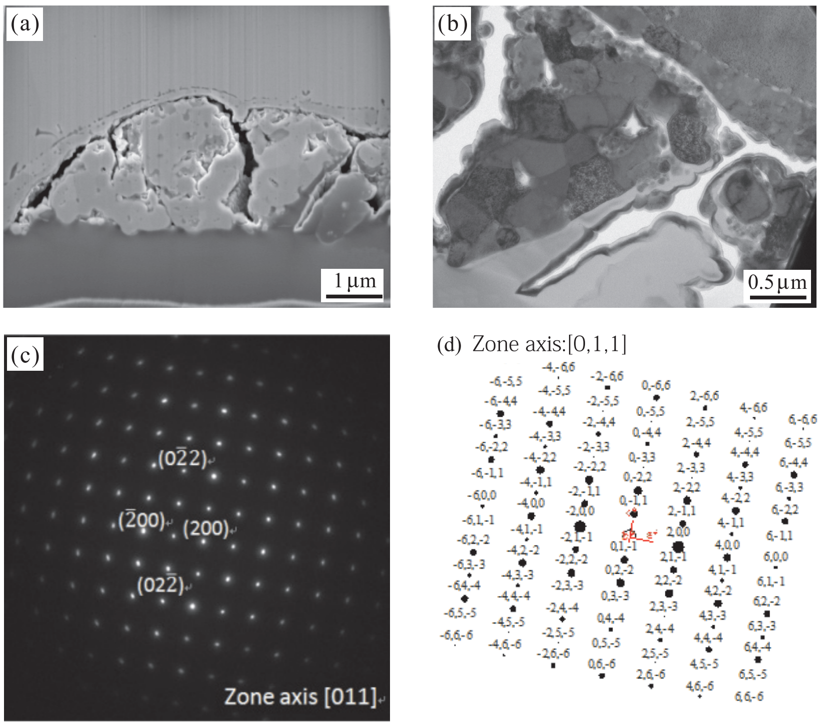
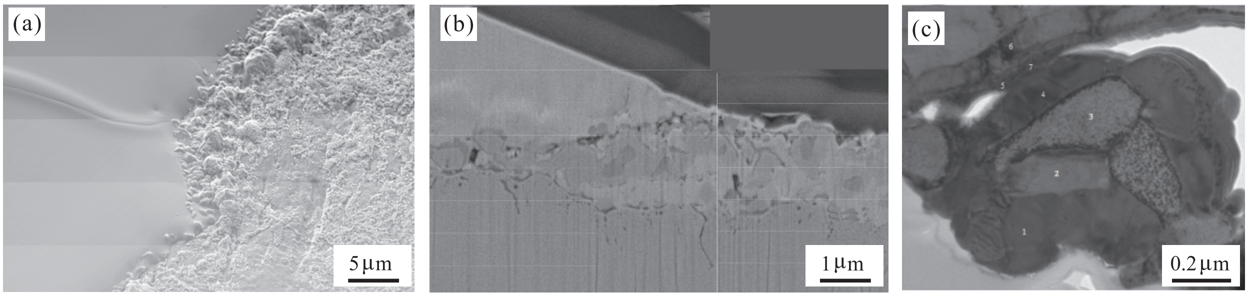


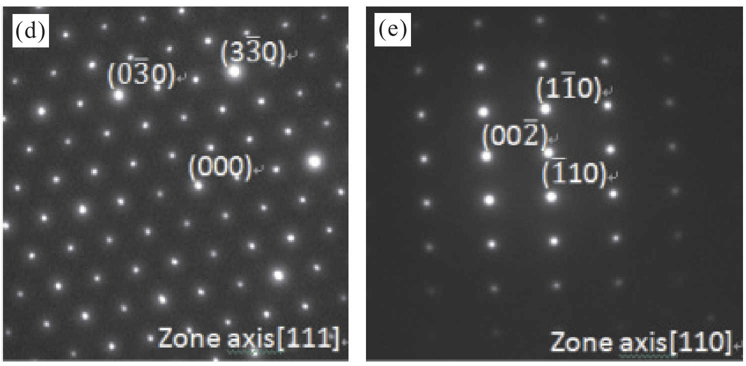
Fig.7. The microstructure analyses of TEM/SAED of the annealed rolled-in scale area.

of the inter-grain substructure. In Fig.7(b), the TEM image of the rolled-in scale shows the distinct substructures which could not be observed by SEM image as shown in Fig.7(a). This indicates that all the oxides were gathered to be an oxide cluster. According to the SAED patterns in Fig.7(c), a specific substructure marked in Fig.7(b) exhibited a Mn_2SiO_4 structure which was identified by the simulated pattern shown in Fig.7(d). Although reducing reaction of the scale oxide occurred in the annealing process, the solid state reaction of SiO_2 and MnO_2 could also be examined. Hence, the oxides, including Fe, in the rolled-in scale such as FeO, SiO_2, MnO_2 and Mn_2SiO_4 played important roles in the following galvanizing process.

3.3 The bare spot of the galvanized DP steel surface

The annealed sample was further galvanized in the simulator held at 460^{o}C in a Zn bath containing 0.2% Al and saturated with Fe. In order to realize the galvanizing behavior of the rolled-in scale, the sampling was chosen to be the bare spot shown in Fig.8(a). An apparent boundary between the galvanized and the ungalvanized areas was observed at the edge of the bare spot. The cross sectional image of the rolled-in scale boundary is shown in Fig.8(b). Even though most area was not covered with zinc, the chinks inside the rolled-in scale could still be filled with zinc. It is of much interest to investigate the reactions of the zinc and the oxides. Consequently, the boundary was further prepared to be analyzed by TEM to result in those shown in Figs.8(c) to 8(e). Fig.8(c) reveals a near surface particle which contained several gathered grains and coated zinc. According to the SAED patterns shown in Figs.8(d) and 8(e), they were identified to be α-ferrite and Γ-Fe_4Zn_9 structures. The EDS analysis shown in Fig.8(c) also revealed oxygen around the particles. This indicates that the inner grains should be a non-stoichiometric Fe_xO_{1-x} with x equaling 0.95. As we know, Γ-Fe_4Zn_9 is always formed at the interface between coated zinc and matrix steel. Hence, Γ-Fe_4Zn_9 is regarded as an intermetallic compound formed by the interfacial diffusion of Fe in the zinc layer. In other words, only when the interface of zinc and iron is exhibited can the Γ-Fe_4Zn_9 be seen formed by interfacial diffusion. However, a phenomenon of direct Γ-Fe_4Zn_9 coating on the Fe or Fe_xO_{1-x} was discovered in this study. In our opinion, molten zinc might react with the iron primarily at the moment of galvanizing and increase the iron concentration. After cooling, Γ-Fe_4Zn_9 adhered to the iron oxide and formed the specific Fe_xO_{1-x}/Γ-Fe_4Zn_9 interface observed in Fig.8(c). Although the diffusion path of the alloying elements is still under investigation, another mechanism of the Zn-Fe diffusion behavior can be predicted and should be considered in the galvanizing process.





	O	Al	Si	Mn	Fe	Zn
1	5.16	0.00	1.02	0.00	30.89	62.93
2	6.24	0.00	1.24	0.00	92.52	0.00
3	7.31	0.00	0.99	0.00	91.71	0.00
4	4.95	0.00	1.10	0.00	32.29	61.66
5	5.85	0.00	1.26	0.00	29.03	63.86
6	7.88	0.00	0.77	0.00	91.35	0.00
7	5.23	0.51	0.94	0.12	26.61	66.59

Fig.8. Cross sectional analysis of galvanized sample by TEM/EDS and SAED.

4. CONCLUSIONS

The rolled-in scale remained on the as-rolled Si/Mn DP steel sheet and was treated by annealing and galvanizing afterwards in the simulator. Microstructure analyses were carried out to investigate the local reactions in the annealing and galvanizing processes. After annealing, various oxides were still found inside the rolled-in scale. In addition, a solid state reaction also took place because of the appearance of the Mn_2SiO_4. All the oxides played important roles in attaching the molten zinc bath in galvanizing process. In this study, we focused on the presence of a $Fe_xO_{1-x}/\Gamma\text{-}Fe_4Zn_9$ interface amongst the surface grains. Theoretically, according to the Fe-Zn phase diagrams, the saturated solubility of iron in molten 0.2 wt% Al-containing zinc is less than 0.02%. In addition, the formation of the $\Gamma\text{-}Fe_4Zn_9$ was based on the diffusion in the Fe/Zn interface. The results indicate that some other mechanisms should be proposed to support the direct $\Gamma\text{-}Fe_4Zn_9$ coating on the Fe_xO_{1-x} grains.

REFERENCES

1. D. Bhattacharya: "Perspectives on Coated Advanced High Strength Steels for Automotive Applications", IL23, 8th International Conference on Zinc and Zinc Alloy Coated Steel Sheet Proceedings, Genova, Italy, June 21-24, 2011.
2. M. B. Moon, S. W. Lee and S. J. Park: "Development of 590Mpa Grade DP GA Steel for Automotive Outer Panel Use", IL24, 8th International Conference on Zinc and Zinc Alloy Coated Steel Sheet Proceedings, Genova, Italy, June 21-24, 2011.
3. Y. Suzuki: "Galvannealed Steel Sheets: Trends and Developments in Japan", IL16, 8th International Conference on Zinc and Zinc Alloy Coated Steel Sheet Proceedings, Genova, Italy, June 21-24, 2011.
4. B. Gleeson, R. K. Singh Raman and D. J. Young: CAMP-ISIJ, 2003, vol. 16, pp. 1345-1348.
5. J. W. Choi and S. J. Kwon: CAMP-ISIJ, 2003, vol. 16, pp. 1357-1359.
6. M. Takeda and T. Onish: Materials Science Forum, 2006, vols. 522-523, pp. 477-488.
7. Y. Tobiyama, Y. Suzuki, K. Kyono and C. Kato: "Improvement in Galvanizability of High Strength Steels by the Suppression of the Selective Surface Oxidation of Alloying Elements During Annealing", pp. 771-781, 6th International Conference on Zinc and Zinc Alloy Coated Steel Sheet Proceedings, Chicago, USA, 2004.
8. T. Yasui, M. Nakazawa and A. Miyasaka: "Factors Affecting Galvannealing Behavior of Si-containing Steel Sheet", pp. 493-498, 7th International Conference on Zinc and Zinc Alloy Coated Steel Sheet Proceedings, Osaka, Japan, 2007.
9. E. Hamada, M. Nagoshi, K. Sato and M. Sakurai: "Initial Stage Fe-Zn Reaction During Hot Dip Galvanizing of Si-Added Steel", pp. 482-486, 7th International Conference on Zinc and Zinc Alloy Coated Steel Sheet Proceedings, Osaka, Japan, 2007.
10. M. Norden, M. Blumenau, R. Schonenberg and K. J. Peters: "Chance and Challenges of Using Pre-oxidation in Hot Dip Galvanizing of AHSS", p. 115, 8th International Conference on Zinc and Zinc Alloy Coated Steel Sheet Proceedings, Genova, Italy, June 21-24, 2011.
11. E. M. Bellhouse and J. R. McDermid: Metall. Trans. A, 2010, vol. 41A, pp. 1539-1553.
12. E. M. Bellhouse and J. R. McDermid: "Selective Oxidation and Reactive Wetting of Al-Si TRIP-Assisted Steels During Heat Treatment in a Galvanizing Simulator", IL26, 8th International Conference on Zinc and Zinc Alloy Coated Steel Sheet Proceedings, Genova, Italy, June 21-24, 2011.
13. F. Menguelti, X. V. Eynde and L. Bordignon: "Effect of Annealing Parameters on Strip Surface State of High Strength Steels and Consequences on Zinc Wetting", 106, 8th International Conference on Zinc and Zinc Alloy Coated Steel Sheet Proceedings, Genova, Italy, June 21-24, 2011.
14. L. Chen, R. Fourmentin and J. R. McDermid: "Short Term Formation of the Inhibition Layer During Continuous Hot-dip Galvanizing", pp. 321-326, 7th International Conference on Zinc and Zinc Alloy Coated Steel Sheet Proceedings, Osaka, Japan, 2007.
15. U. Brinkmann and W. Laqua: Physics and Chemistry of Minerals, 1985, vol. 12, pp. 283-290. □