Effects of Phosphorus in Steel on Galvannealing Behavior of Galvanized Steel

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The alloy phase of the galvanized steel sheets have been examined in order to clarify the effect of phosphorous in steel on the galvannealinmg behavior. SEM observation have revealed that the density of the ζ-ZnFe crystal decreases and the size of the ζ-ZnFe crystal become large as a function of the phosphorous content in the steel. The amount of the Al-Fe alloy as a inhibition layer for the alloying between iron and zinc have been increased as a function the phosphorous content. AES and XPS analyses have revealed that phosphorous in the steel segregates to the surface of the steel and that the amount of segregated phosphorous increases as a function of the phosphorous content of the steel. Phosphorous have been also detected in the Al-Fe alloy layer for the steel having a high phosphorous content. These results suggest that the alloying between iron and zinc is suppressed because the amount of the Al-Fe alloy inhibition layer increased. Therefore, the number of the nucleation site of the ζ-FeZn crystal can be reduced.

1. Introduction

The high strength galvannealed steel sheet are required as a material of the automobile body panel having a good corrosion resistance and strength. Phosphorus is one of the most effective element for the purpose. The galvannealed steel is produced by the following process. The steel sheet is galvanized in the molten zinc bath containing aluminum before the steel sheet is annealed and the galvanized steel sheet is annealed again. At the initial stage of the galvanizing process, the ζ-ZnFe crystals are formed on the Fe-Al alloy layer which is formed as the alloying reaction between iron of the steel and aluminum in the molten zinc bath.

It have been reported that the Zn-Fe alloying reaction was suppressed by adding phosphorus and that the segregation of phosphorus at the surface and / or the grain boundary of the steel might have an important role for the suppression [1]-[4]. However, the effects of phosphorus has not been known.

Moreover, the surface segregation of phosphorous for the phosphorous added steel is not found for the rapid annealing process as the CGL (continuous galvannealing line) process, although the surface segregation is examined for the batch process in which the surface become the equilibrium state [5].

In this paper, the surface segregation of phosphorus during the CGL process and the alloy phases in the galvanized coating have been examined in order to clarify the effect of phosphorus in the phosphorous added steel on the galvannealing behavior.

2. Experimental Procedure

Phosphorus added steels having different phosphorus contents (0.002, 0.024, 0.055, 0.086 mass%P) were prepared by using the laboratory vacuum furnace before the cold rolling. The steel sheets were annealed at 750 °C x 60 sec. in 10% H_2-N_2. The galvanizing was performed to the phosphorus added steel sheets after the annealing. The aluminum content of the zinc bath was 0.12 and 0.2 mass%, the bath temperature was 460 °C and the immersion time in the bath was 3 sec. The phosphorous added steel sheets were annealed at 750 °C x 90 sec. in 10% H_2-N_2 for the measurements of the surface segregation.

The surface morphology of the alloy layer were observed by using SEM (JEOL, JSM840-

F) after the zinc layer was removed by the immersion in a 5% HCl solution. The cross section of the galvanized steel was observed by using TEM. (Philips, EM420).

The surface segregation were examined by using AES (Φ, SAM650) and XPS (VG, ESCALAB MkII). For the AES analysis, the acceleration voltage of the primary electron was 3kV. XPS spectra were measured with the Mg Kα radiation. The spectrometer of XPS was calibrated by Au4f 7/2 line (Au4f 7/2 = 84.0 eV). The peak shift of the binding energy was corrected by adventurous carbon (C 1s = 284.6 eV). The accelerating voltage of the Ar ion was 3 kV for the AES and XPS depth profiling.

The AES depth profiling of the Fe-Al layer was performed after the zinc and Zn-Fe alloy layer was removed by the immersion in a fuming nitric acid [6]. The aluminum content of the Fe-Al layer was measured by using ICP.

3. Results and Discussion

3.1 Galvaniging behavior of phosphorous added steel sheet

The SEM images of the Zn-Fe alloy phase of the phosphorous added steel are shown in Fig. 1. The images were observed after zinc layer was removed by the immersion in the HCl solution. The columnar Zn-Fe alloy phase are seen in every sample. The alloys correspond to the ζ-ZnFe phase. The sparse and coarse crystal of the ζ-ZnFe phase is observed for the steel having a high phosphorous content. The result suggests that phosphorous may delay the nucleation of the ζ-ZnFe crystals.

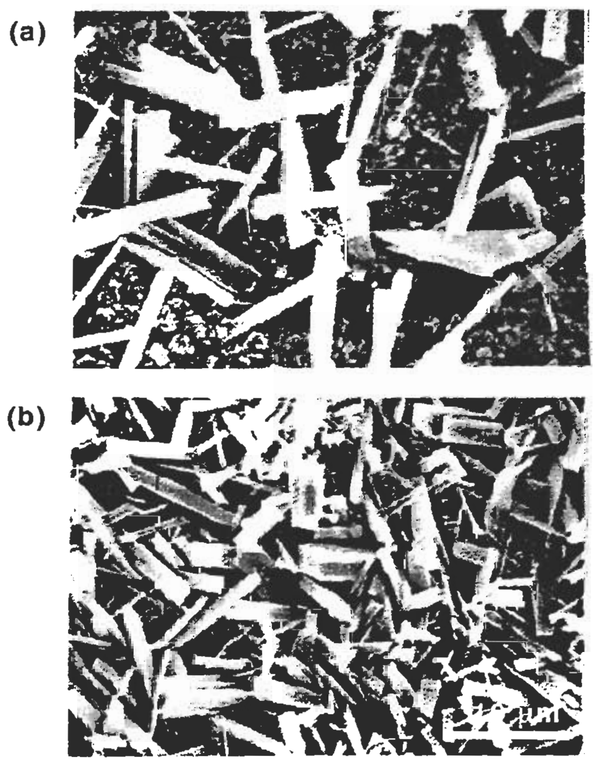

Fig.1 SEM images for intermetallic compounds formed during Galvanizing for phosphorous added steel sheet. (a) 0.086 mass% P and (b) 0.002 mass% P.

Fig. 2 shows the amount of aluminum in the Fe-Al alloy layer of the phosphorous added steel. The amounts of Al increases as a function of the phosphorous content of the steel sheet. Because the aluminum is resulted from the Fe-Al alloy layer which is formed at the interface between the steel and the coating layer, the amount of the Fe-Al alloy layer increase as a function of aluminum content.

3.2 Surface segregation of phosphorous added steel sheet

AES spectra of the phosphorous added steel sheets annealed at 750 °C x 90 sec. in 10% H_2-N_2 are shown in Fig. 3. A P LMM AES line is seen in AES spectrum of the steel having 0.086 mass% phosphorus. Fig. 4 shows AES depth profiles for the phosphorous added steels annealed at 750 °C x 90 sec. in 10% H_2-N_2 having different phosphorous content. The depth profile shows that the phosphorous segregates at the surface only for the steel having high phosphorous content. The amount

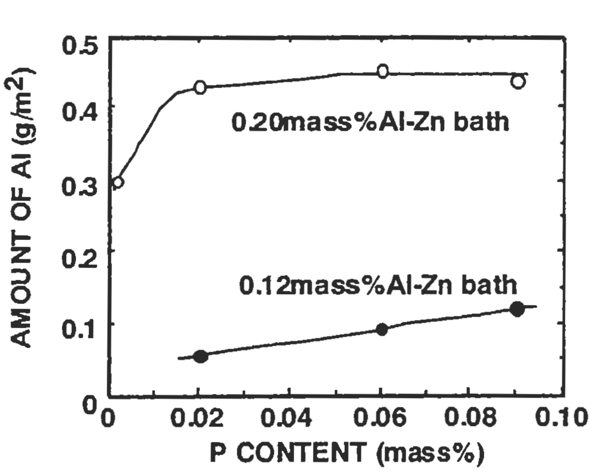

Fig. 2 Amount of Al in Fe-Al alloy layer as a function of P content in the steel sheet.

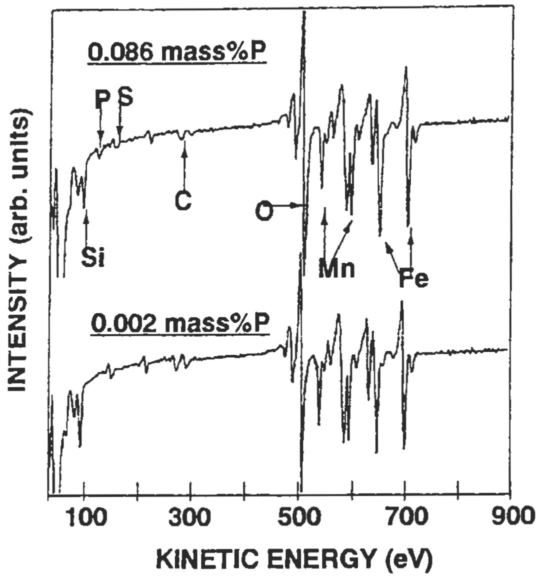

Fig. 3 AES spectra of phosphorous added steel sheet annealed for 90sec. at 750 °C in 10% H_2-N_2. Spectrum is obtained after 2 min. Ar ion sputtering.

of the surface segregated phosphorous increase as the bulk content.

P 2p XPS spectra of the 0.086 mass% phosphorus added steel are shown in Fig. 5. The peak of the P2p XPS spectrum shifts after the Ar ion sputtering. The state of the phosphorous for the as received steel is close to phosphate [7]. At the inner layer observed after 40 min. sputtering, phosphorous exists as phosphide [8]. Although the steel was

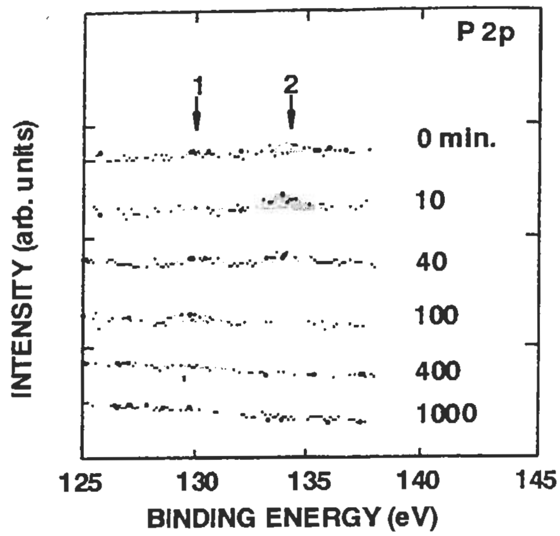

Fig. 5 P2p XPS spectra of 0.086 mass% phosphorous added steel sheet as a function of Ar ion sputtering. Steel was annealed for 90sec. at 750 °C in 10% H_2-N_2.

annealed under the reductive atmosphere, it was exposed to the air before the XPS analysis. Therefore, phosphide changes phosphate at the top surface. These results show that phosphorus segregates as a state close to the phosphide at the surface.

3.3 Mechanism of galvanizing behavior of the phosphorous added steel sheet

The Al-Fe alloy layer at the interface between zinc layer and steel substrate were

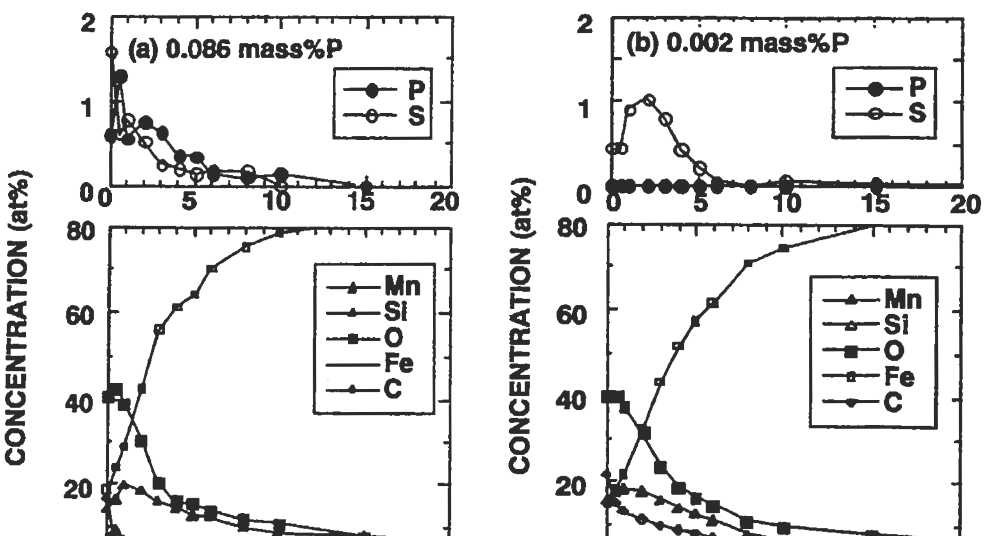

Fig. 4 AES depth profiles for phosphorous added steel sheet annealed for 90sec. at 750 °C. (a) 0.086 mass% P and (b) 0.002 mass% P.

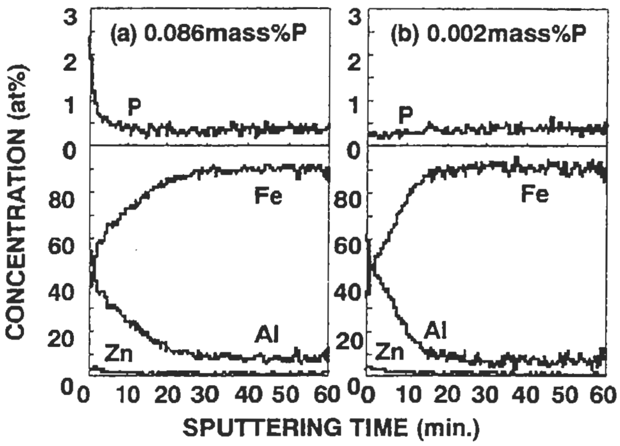

Fig.6 AES depth profiles of Fe-Al alloy layer formed on phosphorous added steel sheet. (a) 0.086 mass% P and (b) 0.002 mass% P.

observed by TEM. The AES depth profiles in the Al-Fe alloy layer for the phosphorous added steels are shown in Fig. 6. Phosphorus is detected in the Al-Fe alloy layer for the only steel having a high phosphorus content. The result suggests that surface segregated phosphorous of the steel moved to the Fe-Al alloy layer during the galvanizing. The crystal structure of the Al-Fe alloy was identified with the Fe_5Al_2 phase by the x-ray diffraction analysis. The number of the phosphorous atom per a unit cell of the Fe_5Al_2 is calculated as about 0.3 from the AES result. The crystal structure of the Fe_5Al_2 alloy reported by shows two holes in a unit cell [9]. Phosphorous can occupy a part of the holes and the mobility of iron and zinc in the layer may be modified. Therefore, the amount of the Fe-Al alloy layer formed on the phosphorous added steel may become large as seen in Fig. 2, by the alternation of the crystal structure.

These results suggest that the segregated phosphorus at the surface during the annealing changes the quantity and structure of the Fe-Al layer which is a suppression layer of the Zn-Fe alloying reaction[10]. Because the Fe-Al layer is altered for the phosphorous added steel, the number of the nucleation site of the ζ-ZnFe crystal can be reduced. Therefore, the ζ-ZnFe crystal can grow coarsely and sparsely.

4. Summary

For the phosphorus added steel, the coarse and sparse ζ-ZnFe crystals which are formed at the initial stage of galvanizing were observed by using SEM. Amounts of Al-Fe alloy at the interface between the Zn coating and the steel increased in the case of the steel having a high phosphorus content.

AES and XPS analyses have revealed that phosphorus segregates as phosphide at the surface of the phosphorous added steel and that the amount of surface segregated phosphorus increases as a function of the phosphorus content. Phosphorus is also detected in the Al-Fe alloy layer for the steel having a high phosphorus content by AES.

These results suggest that segregated phosphorus at the surface during the annealing changes the quantity and structure of Fe-Al layer which is a suppression layer of the Zn-Fe alloying reaction and that the number of the nucleation site of the ζ-ZnFe crystal is reduced. Therefore, the ζ-ZnFe crystal can grow coarsely and sparsely.

References

[1] A. Nishimoto, J. Inagaki and K. Nakaoka, Tetsu to Hagane, **68**, 1404 (1982).

[2] H. Arai, Y. Adachi, T. Nakamori and T. Usuki, Tetsu to Hagane, **83**, 713 (1997).

[3] M. Urai, M. Arimura and Y. Sakai, Tetsu to Hagane, **80**, 545 (1994).

[4] K. Tahara, J. Inagaki and T. Watanabe, CAMP-ISIJ, **6**, 1565 (1993).

[5] M. Takahashi, M. Nishihara and M. Fujino, Tetsu to Hagane, **64**, A167 (1978).

[6] Y. Funabashi, S. Kyoma, N. Yoshida, CAMP-ISIJ, **4**, 1412 (1991).

[7] P. Swift, Surf. Interface Anal., **4**, 47 (1982).

[8] B. Egert and G. Panzner, Suf. Sci., **118**, 345 (1982).

[9] U. Burkhardt, Yu Grin, M. Ellner and K. Peters, Acta Cristallogr., **B50**, 313 (1994).

[10] Von H. Bablik, F. Götzl and R. Kukaczva, Werst Korro., **2**, 163 (1951).