GDOS/XRD Study of Alloying Processes in Zinc Coated Steel Sheet by Annealing at High Temperatures

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GDOS and XRD have been used for investigating alloying processes in zinc coated steel sheet. GDOS depth profiles demonstrate systematic changes of the zinc concentration in the coatings by annealing at high temperatures, while XRD measurements show that the phase formation of zinc-iron alloy layers occurs on the surface of steel sheets with zinc coatings by annealing.

1. Introduction

Zinc coated steel sheets are produced either by electrodepositing or by hot-dipping. Typically, galvannealed steel sheets with zinc-iron alloy coatings, which exhibit superior properties in corrosion resistance, are made by annealing at high temperatures after hot-dipping[1]. These zinc-iron alloy coatings are composed of layers such as ζ, δ_1, Γ_1 and Γ phases, of which the formation strongly depends on annealing conditions.

These coatings are often characterized by X-ray diffraction (XRD) method and glow discharge optical emission spectrometry (GDOS)[1] and so on. However, there are no systematic experiments, and therefore, these data by different methods should be compared mutually for crosscheck. The aim of this work is to characterize the depth profile and crystallographic structures of alloying layers, which are formed by the reaction of a deposited zinc layer with a steel substrate at high temperatures, by using GDOS and XRD. The alloying processes or kinetics of the coatings are also discussed based on those results.

2. Experimental

Samples used were sheets of interstitial free steel, on which a pure zinc layer of about ten micrometers thick was electrolytically deposited. They were annealed in hydrogen gas in the temperature range between 673 K and 873 K for different times, to form zinc-iron alloy layers, and then rapidly cooled to room temperature.

Measurements of GDOS were carried out using RSV analymat 2504, which was operated under the same condition as reported previously [2]. The composition-depth relation was obtained from the data by describing the optical emission intensities for elements and discharging time, that is sputtering time, using a quantitative method [2]. The optical emission intensity for each element sputtered during glow discharge is related to the number of atoms sputtered from the surface per sputtering time in that method.

The conventional XRD measurements with monochromated Cu Kα radiation were performed to identify the crystallographic structure of the alloying layers formed on steel sheets.

3. Results and Discussion

Figures 1 and 2 show quantitative GDOS depth profiles of samples annealed at 673 K and 773 K for different times, respectively. The initial coating was of pure zinc. These results indicate that the zinc concentration in the surface layer decreases with increasing annealing time. Although this alloy system is in a solid state at 673 K, the alloying reaction is found to clearly proceed. In samples

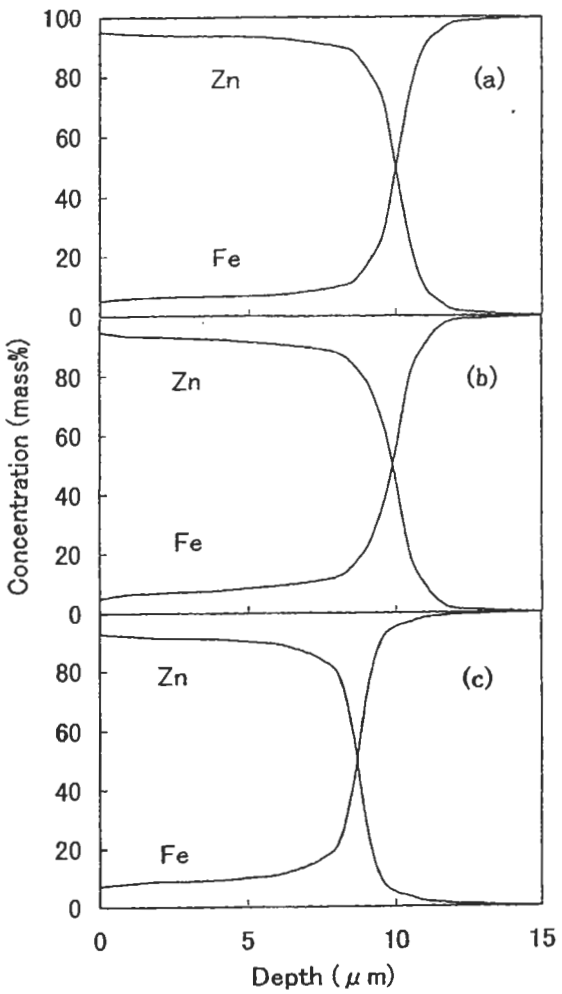

Figure 1. Quantitative GDOS depth profiles for coated steel sheets annealed at 673 K for (a) 300 s, (b) 1000 s and (c) 3000s.

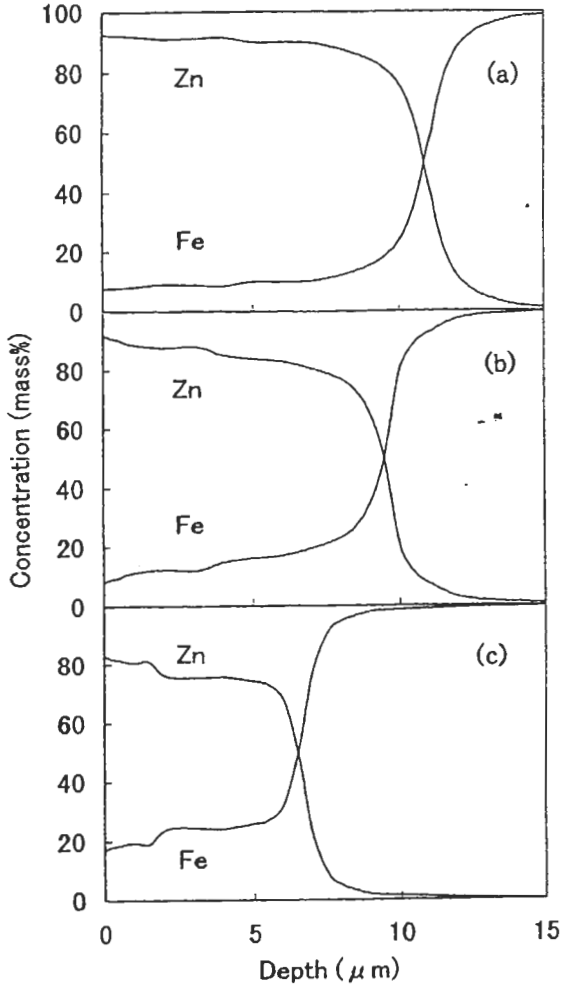

Figure 2. Quantitative GDOS depth profiles for coated steel sheets annealed at 773 K for (a) 300 s, (b) 1000 s and (c) 3000s.

annealed at 773 K, which is the temperature at which pure zinc is melted, alloying layers with different compositions are formed, as shown in Fig.2. The thickness of the coated layer is found to be reduced in a sample annealed for a long time, suggesting that zinc is evaporated from the surface.

Figures 3 and 4 show XRD patterns obtained from samples annealed at 673 K and 773 K, respectively. The amount of ζ phase formed from pure zinc in the initial stage decreases with increasing annealing time at 673 K, whereas the amount of Γ_1 phase increases. This behavior demonstrates that Γ_1 phase is replaced with ζ phase with the alloying reaction. Slight peaks from δ_1 phase was also detected during change from ζ phase to Γ_1 phase. On the other hand, the reaction from Γ_1 phase to Γ phase is observed in samples annealed at 773 K for a long time, as shown in Fig.4.

The compositional results of surface layers in GDOS depth profiles should be compared with the crystallographic data by XRD arising from layers of a few micrometers thick. The composition of ζ,

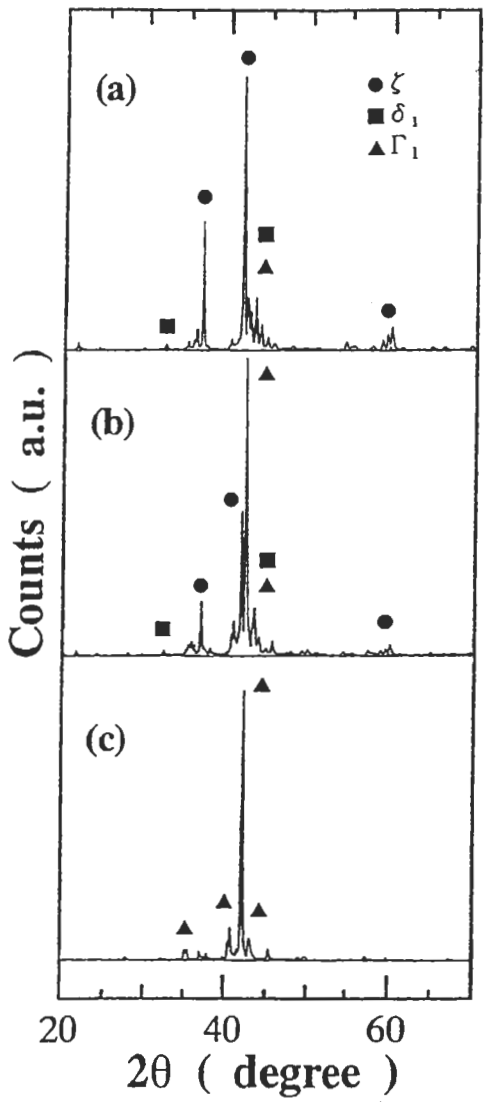

Figure 3. X-ray diffraction curves obtained from coated steel sheets annealed at 673 K for (a) 300 s, (b) 1000 s and (c) 3000s.

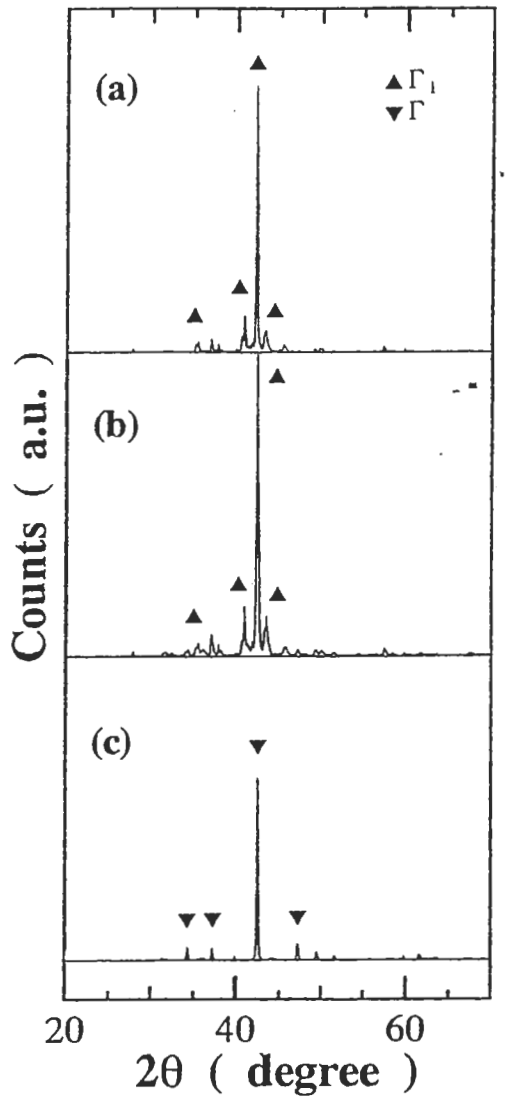

Figure 4. X-ray diffraction curves obtained from coated steel sheets annealed at 773 K for (a) 300 s, (b) 1000 s and (c) 3000s.

δ_1, Γ_1 and Γ phases are 94-95%Zn, 88-93%Zn, 82-83%Zn and 72-73%Zn, respectively. However, the small difference of the concentration in alloying layers, e.g. between ζ and δ_1 phases, is hardly distinguished by GDOS. Nevertheless, it may be accepted that the GDOS results appear to be semi-quantitatively consistent with the XRD results.

In order to understand the kinetics of alloying processes, the time-temperature diagram for phase formation in surface layers in the present steel with zinc coated layer is summarized in Fig.5. By annealing at higher temperatures for longer periods, phases with the higher iron concentration are formed. In addition, it is noted that such annealing induces significant evaporation of zinc. In

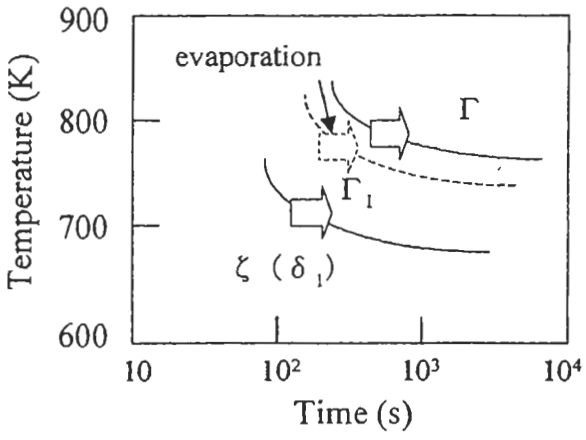

Figure 5. Time-temperature diagram for phase formation on the surface of the steel with a zinc coating of about ten micrometers thick.

these alloying processes, the effect of a small amount of aluminum on the kinetics is neglected. However, the fundamental behaviors of phase formation obtained in this work are consistent with the results by *in-situ* diffraction experiment on alloying processes of zinc coated steel [2].

4. Concluding Remarks

(1) GDOS depth profiles demonstrate systematic changes of the zinc concentration in the zinc coatings by annealing in the temperature range between 673 K and 873 K.

(2) XRD measurements show that the phase formation of zinc-iron alloy layers, which is a series of formation of ζ, δ_1, Γ_1 and Γ phases, occurs on the surface of steel sheets with zinc coatings by annealing.

Reference

[1] W.Warnecke, R.Bode, R.Kothe and L.Meyer, in Zinc-Based Stell Coating System: Metallugy and Performance, edited by G.Krauss and D.K.Matlock, TMD, Pennsylvania, (1990), p.3.

[2] S.Suzuki and K.Suzuki, "Glow Discharge Optical Emission Spectrometry", edited by R.Palying, D.Jones and A.Bengtson, John Wiley, (1997), p.573.

[3] M.Kimura, M.Imafuku, M.Kurosawa and S.Fuji, J.Syncrotron Rad., 5(1998), in press.