Alloying Behavior of Tin-Zinc from Stacked Single Layers

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Tin-Zinc alloy film is a promising substitute for cadmium plating. Conventionally, it is produced from alloy plating using simultaneous electrodeposition (co-electrodeposition) from a certain aqueous solution. The properties depend on the chemical solutions used for plating, however, and this may restrict the flexibility of the process in various ways. We have investigated the possibility of alloy film production by heating stacked single layers of tin and zinc that are deposited distinctively and consecutively on substrates. In this study, we analyzed the alloying behavior by X-ray Diffraction Analysis (XDR), SEM-EDX and Differential Thermal Analysis (DTA), comparing the results with the phase diagram of tin and zinc.

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INTRODUCTION

Cadmium plating has been used as anti-corrosive coating for aircrafts and different mechanical components(1). However, more environment-friendly substitutes for the cadmium plating are required now due to recent environment regulation laws(2). Many kinds of plating such as zinc plating, nickel plating etc. have been proposed and used as substitutes(3). Not only these single phase platings, but also alloy plating such as zinc-nickel, zinc-tin etc. are alternatives. The conventional alloy plating utilizes the alloy co-deposition from a certain aqueous solution. We investigated the alloying from two stacked single layers of the constituents for the alloy films(4)-(8). In our process, the alloying is carried out through heat treatment. Even though the alloying phenomena of thinly stacked layers were studied from the fundamental scientific view point, there was little research regarding its application to the formation of alloy films. Since tin-zinc alloy film is promising as substitute for cadmium plating(2), we investigated the alloying process from stacked single layers of tin and zinc in this experiment(9), (10).

In our experiment, we aimed to identify what occurred to the two stacked single layers of tin and zinc during heat treatment. The alloying process was investigated by X-ray Diffraction Analysis (XRD), Diffraction Thermal Analysis (DTA) and SEM-EDX, and we discussed the mechanism of the process for the tin-zinc system.

EXPERIMENTAL

Pure iron plates (purity:99%) were used as substrate. Tiny samples measuring 10mm × 10mm (0.394 inch × 0.394 inch) were made by cutting the original large plates. Lead wire was attached to one side of each specimen. All sides except the side opposite the wire were coated by epoxy resin. This exposed side was used as an electrode surface. These specimens were polished, degreased and immersed into two kinds of plating baths. The electrodeposition processes were carried as follows. In the first case, specimens were immersed into a tetrafluoroboric acid (TFB) bath. It was composed of 42% tetrafluoroboric acid (18mL), 44.6% tin borofluoride (2mL), and polyethylene glycol of molecular weight 2000 (15mg: 3.31×10^{-5} lb) and the total volume of the bath was 300mL. Tin was electrodeposited first on to the iron surfaces with a current density of 1A/dm^2 (9.29A/ft^2), using a constant current power source. Then the specimens were immersed into the Zinc plating bath at 313°K (40°C, 104°F) {$ZnSO_4$ 80g (0.176lb), boric acid 10g 2.20×10^{-2} lb), sodium chloride 5g (1.10×10^{-2} lb), Aluminum sulfate 80g (0.176 lb), total volume 300mL) and electrolyzed with a current density of 5A/dm^2 (46.5 A/ft^2) in 300s. The electrodeposits were denoted as tin/zinc film in this paper. In the second case, zinc was electrodeposited first and then tin, using the same current densities and solutions. These specimens were expressed as zinc/tin film in this paper. These specimens of two stacked single films were heated in an electric furnace at different temperatures up to 723°K (450°C, 842°F) in 10.8ks. After the heat treatments, the specimens were taken out of the furnace, cooled in the ambient air and tested. The structure analysis of surface layers was investigated by XRD (RINT 2100 made by Rigaku Co.). Copper K_α was used as the X-ray probe. The X-ray voltage was 40kV and the current 20mA. The topographical investigation for the surfaces of specimens were carried out by SEM(S-4300 by Hitachi Co.). The acceleration voltage was 20kV and the current 1×10^{-8}A. As DTA measurement, TG-8100 by Rigaku Co. was used. The surface layer after the heat treatment was detached from the substrate mechanically, powdered, and analyzed by DTA. The powder specimens were heated at a rate of 20°K/min from the room temperature to 773°K (500°C, 932°F) and the results were analyzed and discussed.

RESULTS AND DISCUSSION

Fig.1 and Fig.2 show the XRD spectrum for zinc/tin specimens and tin/zinc specimens without any heating, respectively. In Fig.1, all peaks were composed of those for tin and zinc. Even though the tin layer was the top of the stacked layers, the intensity for tin peaks was not so high. It may be attributable to the tin layer being relatively thinner than the zinc layer. Also, in Fig.2 all peaks belong to those of tin and zinc. However, the intensity of tin peaks was much lower than those in Fig.1, since the tin layer was the under the zinc layer. In Fig.2, the intensity of zinc peaks was high.

The two kinds of specimens were heated to 623°K

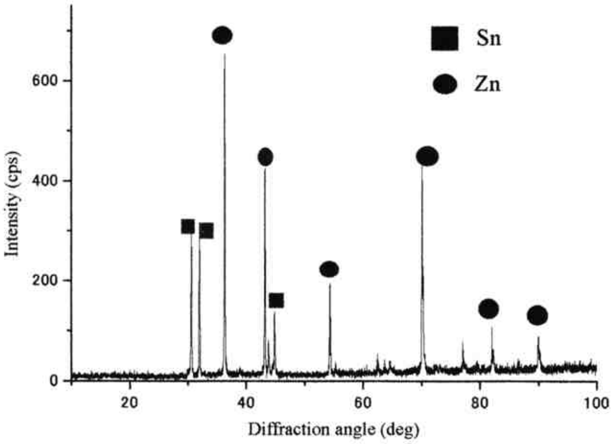

Fig.1 XRD spectrum for zinc/tin specimen without heat treatment.

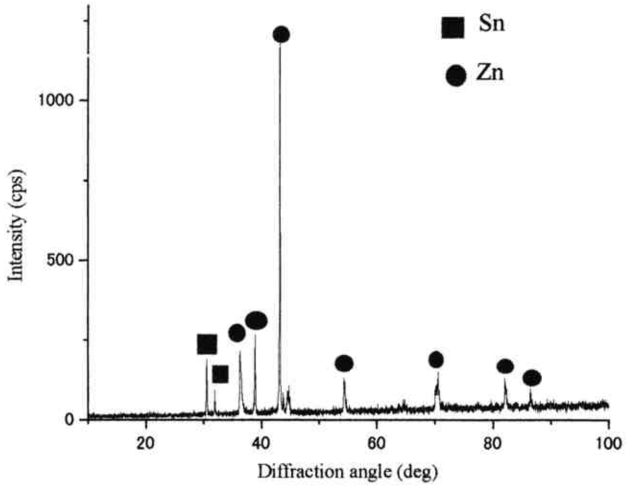

Fig.2 XRD spectrum for tin/zinc specimen without heat treatment.

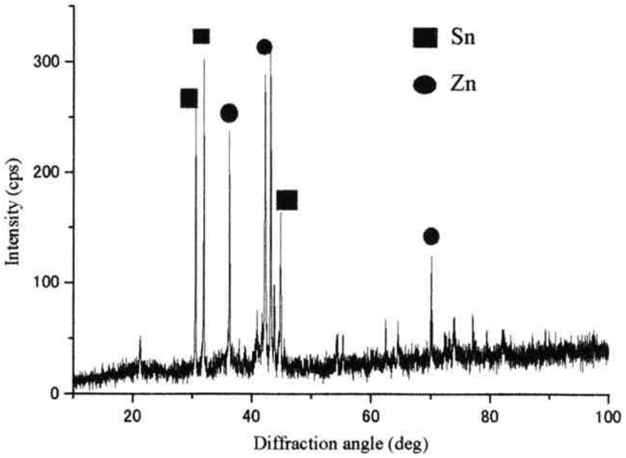

Fig.3 XRD spectrum for zinc/tin specimen heated to 623K.

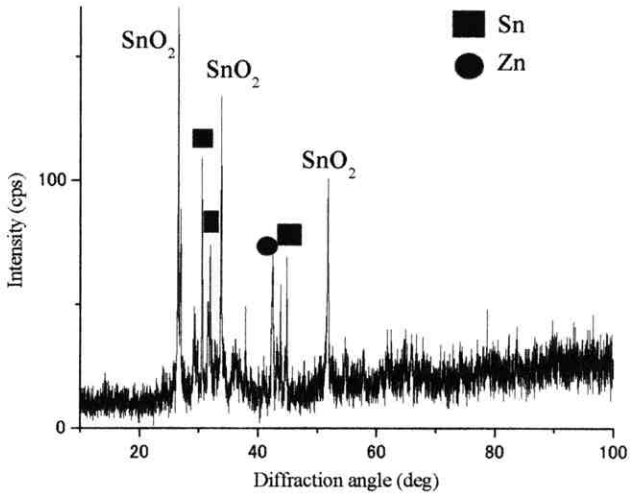

Fig.4 XRD spectrum for zinc/tin specimen heated to 723K.

(350°C, 662°F) and 723°K (450°C, 842°F) in 10.8ks. Fig.3 shows the XRD result for the zinc/tin specimen heated to 623°K (350°C, 662°F). The intensities of all peaks decreased in general. The relative ratio of peak intensities for zinc and tin decreased and the intensities for both peaks almost equalized. These results correspond to the alloying of both tin and zinc films on the steel surface. Fig. 4 shows the XRD result for the zinc/tin specimen heated to 723°K (450°C, 842°F). In this case, the peak intensities decreased to lower than those in Fig.3 and generally became broad. The results suggest progress of the alloying process. In this figure, peaks corresponding to tin oxide, SnO_2 were found which indicates oxidation occurred within the ambient atmosphere in the electric furnace during the heating. Fig. 5 shows the XRD result for tin/zinc specimen heated to 623°K (350°C, 662°F). Compared with the XRD in Fig.2, the intensity of zinc peaks was lower and the relative ratio of the intensities, (I_{zinc}/I_{tin}), was also slightly lower. It suggests that both stacked layers reacted with each other and were alloyed to some extent. Fig.6 shows the result for the tin/zinc specimen heated

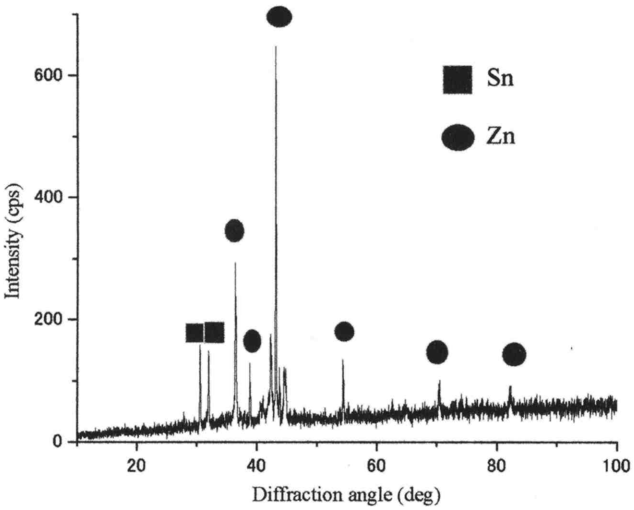

Fig.5 XRD spectrum for tin/zinc specimen heated to 623K.

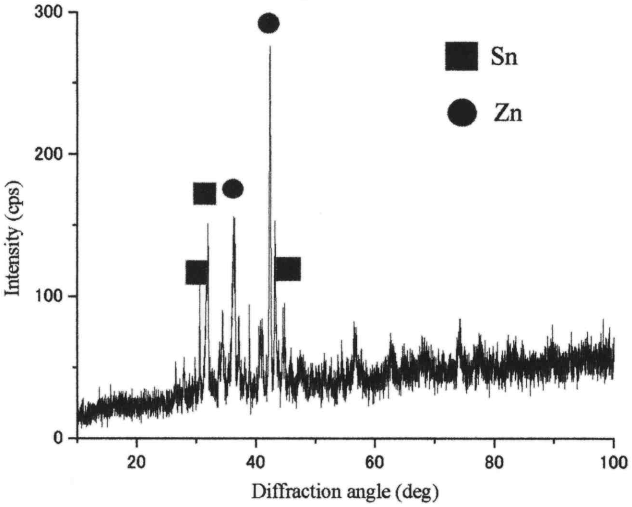

Fig.6 XRD spectrum for tin/zinc specimen heated to 723K.

to 723°K (450°C, 842°F). The tendency recognized in Fig.5 became more remarkable, suggesting that the alloying process progressed further with the increase of temperatures. In this case, oxide formation was not found. Since zinc was the top layer of the specimens, it didn't oxidize at this temperature.

We summed up the progress of the alloying process by the change of XRD spectrum with the increase of heating temperature. For the tin-zinc system, we investigated the alloying process by examining the phase diagram. Fig.7 shows it prepared by ASM (11)(note: the temperature in this figure is shown in Centigrade). The phase diagram is of the simple eutectic type. The equilibrium phases are the liquid (L), the tin terminal solid solution with a maximum solubility of 0.6at % Zn and the zinc terminal solid solution with a maximum solubility of 0.039 at% Sn. The eutectic temperature is 471.5°K (198.5°C, 389.3°F). Therefore, tin and zinc layers are supposed to decrease with the process of heat treating

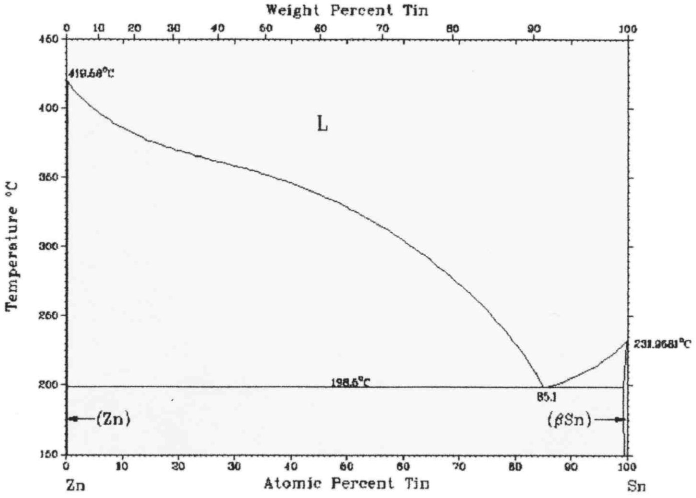

Fig.7 Phase diagram of zinc-tin system.

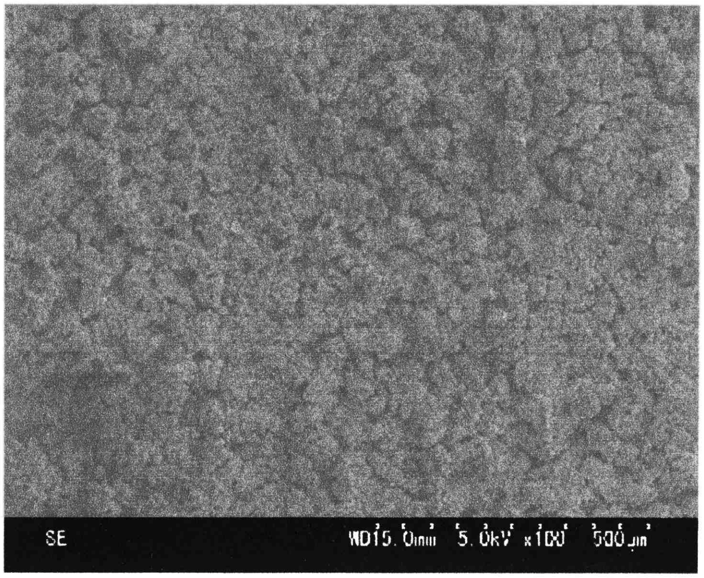

Fig.8 Surface topology for tin/zinc heated to 723°K

to produce the eutectic phase, as well as solid solutions. As a result, mixed phases are produced during the heat treatment. The production of mixed phases corresponds to the change of XRD spectra shown in Fig.3 - Fig.6.

The difference of topographic conditions between zinc/tin and tin/zinc specimens were investigated by SEM. Fig.8 shows the surface of tin/zinc was relatively rough as observed by SEM after heat treatment at 723°K (450°C, 842°F). At all temperatures, the surface of tin/zinc specimens after the heat treatment was relatively rough in general, when the top layer was zinc. On the other hand, Fig.9 shows the surface of zinc/tin specimen observed by SEM after the heat treatment at 723°K (450°C, 842°F). Compared with the surface shown in Fig.8, this figure was smoother. The top layer of tin melted at the treatment temperature, since it was over the melting point. When the process begins, tin melts and flows on the surface to react with the zinc underlayer. As a result, the surface produced after the heat treatment becomes relatively smooth. It is very similar to so called "reflow process" for tin plating.

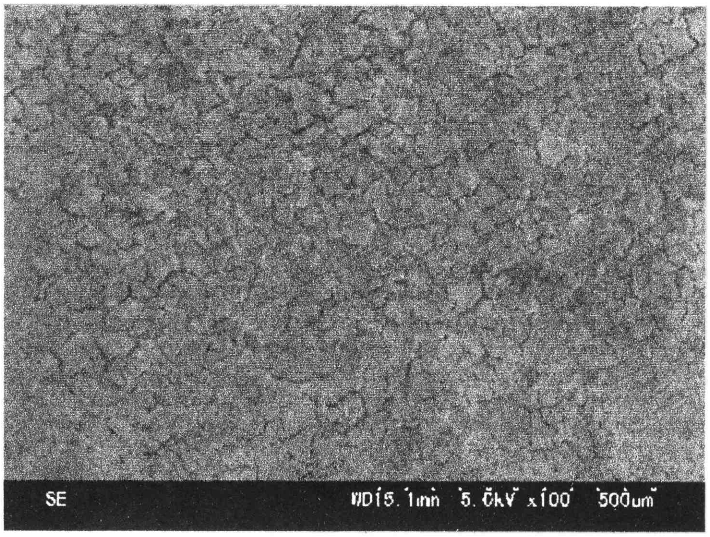

Fig.9 Surface topology for zinc/tin heated to 723°K

The mechanism of the alloy film formation between tin and zinc is basically a liquid (tin phase) - solid (zinc phase) reaction at 623°K (350°C, 662°F). At 723°K, liquid (tin phase) - liquid (zinc phase) reaction may occur. However, the tin phase melts first in any case when the specimens are heated, since the melting point of tin is lower than that of zinc. The phase changes were investigated by DTA. Fig. 10 shows the DTA curve for the zinc/tin specimen. When the specimen was heated, heat absorption was observed at around 373°K (100°C, 212°F). The endothermic peak corresponds to the evaporation of water. There was another endothermic peak at around 500°K (227°C, 440.6°F). It corresponds to the melting of tin, since the temperature overlapped with the melting point of tin. It suggests that the tin phase became a liquid phase first, as expected. Another peak indicating an exothermic reaction was observed at 570°K (297○C, 566.6°F). Since the peak was exothermic, it can't be explained by the melting of

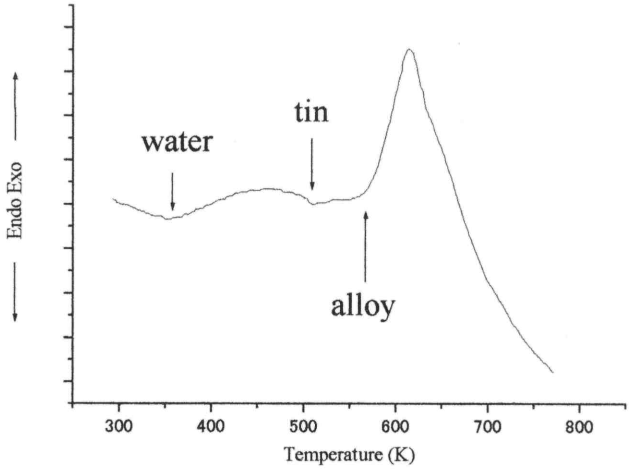

Fig.10 DTA curve for zinc/tin specimen.

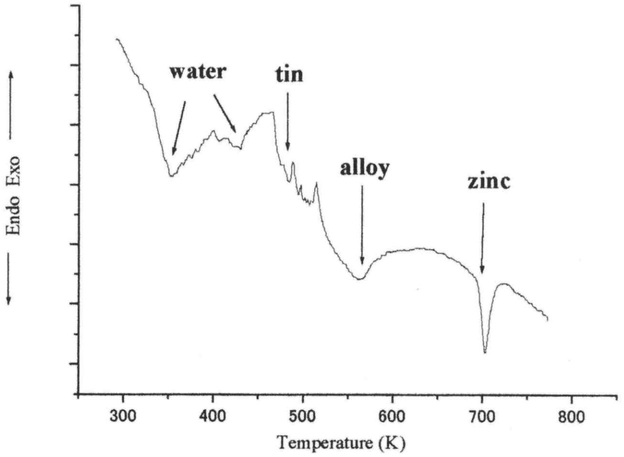

Fig.11 DTA curve for tin/zinc specimen.

zinc after the liquid (tin) - solid (zinc) solution. Currently, the mechanism for the exothermic reaction is not fixed, however, we presume that it corresponds to the starting point of alloying between the liquid tin phase and the solid zinc phase. At a certain composition of liquid tin and solid zinc, the reaction would start and alloying begins. Fig.11 shows the DTA curve for tin/zinc specimen. The endothermic peaks up to 450°K (177°C, 350.6°F) observed in Fig.11 can be also attributed to the evaporation of water, even though the temperatures were higher than the melting point of water, for there are many types of water components. Not only water absorbed or attached to the materials, but also crystal water etc. can contribute to the endothermic peaks found between 373°K (100°C, 212°F) to 473°K (200°C, 392°F). An endothermic peak was also found at the melting point of tin shown in Fig.11. In this case, the tin phase began to melt first. An exothermic peak was also found at 570°K (297°C, 566.6°F). The exothermic reaction can be explained by the same reason described above. The exothermic peak observed around 700°K (427°C, 800.6°F) corresponds to the melting point of zinc. For the tin/zinc specimen, the amount of zinc top layer was large. Therefore, non -reacted zinc remained to some extent after the reaction between the liquid tin phase and the solid zinc one. It should be noted that the specimens for DTA analysis were not the plated phase. For the experiments, the surface films were chipped off from the specimens having the stacked two single films of tin and zinc. If the plating specimens themselves were used, the DTA curves might include the reactions between the underlayer and the substrate iron and the behavior would be more complicated. At any rate, the DTA curves for the surface mixed layers in powder suggest the mechanism of the alloy formation between tin and zinc. Therefore, tin phase becomes liquid first, for both zinc/tin and tin/zinc samples. When the composition reaches a certain value, the liquid tin phase begins to react with the solid zinc phase. The melting of zinc occurs and alloying progresses with time. According to Fig.7, the composition where the liquid-solid reaction begins is around 60at% Sn - 40at%Zn. The conceptual mechanism for the alloying described above is shown in Fig.12. Whatever the exothermic reacion may be, it is true that the drastic reaction between tin and zinc layers occurs over 570°K (297°C, 566.6°F).

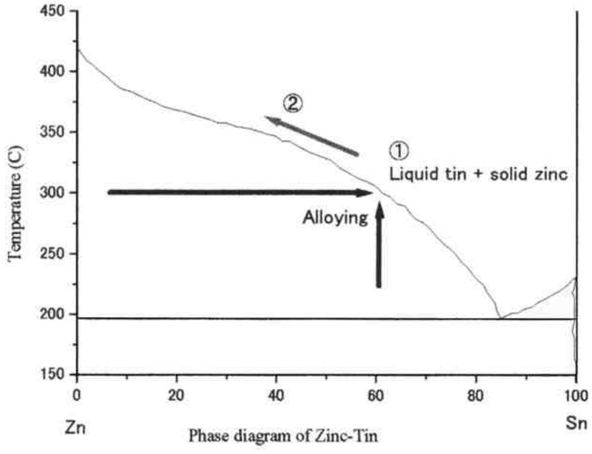

Fig.12 Mechanism of alloying for tin and zinc films.

CONCLUSIONS

Tin and zinc layers were alternately formed on pure iron substrates and were heated to produce alloy as a substitute for cadmium plating. The following results were obtained:

(1)Alloying occurred in both cases.
(2)When the top layer was tin, the surface was smoother.
(3)Thermal analysis indicated that the reaction between the liquid tin phase and the solid zinc phase occurred at 570°K.
(4)The effective alloying from the two stacked single layers of tin and zinc should be heated to temperatures over 570°K (297°C, 566.6°F).

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