Alloying of Tin Plating Film with Silver by Combination of Multistage Plating and Heat Treatment for Antibacterial Property

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Abstract:
The alloy film production of Sn/Ag on steel through heat treatment of stacked single layers was investigated in this study. The specimens used in this investigation were classified into two types. One was tin/silver stacked layered specimen on carbon steels and the other was the same tin/silver stacked layered specimens. However, the copper strike layer between silver and fin layer on steel. For the latter, diffusions of the constituents for the alloy films was inhibited to some extent due to the existence of copper strike layer, which lead to better qualities of product films. As for the alloy films between silver and tin, we confirmed by X-ray Diffraction Analysis that almost the same compounds were formed at each heat treatment temperature. The number of compound layers increased with heat treatment temperatures, while the single element layers disappeared with increasing temperatures. The antibacterial property was investigated and discussed as well as surface color tones, hardness, and corrosion resistance.

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INTRODUCTION

Tin plating has been used in food processing industries very widely. Recently, the safety of food products impress Japanese people through several practical cases such as serious food poisoning, the interfusion of harmful extraneous substances into food products etc. Generally speaking, the cost for the safety does not burden on consumers, but manufacturers. Therefore, the increase of the safety for food products leads not only to the improvement of good hygiene, but also to the cost reduction as well as the social credibility. Generally speaking, tin plating does not show any significant antibacterial property[(1)]. Therefore, some of the authors investigated the antibacterial possibility for the alloying of tin and copper on steel surfaces, applying our proprietary process to the plating system[(1),(2)]. In the process, the stacked single layers of tin and copper were produced firstly. Then the stacked layers were heated to higher temperatures beyond the melting point of tin to form the alloy film through thermal diffusion. The alloy film of tin and copper showed high antibacterial property, even though the original tin plating didn't show it at all.

In this study, the authors tried to add the same or higher antibacterial effect to tin plating by alloying of silver, using the same heating stacked single layers process (HSSL[(3)-(5)]). And the antibacterial property as well as other surface properties were measured and discussed.

EXPERIMENTAL

Commercial tin plated steels were used for this experiment. The substrate was a carbon steel (Japan Industrial Standard SS400) and the thickness of tin plating was about 5 micrometers (200 micro inches). Then some specimens were plated with silver from a cyanide bath directly. On the other hand, a very thin copper was plated on the tin layer, being followed by the same silver plating. The first specimens group had two layers composed by silver and tin. However, the two layer constitution was broken in some surface sites. As for the second specimen group, each had a solid multilayer composed of silver, copper and tin plating. All of these specimens were cut by a Shearing Machine (SHS3X125, Komatsu Co.) into small sheets (10mm x 10mm, 0.4 inch x 0.4 inch) and served for various tests.

An electric furnace (Muffle type furnace FP31, Yamato. Co) was used for the heat treatment of specimens. 200, 250, 300 and 350 degrees Centigrade were chosen as heat treatment temperatures and specimens were heated to them in the furnace whose atmosphere was not regulated. The heat treatment time was 2 hours and after the heat treatments, all specimens were cooled in the ambient air.

The color tone of the specimen's surfaces was measured by a colorimeter (CR-13, Konica-Minolta Co.). The measurement standard used for the observation was L-a-b system and the results were shown three-dimensionally by L-a-b system.

The surface structures for all specimens were analyzed by X-ray Diffraction Analysis (XRD). The apparatus used for the analysis was RINT 2100 (Rigaku Co.). The electrode was copper. The X-ray voltage was 40kV and the current 20mA. The peaks were measured in the range from 20 degrees and 100 degrees. The scan rate for the diffraction was 2 degrees/min.

Antibacterial properties for the surface films were measured by Film Adhesion Test (Japanese Industrial Standard Z2801). The specimens were put in petri dish, while the bacterial solution was prepared as follows. The bacteria were incubated in 10ml aqueous culture in 24 hours at 37 degrees Centigrade and then they were diluted two-thousand fold by sterile water and established as bacterial solution. 16 micro litters per square centimeter of the diluted bacterial solution were put on the specimen and then the polymer film was attached on the solution. It was kept in an incubator in 24 hours at 37 degrees Centigrade. After the incubation, 10ml sterile water with 200 micro litters Tween 80 was introduced into the petri dish and the bacteria attached to the polymer film was washed into the aqueous solution. It was diluted one hundred fold more by sterile water and the diluted solution was inoculated on the usual agar medium and incubated in 24

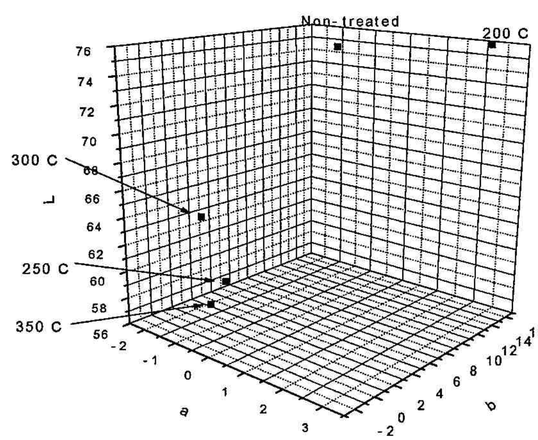

Fig.1 L-a-b values for tin-silver specimens.

hours at 37 degrees Centigrade. Then the final number of the colony formation unit was measured to evaluate the antibacterial properties.

RESULTS AND DISCUSSION

Color Tones

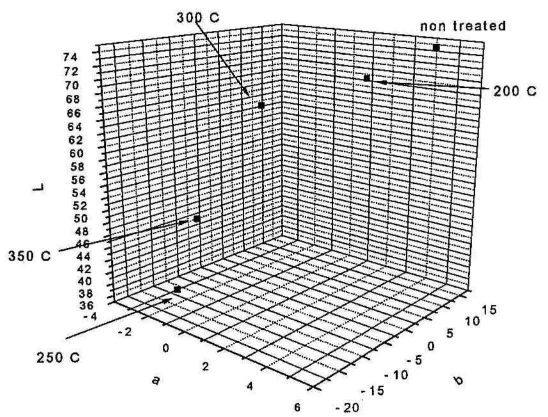

Fig.2 L-a-b values for tin-copper-silver layers specimens

Firstly, the color tones for all of the heat treated specimens were measured by the colorimeter. Fig.1 and 2 were those results for silver-tin plating specimens and tin-copper-silver plating specimens, respectively. For all of heat treated specimens, the brightness corresponding to L values decreased after the heat treatment. It indicates the thermal diffusion made the surfaces more irregular on the microscopic level. For all heat treated specimens, the surface color changed in the negative direction of a and b. It means that the surface color changed to green or blue. And particularly for tin-copper-silver specimens, the tendency was very remarkable and the surface was quite blue for the specimens heat treated at 300 and 350 degrees Centigrade. Therefore, the surface color tone changed to dark blue ones through the heat treatment process.

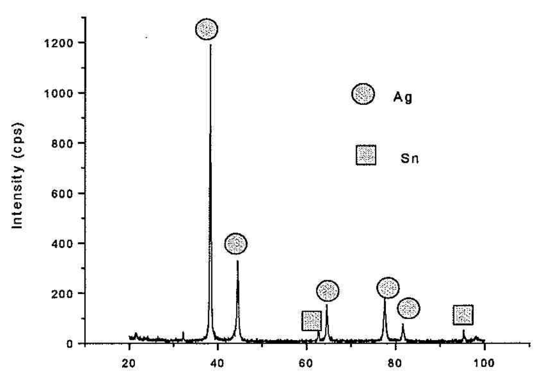

Fig3. XRD result for non-heat treated Sn-Ag film specimen.

X-ray Diffraction (XRD) analysis

Fig.3 shows the result of XRD analysis for the non heat treated specimen which had the multi-layer of tin-silver. All X-ray peaks were composed of tin and silver. And the peak intensity of tin was much lower, being compared with that of silver. All of these tendencies show that the surface layer was composed of tin and silver and the silver existed in the surface layer much closer to the substrate.

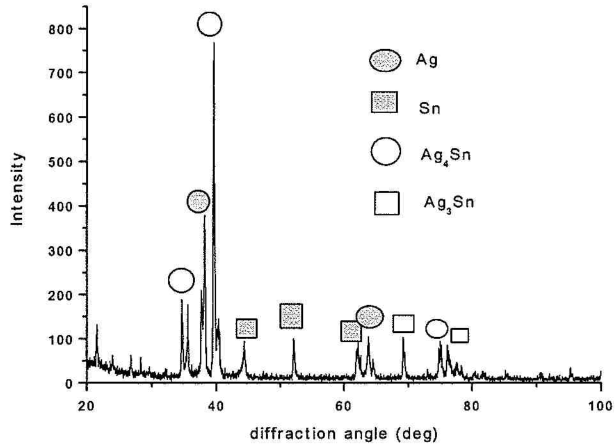

Fig.4 XRD result for Sn-Ag film specimen heat treated at 200 C.

Fig. 4, 5 6 and 7 show the results of XRD analyses for heat treated specimens of tin-silver surface layer specimens. For the heat treated specimen at 200 degrees Centigrade (Fig.4), the peaks of some intermetallic compounds, Ag_4Sn and Ag_3Sn, were observed, even though tin and silver peaks were still observed. It indicates that the intermetallic compound films were formed through the heat treatment and also that the unreacted tin and silver remained to some extent. Since the diffusion occurred under the melting point of tin, all reactions proceeded through solid phase diffusion. Fig.5 shows the result for the specimen heat treated at 250 degrees Centigrade. The intensity of the intermetallic compounds for tin and silver increased relatively. It suggests that the formation reaction of those intermetallic compounds proceeded at this temperature rather than at the lower temperature. Fig.6 and 7 show the result for the specimen heat treated at 300 and 350 degrees Centigrade, respectively.

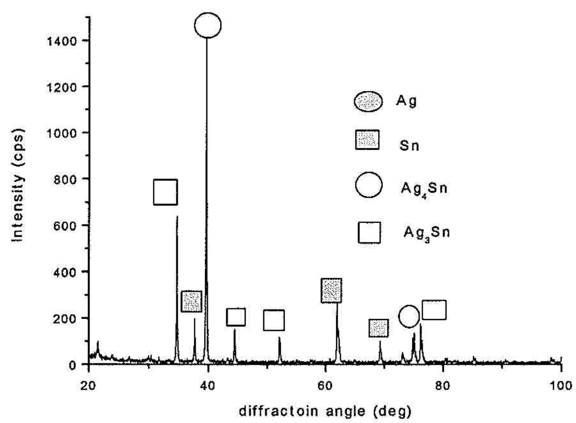

Fig.5 XRD result for Sn-Ag film specimen heat treated at 200C.

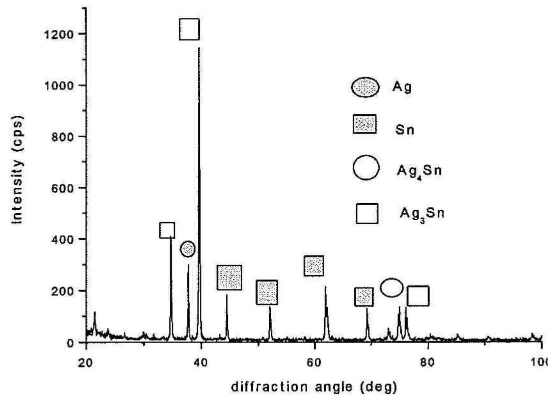

Fig.6 XRD result for Sn-Ag film specimen heat treated at 300 C.

Even though the peaks for tin and silver still remained, the relative intensities for the intermetallic compounds of tin and silver increased more. Since these temperatures were above the melting point of tin, the diffusion occurred between liquid tin and solid silver. The diffusion of the solid element into the liquid phase is generally easier, since the Brownian motion generally helps those atoms to move and diffuse in liquid phases generally.

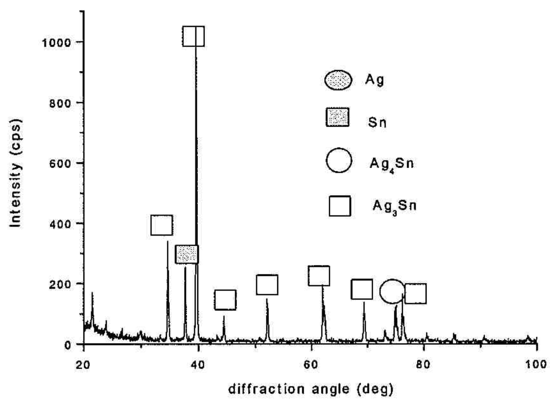

Fig.7 XRD result for Sn-Ag film specimen heat treated at 350 C.

Fig. 8 shows the result of XRD analysis for the tin-copper-silver surface layers specimens before heat treatments. Like the result shown in Fig.3, the peaks for tin and silver could be observed. However, copper was also observed additionally, even though the peak was very small. These specimens had three single layers of tin, copper and silver. The structure was reflected on the XRD result.

Fig.9, 10, 11 and 12 show the results of XRD analyses for the tin-copper-silver surface layers specimens heat treated at various temperatures. Fig.9 shows the result for the specimen heat treated at 200 degrees Centigrade. Since the heat treatment temperature was lower than the melting point of tin, the reaction occurred through diffusion between the solid phases. However, the formation reaction for the intermetallic compounds occurred to some extent and the intermetallic compounds between tin and silver were observed also in this case (Ag_4Sn and Ag_3Sn). However, the intermetallic compound of tin and copper was also observed (Cu_3Sn). Fig.10 shows the result for the same specimen heat treated at 250 degrees Centigrade. Since the intensities for the intermetallic compounds of tin and silver increased, we can presume that the amount of intermetallic compounds increased through the proceeding of diffusion. At the same time, the peak ratio of tin and silver decreased and copper peaks could not be observed. It suggests that the single layers were going to disappear through diffusion reaction at this temperature. And it also indicates that the main compounds of tin and silver changed from Ag_4Sn to Ag_3Sn and also that those of copper and tin changed from Cu_3Sn to Cu_6Sn_6. For both cases, the compounds were changed to tin rich ones due to the proceeding of diffusion reaction at higher temperatures. Fig.11 and 12 show the results for the specimens heat treated at 300, and 350 degrees Centigrade, respectively. In both cases, the tendency for XRD peaks was almost the same. The compounds of tin and silver were Ag_3Sn, while any compound of tin and copper were not observed. At higher temperatures, tin was consumed mostly to form the intermetallic compound of tin and silver. Copper didn't form any significant intermetallic compound with tin in this case. However, the single layer of tin still remained as unreacted parts. As described above, the copper layer was inserted between tin and silver, so that the silver layer was plated well on the tin layer. However, tin penetrated through the copper layer

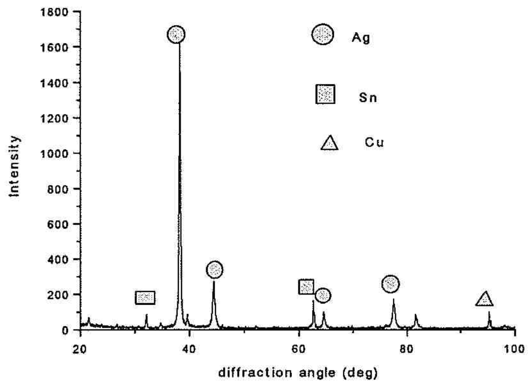

Fig.8 XRD result for non-heat treated Sn-Cu-Ag specimen.

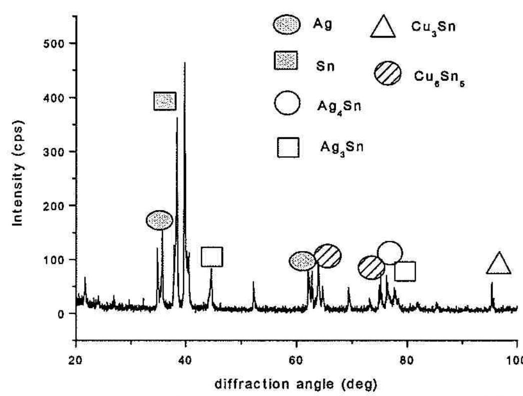

Fig.9 XRD result for Sn-Cu-Ag specimen heat treated at 200C.

to react with the upper silver layer and the result was almost the same with the stacked layers without the intermediate copper layer, when the heat was applied to the stacked single layers.

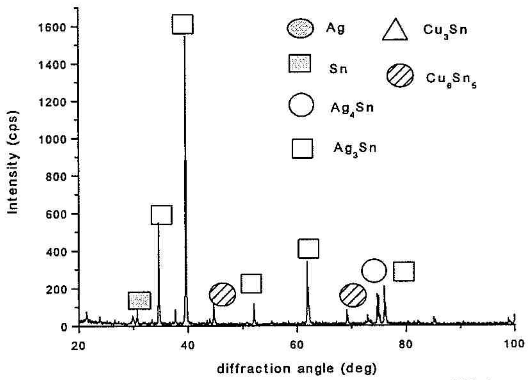

Fig.10 XRD result for Sn-Cu-Ag specimen heat treated at 250 C.

Antibacterial Property

Fig.13 shows the results of antibacterial property measured for tin-silver surface layers specimens. Usually, one can judge the specimen as antibacterial, when the number of CFU (Corrosion Formation Unit) was lower than that of controls in the order of 10^2. From the viewpoint, all specimens except the one heat treated at 200 degrees Centigrade showed the antibacterial property.

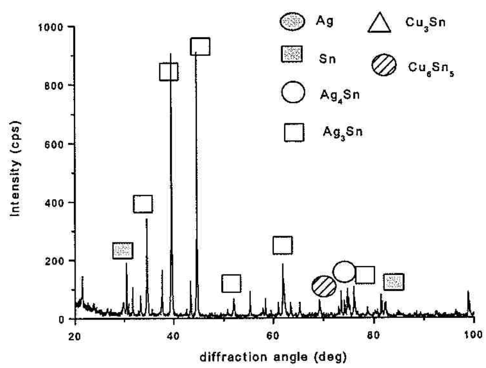

Fig.11 XRD result for Sn-Cu-Ag specimen heat treated at 300 C.

Fig.14 shows the results of antibacterial property measured for tin-copper-silver surface layers specimens. These results also indicate that all specimens except that heat treated at 200 degrees Centigrade showed antibacterial property. The specimen heated at 200 degrees Centigrade was also an exception. However, all other specimens showed antibacterial properties, even though the extent of CFU decreases in Fig.14was not so remarkable than that in Fig.13.

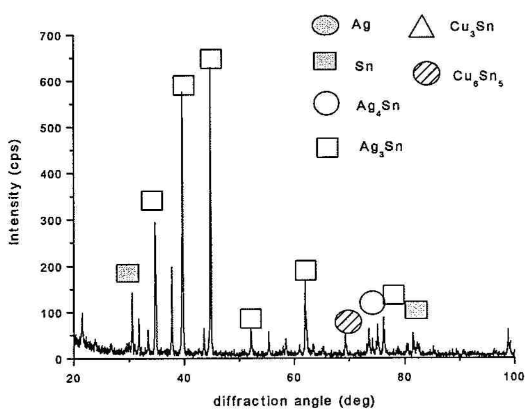

Fig.12 XRD result for Sn-Cu-Ag specimen heat treated at 350 C.

For the specimen heated at

200 degrees Centigrade, the reflow of tin occurred and it could prevent the dissolution of substrate iron. For silver-tin surface layer specimens, many amount of substrate iron was dissolved into the culture fluid, since the stacked single layers were formed imperfectly. They could have many defects in the surface layers which lead to the iron dissolution. Therefore, the antibacterial properties shown in Fig.13 may be given not by the silver element, but by the iron to much extent. And at the same time, the results show that the surface film for silver-tin system would have a technical problem for practical applications. On the other hand, tin-copper-silver films have sound stacked single layers and the condition could be kept after the heat treatment, even though chemical reaction occurred through diffusion processes.

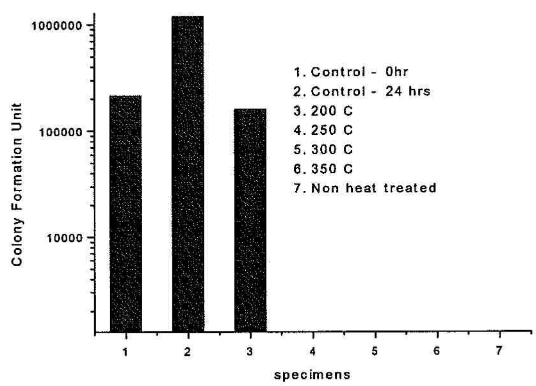

Fig.13 Antibacterial properties for Sn-Ag specimens.

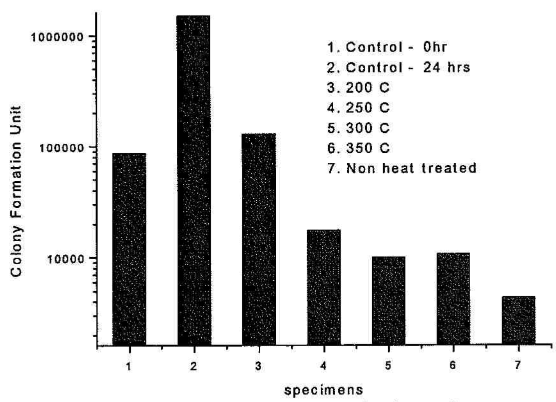

Fig.14 Antibacterial properties for Sn-Cu-Ag specimens.

CONCLUSIONS

Silver was plated on commercial tin plating steel to form stacked single layers of tin and silver on the steels. Then they were heated to 200-350 degrees Centigrade. The structures, surface color tones and antibacterial properties were measured. As a result, all of specimens which had tin and silver on the surfaces formed intermetallic compounds of tin and silver by heat treatments and showed antibacterial properties to some extent mostly. However, copper interlayer was required to form sound stacked single layers which would lead to the desirable formation of alloy films.

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