Alloy Film Production of Tin-Copper Through Heat Treatment of Stacked Layers

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Tin-copper alloy films have the potential as a substitute for nickel plating, which may cause skin irritation. However, in most cases, deposition of this alloy requires the use of cyanide chemistry, which leads to other environmental problems. We have developed a unique process to produce the alloy, by producing stacked, alternating layers of tin and copper from non-cyanide solutions, and subjecting the multilayers to a diffusion heat treatment. In this study, we studied the relation between heat treatment conditions, the film thicknesses and the metallurgical phases produced. We also discuss the possibility of applying this technology.

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INTRODUCTION

Chromium, Cadmium etc which are harmful to natural environment, is going to be restricted for their application uses. Therefore, those environment-unfriendly metal elements may be replaced significantly by more environment-friendly substitutes according to regulations and laws in the future. One of the promising substitutes is alloy plating. However, the process requires a certain special combination of chemicals which may be also harmful to environment. In addition, it is often difficult for the condition of production to be realized. We have proposed another proprietary process to produce substitute alloy films so far.[(1)-(7)] It has been called Heating Stacked Single Layers Process (HSSL Process). In the process, stacked single layers (two or more) are alloyed through heat treatment. This process makes it possible for us to choose any process for the production of single stacked layers. As a result, we can select environment-friendly chemicals for the whole process.

In this study, we focused on the productions of alloy film between tin and copper. Tin-copper alloy films have the potential as a substitute for nickel plating, which may cause skin irritation. Conventionally, the alloy film is often produced in cyanide bath. However, the bath has a safety and environmental problem due to its high toxicity. On the other hand, the application of our HSSL process to the alloy film formation can avoid the environmental problem and lead us to the successful alloy formation technically. Therefore, we investigated the phenomenon how alloying behavior would take place through heating stacked single layers of tin and copper on steel substrates.

EXPERIMENTAL

Specimens

Carbon steel (JIS SS 400) was used as substrate. Copper was plated on them at first. The bath for the copper plating was copper sulfate solution (copper sulfate; 150g/L, sulfuric acid; 40-60g/L) at 25 degrees Celsius (77 degrees Fahrenheit). We got 10 micrometers (400 microinches) copper layer by the electroplating under the condition of 1A/dm^2 and three minutes. Then we coated the specimen by tin plating in the bath composed of tin sulfate (30g/L) and sulfuric acid (180g/L) where the current density of 1A/dm^2 was applied at the bath temperature of 20 degrees Celsius (68 degrees Fahrenheit). The thickness of tin layer which were produced by changing the plating time was finally 1 micrometer (40 microinches, plating time: 2 minutes), 5 micrometer (200 microinches, plating time: 10 minutes) and 10 micrometer (400 microinches, plating time: 20 minutes). The specimens were cut by a shearing machine to produce small plates whose dimension was 1.5cm x 1.5cm (0.6 inches x 0.6 inches)

Heat Treatments

Each specimen having two plating layers of tin and copper was heat treated in a muffle furnace (Yamato, FR31). The atmosphere was not regulated during the heat treatment. The heating temperatures were 200, 250, 300 and 350 degrees Celsius (392, 482, 572 and 662, respectively). And the heat treatment times were 1, 3 and 5 hours at each temperature.

Surface Analysis

The structures of surface layers for stacked layers of tin and copper on steels before and after the heat treatment were analyzed by X-ray Diffraction Analysis (XRD: RINT 2100). Copper electrode was used as X-ray target. The measurement condition for XRD was as follows: X-ray voltage – 40kV, X-ray current – 20mA. The measurement diffraction angle 2θ: 10 degree – 100 degree. For element analysis of surface layers, SEM (Hitachi, S-4300) – EDX (Horiba EMAX-7000) was used. The experimental conditions were as follows: Acceleration voltage - 20kV, the current – 1 x 10^{-8}A. The experimental process was shown in Fig.1 as a flow chart.

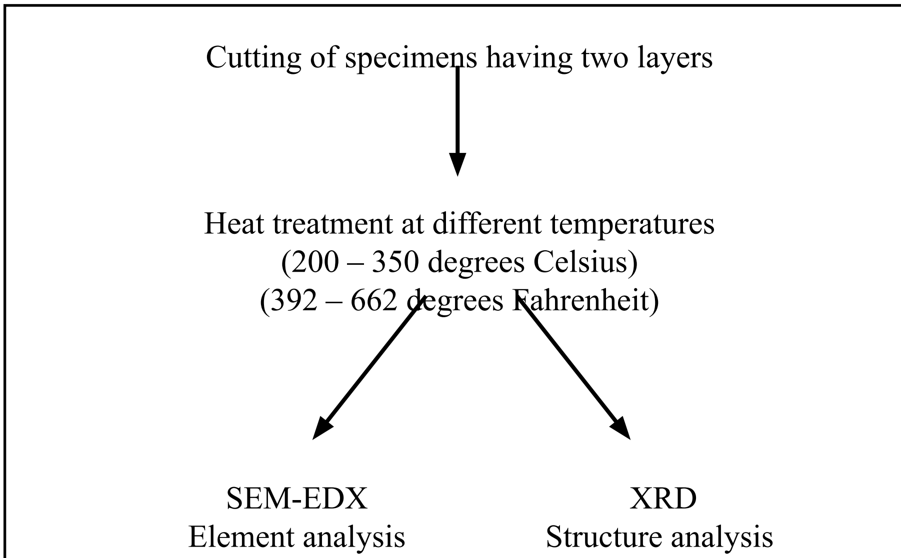
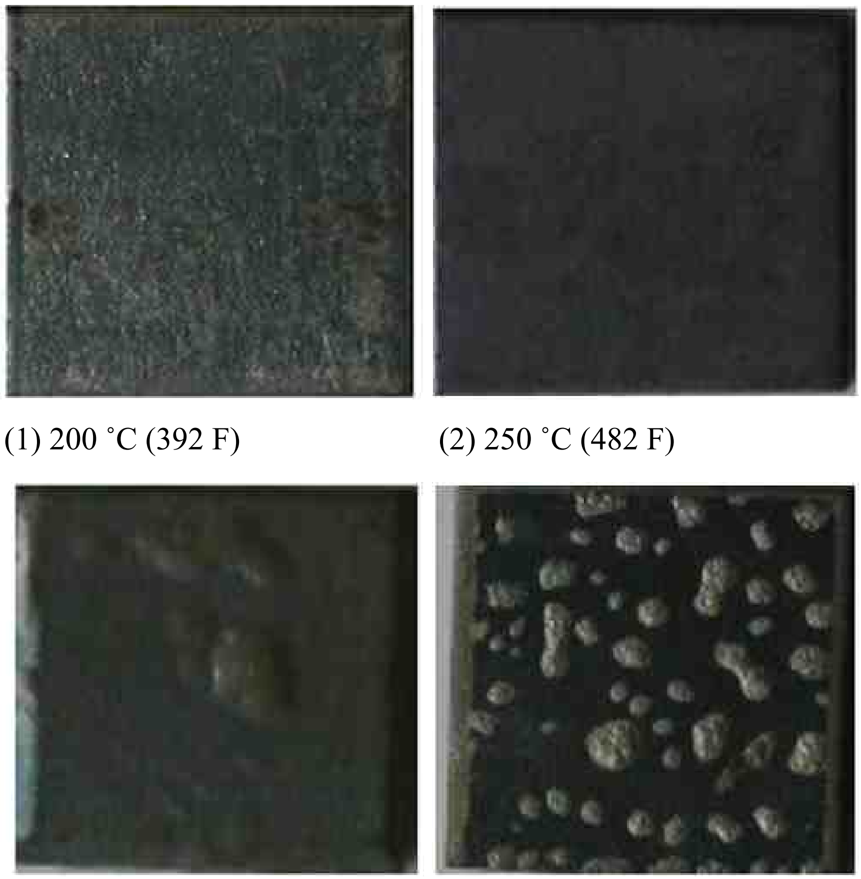


Fig.1 Flowchart for the experimental procedure.

RESULTS AND DISCUSSION

Change of Surface Conditions with Heat Treatments

Fig.2 shows the surface condition of the specimen before heat treatment, taken by a digitizing camera. And Fig.3 shows that for the specimens having 10 micrometer (400 microinches) tin layer which was heated in an hour at various temperatures from 200 to 350 degrees Celsius (from 392 to 662 degrees Fahrenheit). For the specimen heated at 200 degrees Celsius (392 degrees Fahrenheit, Fig.3-(1)), the surface condition was almost the same with that before heat treatment. For that heated 250 degrees Celsius (482 degrees Fahrenheit, Fig.3-(2), the surface looked more blackish than that at 200 degrees Celsius (392 degrees Fahrenheit) due to the progress of oxidation. For the specimen heated at 300 degrees Celsius (572 degrees Fahrenheit, Fig.3-(3)), the surface layer bulged and exfoliated partly. For the specimen heated at 350 degrees Celsius (662 degrees Fahrenheit), tin atoms were observed to be nucleated in granular



(1) 200 ˚C (392 F) (2) 250 ˚C (482 F)

(3) 300 ˚C (572 F) (4) 350 ˚C (662 F)

Fig.3 Surface conditions of specimens heat treated at various temperatures.

shapes. As for the change by heat treatment, we could observe that any change didn't occur at 200 degrees Celsius (392 degrees Fahrenheit, Fig.3-(1)) and that the nucleation became more obvious with increasing temperatures. Focusing on the correlation between the nucleation and thickness of the original surface stacked layers, we made clear that the tendency mentioned above became remarkable with increasing thickness.

X-ray Diffraction Analysis

Each specimen was analyzed by X-ray Diffraction Analysis (XRD). Some of these results are shown in Fig.4 and 5. Fig.4 shows the result of XRD for the

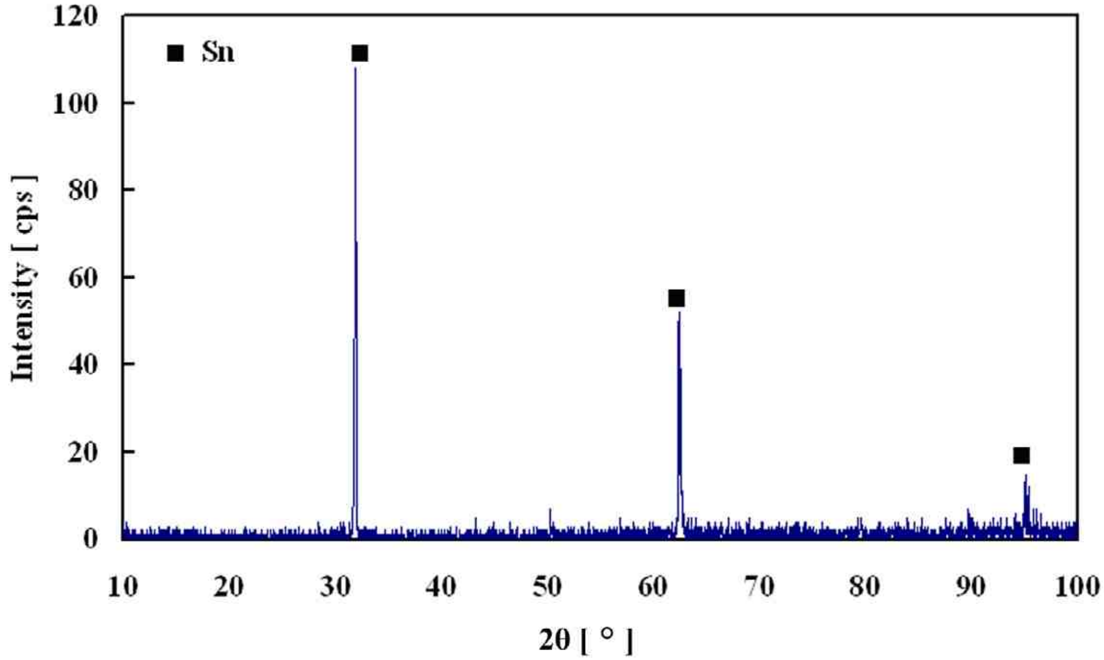


Fig.4 XRD for the specimen before heat treatment.
(tin thickness: 5 micrometers:200 microinches)

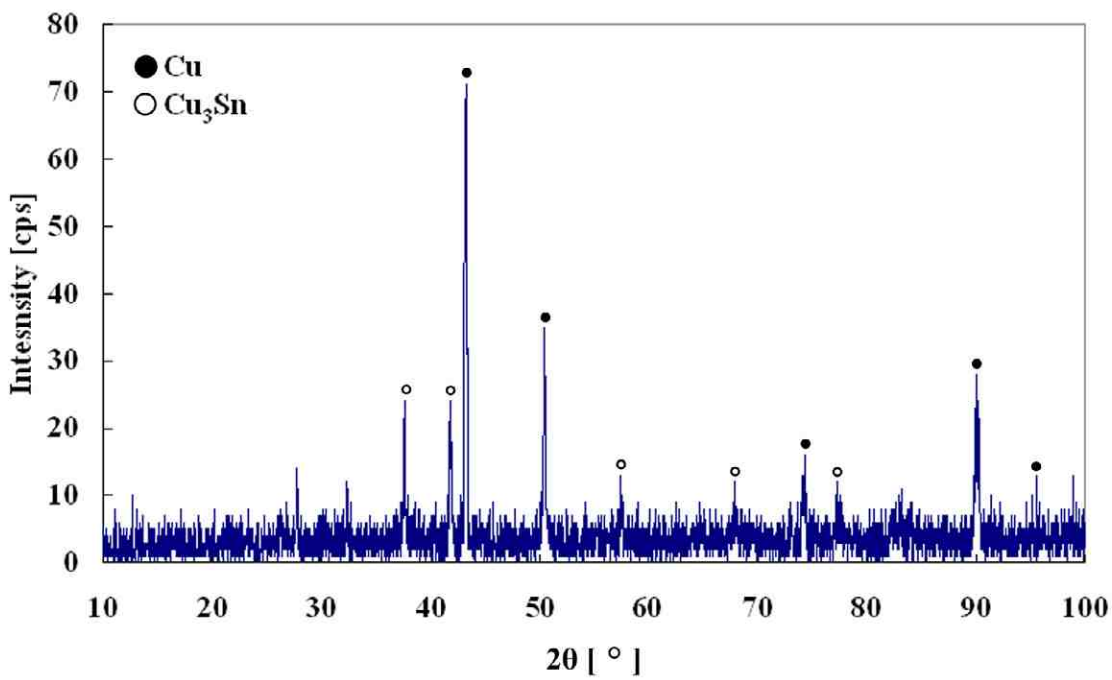


Fig.5 XRD for the specimen heat treated at 250 ˚C (482 ˚F)
(tin thickness: 5 micrometers:200 microinches)

specimen of 5 micrometer (200 microinches) tin layer before heat treatment. And Fig.5 shows that for the same specimen after being heat treated at 250 degrees Celsius (482 degrees Fahrenheit) for 5 hours. While the peaks corresponding to the existence of tin was observed in Fig.4, they were not seen in Fig.5. Instead, some peaks for Cu_3Sn and copper were observed in this case. It indicates that the diffusion of tin and copper occurred in the surface layers leading to the formation of intermetallic compound, Cu_3Sn.

Table 1 XRD results for the heat treated specimens.

200 ˚C (392 ˚F)	1h	3h	5h
1µm (40 microinches)	Cu_3Sn Sn Cu	Cu_3Sn $Sn0_2$ Cu	Cu_3Sn Cu Sn
5 µm (200 microinches)	Sn Cu	Sn Cu	Cu Sn
10 µm (400 microinches)	Sn	Sn	Sn
250 ˚C (482 ˚F)	**1h**	**3h**	**5h**
1 µm (40 microinches)	Cu Sn SnO_2	Cu SnO_2 Cu_6Sn_5	Cu_6Sn_5 Cu_3Sn SnO_2
5 µm (200 microinches)	Cu Sn Cu_6Sn_5	Cu_6Sn_5 Cu_3Sn SnO_2	Cu_3Sn SnO_2
10 µm (400 microinches)	Cu Cu_3Sn Cu_6Sn_5	Cu_3Sn SnO_2 Sn	Cu_3Sn SnO_2
300 ˚C(572 ˚F)	**1h**	**3h**	**5h**
1 µm (40 microinches)	Cu Sn SnO_2	Cu SnO_2 Cu_6Sn_5	Cu_6Sn_5 Cu_3Sn SnO_2
5 µm (200 microinches)	Cu Sn Cu_6Sn_5	Cu_6Sn_5 Cu_3Sn SnO_2	Cu_3Sn SnO_2

10 μm (400 microinches)	Cu Cu_3Sn Cu_6Sn_5	Cu_3Sn SnO_2 Sn	Cu_3Sn SnO_2

350 ˚C(662 ˚F)	1h	3h	5h
1 μm (40 microinches)	Cu_3Sn Cu	Cu_3Sn Cu SnO_2	Cu_3Sn Cu
5 μm (200 microinches)	Cu_3Sn SnO_2	Cu_3Sn SnO_2 Cu	Cu_3Sn SnO_2
10 μ m (400 microinches)	Cu_3Sn Cu_6Sn_5 SnO_2	$CuSn_3$ SnO_2 Cu	Cu_3Sn SnO_2

Table 1 listed the kinds of produced phases after heat treatments for various specimen having stacked single layers of tin and copper on steels. For the specimen of 1 micrometer thickness tin layer, the intermetallic compound, Cu_3Sn, was formed only at 200 degrees Celsius (392 degrees Fahrenheit), and at other temperatures, any compounds except for tin oxide were not observed and the results suggest that the temperatures below the melting point of tin would be not enough to make the alloying take place. At 300 degrees Celsius (572 degrees Fahrenheit), tin oxide was observed for all of specimens having various tin layer thicknesses. It indicates that the melting of tin accelerated the oxidation process. However, the intermetallic compounds were also accelerated at the same time, which lead to the formation of plural compounds of tin and copper. The compounds were mainly consisted of tin-enriched compound (Cu_6Sn_5) and tin-unenriched compound (Cu_3Sn) at this temperature (300 degrees Celsius: 572 degrees Fahrenheit). The stacked layers of tin and copper tended to form Cu_3Sn rather than Cu_6Sn_5, when tin oxide was formed. The oxide formation generally requires the certain amount of tin element and therefore, the produced intermetallic compound tends to have lower content of tin. At 350 degrees Celsius (662 degrees Fahrenheit), the tin-enriched compound, Cu_6Sn_5 was seldom observed and the main compound was Cu_3Sn, since the formation of tin oxide occurred very easily. And also for the specimens having 1 micrometer (40 microinches) tin layer, the formation of Cu_6Sn_5 seldom occurred, since the feeding of tin to the compound was not enough.

SEM-EDX Analysis

The results of SEM-EDX analyses for the specimen having 10 micrometer (400 microinches) tin thickness were shown in Fig. 6, 7 and 8. All of these figures are consisted of SEM images and element mappings. At every

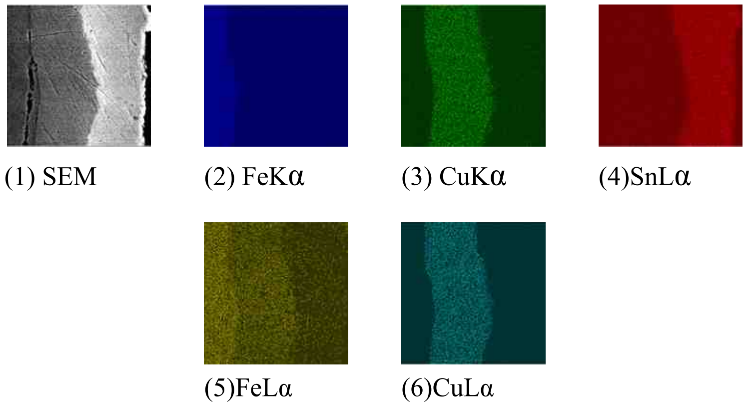


Fig.6 SEM-EDX analysis for the single stacked layers specimen before heat treatment.

upper stand of each figure, a SEM image, the element mappings for iron (Kα), copper (Kα), tin (Lα) are aligned from left to right, while the element mappings for

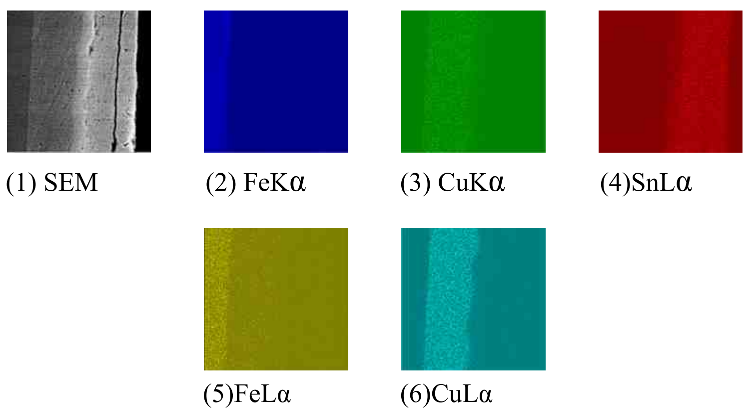
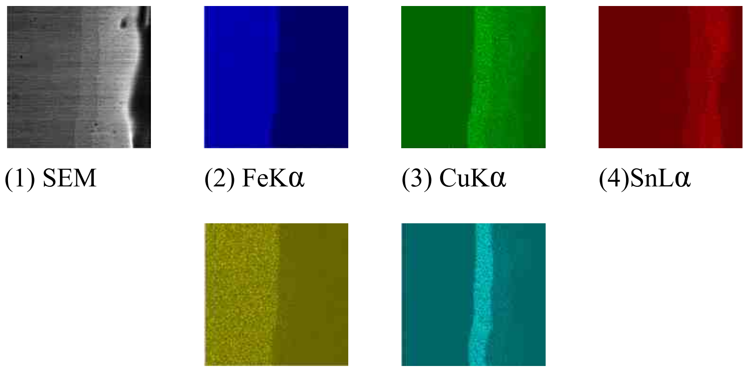


Fig.7 SEM-EDX analysis for the single stacked layers specimen heat treated at 200˚C (392˚F) for 5 hours.



(1) SEM (2) FeKα (3) CuKα (4)SnLα

(5)FeLα (6)CuLα

Fig.8 SEM-EDX analysis for the single stacked layers specimen heat treated at 250˚C (482˚F) for 5 hours.

iron (Lα1), copper (Lα1) are aligned from left to right at the lower stand of each figure. Fig.6 shows the analysis result for the cross section of the specimen having 10 micrometer (400 microinches) tin layer before heat treatment. In each photo of the figure, the specimen's surface corresponds to the right side. And the same kind of specimen heated at 200 degrees Celsius (392 degrees Fahrenheit) for 5 hours and that heated at 250 degrees Celsius (482 degrees Fahrenheit) for 5 hours are shown in Fig.7 and 8, respectively. At 200 degrees Celsius (392 degrees Fahrenheit, Fig.7), four phases iron substrate, copper, tin and intermetallic phases, were observed. At 250 degrees Celsius (482 degrees Fahrenheit, Fig.8), the surface layers composed of three phases were observed. Being compared with the results by XRD, the figure indicates that the surface layers were divided into copper phase and intermetallic one. At any rate, these results suggest that copper diffused into the tin phase much more than the latter diffused into the former. And at 250 degrees Celsius (482 degrees Fahrenheit, Fig.8), tin phase melted and the counter diffusion between tin and copper occurred vividly which lead to the formation of intermetallic compound phase by completely consumption of tin phase.

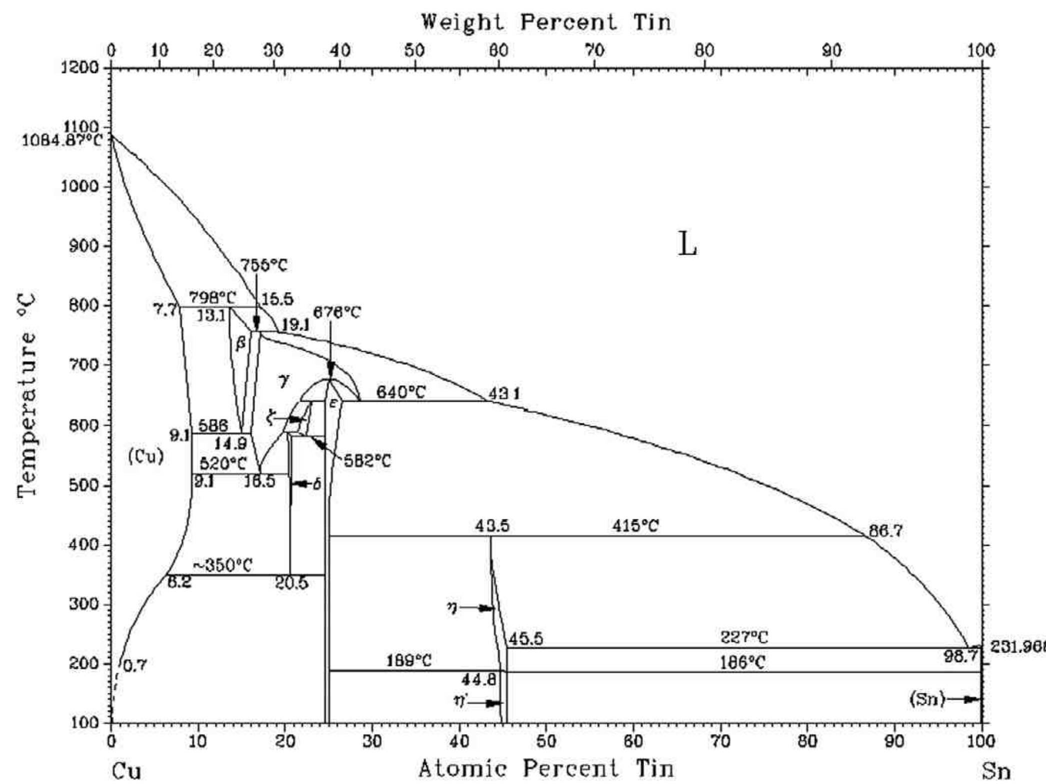


Fig.9 Phase diagram of tin and copper.

Fig.9[8] shows the binary phase diagram of copper and tin. At temperatures below 350 degrees Celsius (662 degrees Fahrenheit), an intermetallic compound of tin and copper, Cu_3Sn (ε phase), forms at the tin concentration of 37 wt% and another compound, Cu_5Sn_6 (η phase) at the tin concentration of 60 wt%. These two phases were observed in this study. Which compound dominates finally in the surfaced layers? It depends on the amount of tin relating to the formation of intermetallic compound. Concretely speaking, it depends on the originally thickness of tin layer and the extent of tin oxide formation.

CONCLUSIONS

Heating Stacked Single Layers Process (HSSL) was applied to Copper-tin alloy film formation for the application of anti-corrosion characteristics and wear resistance. Copper and tin were stacked separately on steels and they were heat treated at various temperatures. We analyzed the surface layers before and after the heat treatments and investigated the correlation between the produced phases and experimental conditions, using X-ray Diffraction Analysis and SEM-EDX. We got the following results in this study.

(1) XRD and SEM-EDX results indicate that two kinds of intermetallic compounds between tin and copper, Cu_3Sn and Cu_6Sn_5 formed on steels after heating stacked single layers of tin and copper.

(2) The formation of the intermetallic compounds depended on the thickness of the original tin layer, heat treatment temperature, heat treatment time and the extent of tin oxide formation.
(3) With increasing heat treatment temperatures, the formation of tin oxide was accelerated.
(4) When tin oxide formation occurred vividly, the tin enriched intermetallic compound (Cu_5Sn_6) was hard to be formed. In that case, Cu_3Sn was formed more easily.

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