Thermal Alloying of Tin/Nickel Films as Substitutes for Chromium Plating

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Chromium is one of harmful elements and substitutes for chromium plating is being required urgently. Tin-Nickel alloy plating is one of such substitutes. However, the phase being produced by alloy electro-deposition is non-equilibrium and the composition is always fixed (NiSn), which seems to limit the application of this alloy film to certain extent. In this research, we investigated the possibility of Tin-Nickel alloy films from multilayer Tin/Nickel films through thermal diffusion process. Tin(from fluoroboric bath) and Nickel film (from Watt bath) were electro-deposited on copper or iron substrates layer by layer and then they were heated at 313K (284F, 140C) - 473K (392F, 200C) in 86.4ks (1 day) - 864ks (10 days). We characterized film structures by Both X-ray and SEM-EDX, and evaluated the hardness for each specimen by Vickers hardness testing machine. In the case of Nickel/Tin films on substrates, the tin layer became thinner due to the dissolution of tin, when copper with deposited tin was immersed into Watt bath for nickel formation. X-ray diffraction analysis (XRD) showed that the peaks of tin disappeared with time being through the heating process, however any peaks corresponding to intermetallic compounds between tin and nickel could not be found. The diffusion of tin into nickel layer was seen and the Vickers hardness of surface layers increased through heating process. On the other hand, the order of precipitations was changed so that the proportion of tin in the multiplayer increased. In this case, the peaks of tin were remained through heating process under the same condition. However, the amount of tin layer decreased and the other peaks suggesting the existence of alloying phase appeared through the thermal process.

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Introduction

Nowadays, every material is required to be environmental-friendly. From the viewpoint of environment and natural resources protection, every material design or process should be developed in coming 21st century. The tendency and idea will make some of plating materials and processes change inevitably. As a matter of fact, the use of some plating metals like lead, chromium, cadmium etc. are being regulated or going to be regulated all over the world. In the future, some metals like those will be used for plating restrictedly.

Chromium hard plating is one of those processes that should be reexamined, since chromium is considered as one of harmful elements for environments. Among various processes for the chromium substitutes, some systems for tin alloys have been paid attention. Tin-Nickel alloy has been one of those systems[1]. Although the hardness cannot reach the value of plated chromium, it is much more environment-friendly. The alloy film has been produced through alloy electrodeposition so far. This technique always provides only a certain phase, NiSn with 10wt%Ni, regardless of experimental conditions or any added components. However, the phase cannot be found in the equilibrium phase diagram (Fig.1)[2]. The truth may restrict the application of the substitute alloy to a certain extent. And in addition, the film can be unstable thermodynamically and may be changed through thermal process like friction and so on. Generally speaking, the alloy electrodeposition can involve some harmful chemicals as bath components to make an appropriate co-deposition of plural elements possible. To avoid all of these potential demerits for alloy electrodeposition process, we investigated another process as substitute for chromium plating. The background and the aim for this study are explained schematically in Fig. 2.

In this study, multi-layers of tin and nickel were produced on copper and iron substrates at first. Then the multi-layers were heated in the furnace and the alloying behavior of multi-layer composed of tin and nickel through thermal-diffusion processes was observed and investigated. For some very thin multi-layer films deposited by sputtering etc., the diffusion process has been examined[3-5]. And for the thermal diffusion of tin film onto the substrate copper, several observations have been reported[6,7]. However, the application of the phenomenon to the formation of a relatively thick alloy film has not been investigated closely so far. In this study, we observed the fundamental behavior of alloying through thermal diffusion in relatively thick multi-layers composed of tin and nickel. And the hardness of the films produced by thermal process was investigated.

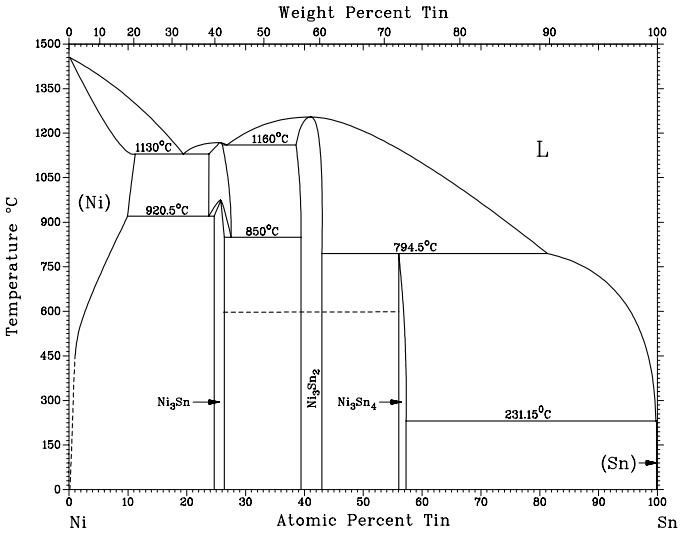

Fig. 1 Phase diagram for Ni-Sn.

Experimental

Specimen and plating bath

Pure copper (99.9 wt%) and iron sheets (99.8 wt%) were used as specimen. The thickness was 2mm (0.0787 in.) for both specimens. Tiny coupons of 10mm x 15mm (0.3937 in. x 0.5906 in.) were cut from original sheets and used as substrate. Lead wires were attached electrically to one side of every substrate, respectively and all surfaces except for the opposite side of the lead wire were covered by epoxy resin. Those coupons as cathode were immersed into plating bath made of Pyrex glass beaker of 300ml. The opposite electrode, the anode, was made of pure copper mesh. It was set along the inner surface of the beaker so that it surrounded the anode coupons placed at the center of the bath. Both electrodes were connected to a constant current power source (Kenwood PA36-3A) and the current value was regulated by it.

For tin plating, tetrafluoroboric acid (TFB) was used. The total amount of the bath solution was 300mL. The solution was made so that it contained tetrafluoroboric acid of 18mL (42%HFB_4) and fluoroboric tin acid of 2mL (43%$Sn(BF_4)_2$). And polyethylene glycol (molecular weight 2000) of 15mg was added into the bath to enhance the deposition condition. On the other hand, Watt bath was used for nickel plating. It contained $NiSO_4$

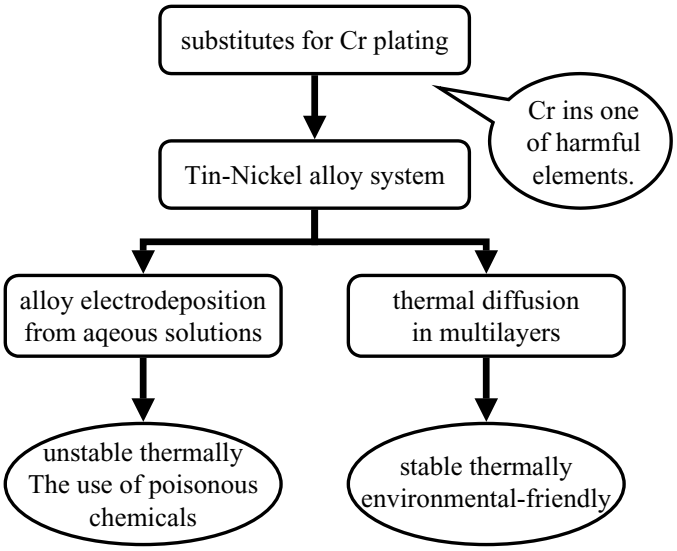

Fig. 2 The aim of the current study.

of 90g, $NiCl_2$ of 15g, H_3BO_3 of 12g, and the total volume was also 300ml. Tin was electroplated in TFB at room temperature and on the other hand, nickel was plated in Watt bath at 323K (50C, 122F). The current density for electrodeposition ranged from 1A/dm^2 to 10A/dm^2, and the plating time used for each case was 300s (5 minutes).

Experimental Procedure

The experimental procedure was explained schematically in Fig.3. Tin and nickel were electroplated on copper or iron substrates in this order or in the opposite one at a certain current densities and in a certain time mentioned above, using their own plating baths, respectively. Being washed, dried and separated from lead wires and epoxy resin, the specimens were put into crucibles filled with silicon oil and heated in an electronic furnace. The temperature of silicon oil was kept at 413K (140C, 284F) or 473K (200C, 392F) and they were heated up to 864ks (10 days) at most. Specimens were taken out of the furnace at a certain heating time within 864 ks and cooled slowly in the air. Specimens being washed by acetone and water, and dried thoroughly, the structure of the surface layers were analyzed by X-ray diffraction (XRD) apparatus (Hitachi Rint 2100) and SEM(Hitachi S-4300) - EPMA (Horiba EMAX-7000). For XRD analysis, copper electrode was used and the diffraction patters were obtained, X-ray voltage of 40kV and the current of 20mA were applied. And the hardness of surface layers was measured by Vickers hardness testing machine (Akashi Model AVK). The loads ranging from 50g (11.02 x 10^{-2} lb) to 1kg (2.20 lb) were applied to the surfaces of specimens. And the values obtained for five different spots were averaged and the Vickers hardness was calculated for each specimen.

Results and Discussion

Nickel/Tin Electroplating on Copper

Tin was electroplated on copper at several current densities ranging from 1A/dm^2 to 10A/dm^2 in TFB bath. The thickness was expected to increase with the current densities. However, the XRD results indicate that few amount of tin film was produced at the highest current density. TFB is generally well known for the high deposition rate of tin deposition and the high current density can make the deposited grain coarse and the film more dendrite-like, which can lead to the poor adherence of the film. Therefore, deposited grains dropped off immediately after the deposition and any film was not produced significantly in the case. SEM observation indicates that the deposition for the current density, 1A/dm^2, provided the optimum thickness of 8 x 10^{-5} m - 9 x 10^{-5} m (3.1 x 10^{-2} in. - 3.5 x 10^{-2} in.). Fig.4 shows the result of XRD for the specimen on which tin was electroplated at 1A/dm^2. Some peaks for copper were found remarkably, since X-ray penetrated into the substrate. However, the peaks of tin could be confirmed around 30 degree in the diagram. On the other hand, we confirmed in advance that nickel film of 6 x 10^{-5}m (2.4 x 10^{-2} in.) was produced at the current density of 5A/dm^2 from Watt bath. Therefore, the current density was applied to the electrodeposition of nickel on copper with tin film.

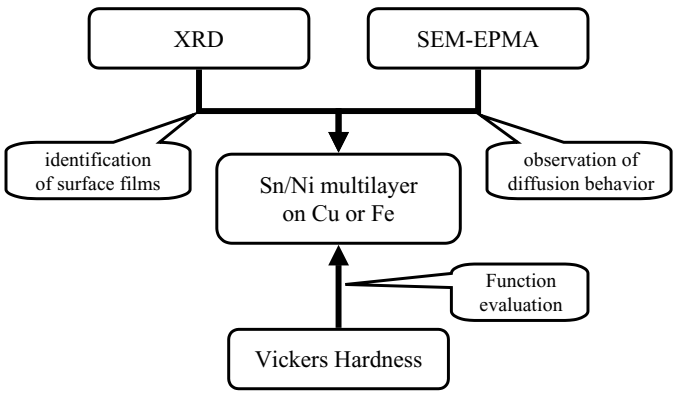

Fig. 3 Experimental procedure.

Fig.5 shows the XRD result for the copper specimen with tin film on which nickel was electroplated at 5A/dm^2 from Watt bath. Being compared with Fig.4, this diagram indicates that peaks for nickel were added. Both nickel and copper have face cen-

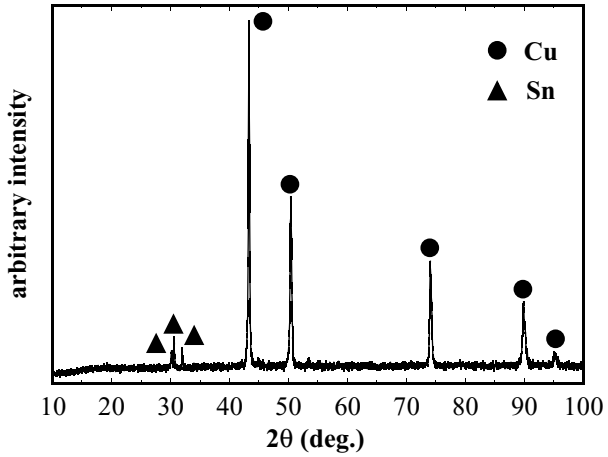

Fig. 4 XRD result for Sn plated copper (at 1 A/dm^2).

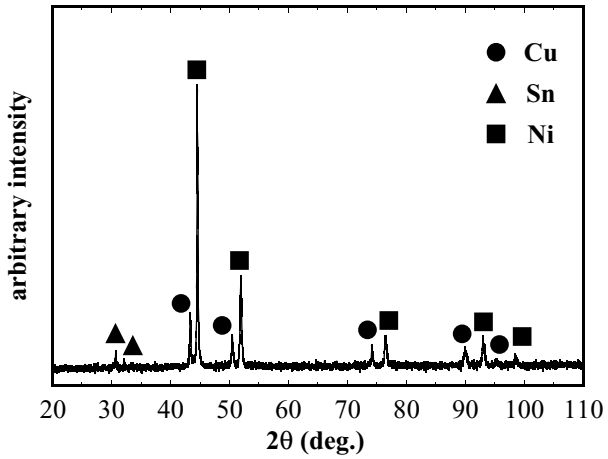

Fig. 5 XRD result for Ni/Sn multilayered copper before heating (Sn: 1 A/dm^2, Ni: 5 A/dm^2).

tered cubic (fcc) crystal structure and therefore, both peaks appeared in pairs from 40 degree to 100 degree. The peaks for tin were still observed around 30 degree, which assured the presence of tin in the surface films. However, one of those peaks disappeared and the intensities of others also decreased in this case. These results suggest that the amount of tin phase decreased with deposition of nickel. Since there were no peaks for other compounds among composed elements, we presumed that tin disappeared to some extent. SEM images supported the assumption. According to the image, the thickness of nickel film was about 6×10^{-5} m (2.4×10^{-2} in.), although tin layer had only several micrometers thickness under it. The element analysis by EDX confirmed that tin was dispersed into nickel layer and a lot of tin was scattered in it. These results provide us a picture that the copper specimen has very thin film for tin right above it and relatively thick nickel film with a lot of scattered tin at the top of the surface. The change of tin layer with nickel plating can be attributed to the corrosion susceptibility of tin to acid Watt bath. When the specimens with tin surface film were immersed into Watt bath for nickel electroplating, tin can dissolve anodically at high rate in the bath.

Fig.6 shows XRD results for the specimens with nickel/tin films heated at 413K (140C, 284F). Fig.6-(a) corresponds to the result obtained after the heating in 259.2ks (3 days) and Fig.6-(b) to that in 864ks (10 days). The peak pairs of nickel and copper were found also in both diagrams, as the result for the specimen before heating. However, the peaks for tin became less remarkable. In Fig.6-(a), the intensities and sharpness of tin peaks decreased remarkably, although they were still recognized with difficulty. However, the peaks for tin were not found at all in Fig.6-(b). It indicates that tin layer disappeared with time being during the heating process. EDX analysis showed that the density of tin in the nickel layer decreased as a whole and that the existence of tin layer became vague remarkably. These results suggest that the tin layer disappeared with time being during heating and that tin was scattered into the nickel layer.

Fig.7 shows XRD results for the specimens with nickel/tin films heated at 473K (200C, 392F). Fig.7-(a) shows the result obtained after the heating in 259.2ks (3 days) and Fig.7-(b) that in 864ks (10 days). In Fig.7, the tendency was very similar with that in Fig.6. Although tiny peaks for tin were still remained, the tin layer was disappeared almost completely. The phenomenon was also supported by EDX result.

Fig.8 shows Vickers hardness for the specimens with copper substrates after the heat treatments. In this figure, the vertical axis corresponds to Vickers hardness and the horizontal one to weight applied for the measurement of hardness. When heavier weight was applied, the Vickers hardness was almost

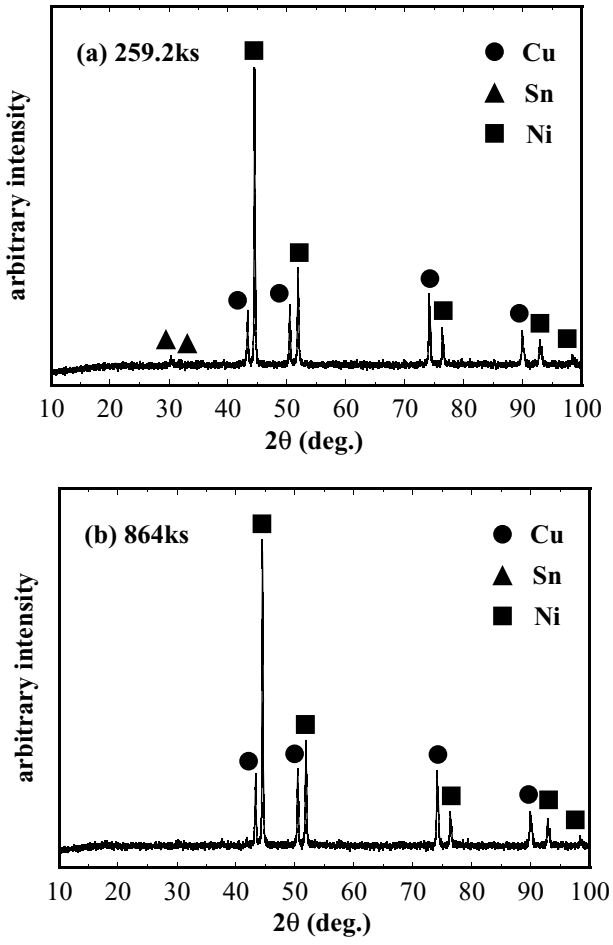

Fig. 6 XRD result for Ni/Sn multilayer on copper heated at 413°K.

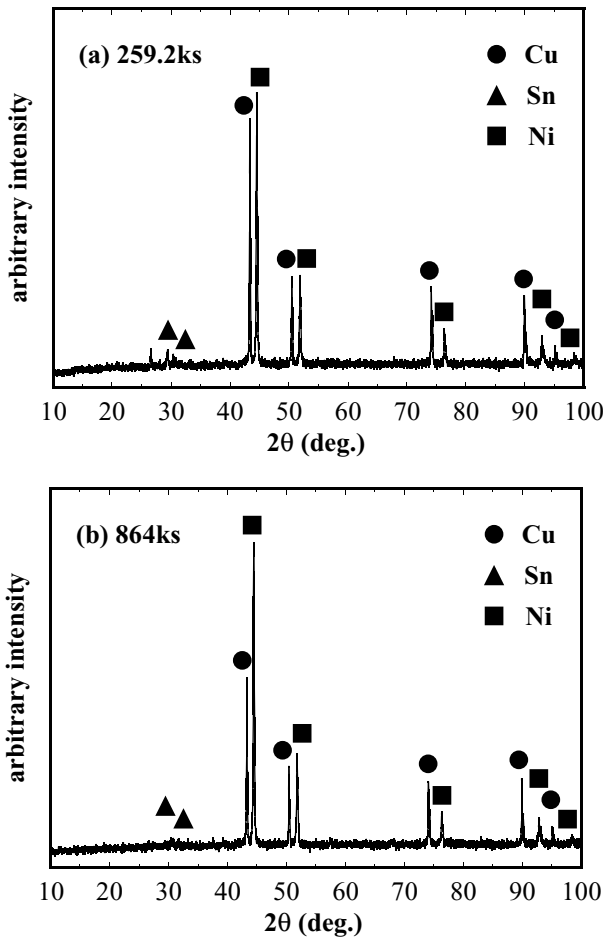

Fig. 7 XRD result for Ni/Sn multilayer on copper heated at 473°K.

the same for all of the specimens, because the test with heavier weights measures the hardness for the inner parts of the specimens generally. The values that were obtained with heavier weights belong to the copper substrates on the other hand. In the case of 50 g (11.02 x 10^{-2} lb) as applied weight, some specimens had higher hardness. Particularly, the specimen heated at 473K (200C, 392F) in 864ks (10 days) had the highest hardness. The values at 50 g (11.02 x 10^{-2} lb) belong to the surface films relatively well. Therefore, the higher hardness for the specimen heated in 864ks (10 days) at 473K (200C, 392F) suggests that the surface layer was hardened through the diffusion process of tin into the nickel layer. Although any significant intermetallic compounds were not confirmed, the dissolution of tin into nickel phase or its local alloying might harden the surface films.

Tin/Nickel Electroplating on Iron

As mentioned above, tin film can dissolve anodically, when specimens were immersed into Watt bath. To minimize the anodic dissolution, iron was used as substrate. Since iron is more negative than tin electrochemically, we expected that the rate of the dissolution would be suppressed to some extent due to the sacrificial dissolution of substrate. However, XRD results showed the same tendency with those for copper substrate in Fig.5. And the tiny peaks for tin disappeared with time being during heating in the same way with that in Fig.6 and 7.

We had another try for the same purpose. Nickel was electrodeposited on iron substrate from Watt bath at first. Then the specimens were immersed into TFB bath and had the electro deposition of tin on the top of the specimens. Fig.9 shows XRD result for the specimen just after the nickel-tin electro deposition. Since copper electrode was used as X-ray source, any peaks of iron as substrate could not be found in this figure. Some Nickel peaks were still found from 40 degree to 100 degree remarkably. Several peaks corresponding to tin were also found around 30 degrees. However, the sharpness and intensities for the tin peaks were much higher than those in Fig.4 - 7. It suggests that relatively thick tin layer was produced on the nickel film. Fig.10 shows the XRD result for Tin/Nickel/steel specimen heated at 473K (200C, 392F) in 864ks. The nickel peaks remained unchanged also in this figure. For tin peaks, the intensities decreased after the heating. And in addition, several new peaks were found around 30 degrees, which suggests the formation of new phases among plating elements and substrates. It is noteworthy that the alloying behavior in this case was different from the former results. The same amount of both elements in the surface layers made the difference possible. These results will make it possible to produce various intermetallic phases under some experimental conditions.

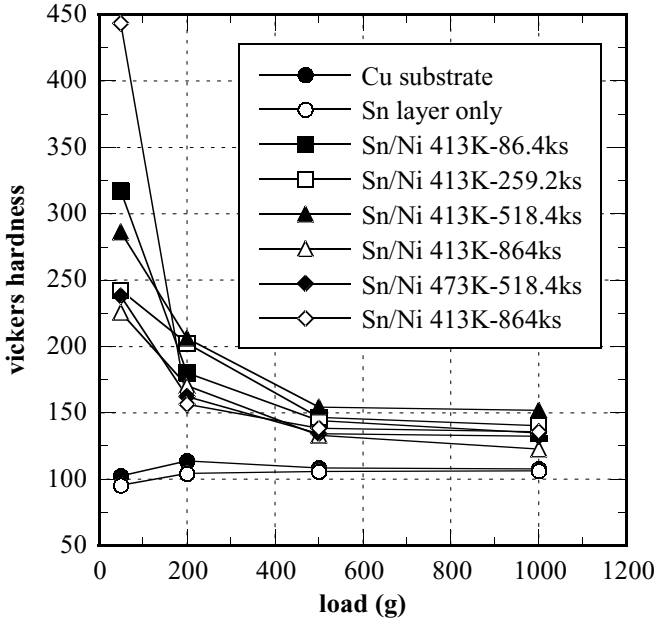

Fig. 8 Vickers hardness of specimens with Cu substrates.

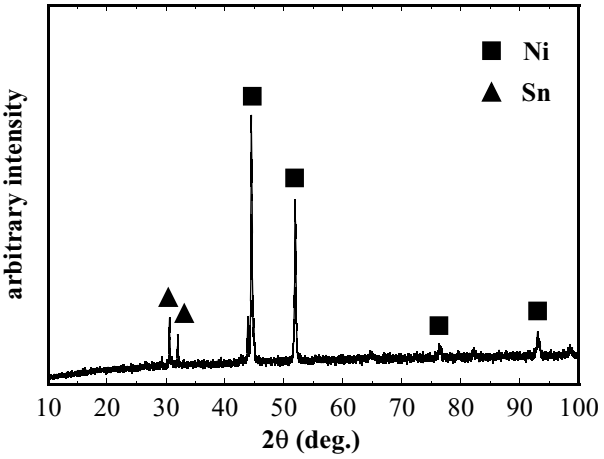

Fig. 9 XRD result for Sn/Ni/Cu before heating.

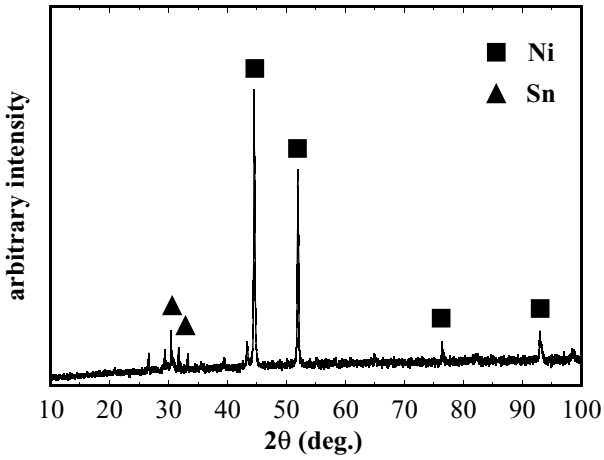

Fig. 10 XRD result for Sn/Ni/Cu heated in 864ks.

Conclusions

Tin nickel alloy film is one of the potential substitutes for chromium hard plating from the viewpoint of environment friendliness. The alloy film is usually produced, using co-electrodeposition. However, the phase through the alloy electrodeposition has been restricted to only one phase, regardless of plating conditions and unstable thermodynamically. Therefore, we investigated the alloying behavior of multi-layers composed of tin and nickel through a thermal diffusion process. At first, tin and nickel were electroplated on copper substrate one by one in this order. Although the tin layer was diminished due to it's dissolution in Watt bath, tin diffused into nickel layer and increased the hardness. However, any intermetallic compounds were not found. Therefore, we had another try to make the multi-layer, using iron substrate. At first, nickel was electroplated in Watt bath and then tin was electrodeposited on the top of the specimens. This process made the tin layer more stable and thick. Heating those specimens lead to the formation of various phases.

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