Tin-Nickel Alloy Films Produced from Stacked Single Layers by Heating & Their Characteristics

Hideyuki Kanematsu, Dr. Eng., MIMF, Tatsumasa Kobayashi, Dr. Eng. & Noriyuki Wada, Dr. Eng., Dept. MS & E., Suzuka National College of Technology, Shiroko-cho, Suzuka, Mie 510-0294, Japan Takeo Oki, Dr. Eng., Professor Emeritus, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

Tin-nickel alloy films have been evaluated as environmentally friendly substitutes for chromium plating. Conventionally, the film has been produced by using co-deposition from an aqueous solution. On the other hand, another process was invented in which single stacked nickel and tin single layers were heated in the furnace to produce the alloy film. Basically, several phases between tin and nickel were already confirmed by X-ray Diffraction Analysis (XRD). However, in this study, we investigated the alloying behaviors under various heat treatment conditions by SEM-EDX and Differential Thermal Analysis (DTA). In addition, we measured the various characteristics of formed ally films and discussed the possibility of the application to the practical purposes.

For more information, contact: Hideyuki Kanematsu, Dr. Eng., MIMF Dept. MS & E., Suzuka National College of Technology Shioroko-cho, Suzuka, Mie 510-0294, JAPAN voice/fax: +81-593-68-1849 (direct) email: <u>kanemats@mse.suzuka-ct.ac.jp</u> web: <u>http://marquiswhoswho.net/KANEMATSUH/</u>

INTRODUCTION

Recently, environmental protection is the first policy for energy technology, and the plating industry must take it into account, so that it will benefit us as a sustainable technology in the future. Lead, chromium and several other metal elements tend to be avoided, even though they haven=t been completely banned. We focused on chromium plating in this paper and investigated tin-nickel film as a substitute. Conventional studies have dealt with alloy electrodeposition where plural metal elements precipitate simultaneously from a certain mixed aqueous solution by electrodeposition⁽¹⁾. For tin-nickel alloy film, most of the formed layer was NiSn, although the phase can=t be found in the tin-nickel phase diagram (Fig.1)⁽²⁾. This means that the formed layer is unstable thermodynamically.



In addition, the co-electrodeposition requires a certain combination of chemicals, which leads to the restriction of choice for methods.

We aimed to produce the alloy film from two stacked single layers of tin and nickel. In the thermal process, the diffusion of elements plays an important roll for the formation of alloy film. Even though there are few studies on the phenomenon, Yoshitake et.al⁽⁴⁾⁻⁽⁷⁾ investigated and discussed the mutual diffusion for different combination of metals from the general view point. Gabe et al⁽⁸⁾⁻⁽¹⁰⁾ investigated alloy layers of tin on steel substrates. For the multilayer of tin and nickel, many other researchers investigated the multilayer system, since nickel layer could be used as an underlayer for the tin overlayer⁽¹¹⁾⁻⁽¹⁴⁾. Then many researchers followed their study.

We have made an effort to apply the stacked layer as a substitute alloy film for chromium plating. In this process, the stacked layers were heated to under the melting point of tin initially^{(15), (16)}, then heated to a temperature slightly over it⁽¹⁷⁾. Since there were many interesting results from the process, we have applied our method for several patents in the USA^{(18), (19)} and Japan^{(20), (21)} so far.

In this experiment, we focused particularly on the liquid (tin) - solid (nickel) reaction for the formation of alloy films and discussed the diffusion phenomena. Then we investigated the formed alloy phases with temperatures and characterized some properties for the produced films.

EXPERIMENTAL

Steel plates were used, on which nickel and tin were deposited in layers in this order. These specimens were produced electrochemically from aqueous solutions by Hatsumec Co.(Eba, Kuwana-city, Mie 511-0836). The

nickel layer was precipitated directly on the steel substrates and tin was produced on it as overlayer. Each of the stacked tin and nickel samples had a thickness of 10im (3.94×10^{-4} inch) exactly which SEM(S-4300 made by Hitachi Co.) -EDX (EMAX-7000 made by Horiba Co.) confirmed in advance. Each specimen was cut from the main sheet with a thickness of 0.6mm ($2.36 \text{ H } 10^{-2}$ inch), and used as a tiny sample with dimensions of 10mm H 10mm (0.394 inch H 0.394 inch.) They were heated in an electric furnace to the temperatures, 623 "K (350"C, 662"F), 723"K (450"C, 842"F) and 823"K (550"C, 1022"F). Heat treatment time was 10.8ks for all cases. And these heat treated specimens were analyzed by X-ray Diffraction Analysis, SEM-EDX, Differential Thermal Analysis, hardness testing and color measurement.

The structures of surface layers were investigated by X-ray Diffraction Analysis (XRD; RINT 2100 made by Rigaku Co.). Copper K_{a} was used as the X-ray probe. The X-ray voltage was 40kV and the current was 20mA for every measurement.

Thermochemical characteristics for the specimen were analyzed by Differential Thermal Analysis (DTA, TG-8110 by Rigaku Co.). The specimen was heated from room temperature to 1073 "K (800 "C, 1472 "F) at the rate of 20 "K/min.

The hardness was measured by Micro-Vickers hardness testing machine (MVK-E made by Akashi. Co.). The specimens heated at different temperatures were cut and the hardness of the cross sections of these specimens were measured from the circumference of the cross sections to the inner area at every 5 im (1.97 H 10^{-4} inch). The load was 10g (2.20×10⁻² lb) for all cases.

The color tones of the specimens were measured by the color testing machine (SP-80 made by Tokyou Denshoku Co.). The light source was a halogen lamp (6V-10W, 2000H) and they were measured under the condition of integrating sphere 0-d method (JIS-Z8722).

RESULTS AND DISCUSSION



Fig.2 XRD result for the stacked films of tin and zinc.

Firstly, the stacked films on the steel were measured by X-ray analysis. Fig.2 shows the XRD spectrum. Table 1 indicated the result for the comparison between all of the peaks in Fig.2 and the

Peak No.	2θ in the experiment	2 θ (JCPDS card)	structures
1	30.463	30.643	Sn
2	32.017	32.017	Sn
3	44.90	44.900	Sn
4	62.535	62.535	Sn
5	79.460	79.466	Sn

Table 1 The identification of peaks in Fig.2.

standard peaks in JCPDS (Joint Committee on Powder Diffraction Standards) cards and the identification of all these peaks. Even though two stacked single layers of tin and nickel were confirmed on the surface of steel by SEM-EDX, XRD indicated the peaks only for tin. Since the thickness of tin overlayer was about 10im $(3.94 \times 10^{-4} \text{ inch})$, peaks for the nickel underlayer and the substrate could not be found.



Fig.3 XRD result for the stacked films of tin and zinc heated to 623K.

Fig.3 shows the XRD spectrum for the specimen heated to 623 "K (350 °C, 662 "F). Table 2 indicates the comparison between the observed peaks in Fig.3 and the standard peaks in JCPDS cards. The peaks for tin were still observed. (Peak 2, 9, 12). This indicates that a part of the tin overlayer still remained on the top of the specimens after the heat treatment at

Peak No.	2θ in the experiment	2 θ (JCPDS card)	structures
1	29.96	29.846	NiSn
2	30.56	30.643	Sn

3	31.8	31.439	NiSn
4	33.44	33.329	NiSn
5	39.52	38.956	Ni ₃ Sn ₄
6	40.68	40.660	NiSn
7	43.54	43.536	Ni ₃ Sn ₂
8	44.74	44.597	Ni ₃ Sn ₄
9	55.4	55.328	Sn
10	58.48	58.312	NiSn
11	61.04	61.072	NiSn
12	62.78	62.535	Sn
13	65.3	65.284	NiSn
14	73.5	73.324	Ni ₃ Sn ₄
15	74.018	74.399	NiSn
16	75.1	75.369	Ni ₃ Sn ₄

623 [°]K (350 [°]C, 662 [°]F). However, Fig.3 shows different intermetallic compounds between nickel and tin were formed on the surface area of the specimens. NiSn, which is often observed in alloy electrodeposition from aqueous solutions, was also found in this case. Peaks1, 3, 4, 6, 10, 11, 13 and 15 correspond to the unstable chemical compound between tin and nickel. Even though there were other types of intermetallic compounds on the surface of the specimens like N_bSn₄ (peaks 5, 8, 14 and 16) or N_bSn₂ (peak 7), NiSn was the main phase in this case. Since the temperature was much lower than the melting point of nickel, the nickel underlayer was supposed to be still stable and this was confirmed by SEM-EDX. The temperature for the heat treatment was over the melting point of tin. Therefore, the reaction between tin and nickel was liquid (tin) - solid (nickel). The liquid tin diffused into the nickel layer and formed NiSn, as well as other types of intermetallic compounds between tin and nickel.



zinc heated to 723K.

Fig.4 shows the XRD spectrum for the specimen heated to 723[°]K (450[°]C, 842[°]F) and table 3 shows the list of observed peaks and standard peaks in JCPDS cards. Both this figure and table indicate that the unstable compound NiSn disappeared and N_bSn₂ and N_bSn₄ phases were mainly produced instead. The N_bSn₂ corresponds to the peaks, 2, 7, 9, 10 and 12. On the other hand, N_bSn₄ corresponds to the peaks, 3, 6, 8, 11 and 13. At 723K (450[°]C, 842[°]F), NiSn which was formed mainly at the lower temperature disappeared and more stable compounds like N_bSn₂ and N_bSn₄ appeared. Higher temperature made tin

and nickel diffuse more easily and was the reason why thermodynamically stable compounds were formed at this temperature. A type of tin oxide, Sn_3O_4 was

Peak No.	2θ in the experiment	2 θ (JCPDS card)	structures
1	27.02	27.709	Sn ₃ O ₄
2	30.36	30.773	Ni ₃ Sn ₂
3	31.6	31.473	Ni ₃ Sn ₄
4	32.94	32.314	Sn ₃ O ₄
5	33.32	33.013	Sn ₃ O ₄
6	33.88	33.406	Ni ₃ Sn ₄
7	43.40	43.536	Ni ₃ Sn ₂
8	44.6	44.597	Ni ₃ Sn ₄
9	55.16	55.040	Ni ₃ Sn ₂
10	57.84	57.673	Ni ₃ Sn ₂
11	73.30	73.324	Ni ₃ Sn ₄
12	73.94	73.390	Ni ₃ Sn ₂
13	81.34	81.499	Ni ₃ Sn ₄

Table 3 The identification of peaks in Fig.4.





formed on the top of the surface. The atmosphere was not regulated through heating in the furnace. Therefore, a thin oxide was formed on the top of the alloy films. SnO and SnO₂ are typical tin oxides, however, the oxide was composed of both trivalent and quadravalent tin ions. Since the heating temperature was relatively low from the view point of oxidation, the divalent tin ion was stable and Sn_3O_4 was formed on the surface due to oxidation of the surface tin layer. However, the formation of the tin layer was not so extensive and the oxide layer was restricted only to the vicinity of the surface area. Fig.5 shows the XRD spectrum for the specimen heated to 823 "K (550 "C, 1022"F) and table 4 lists the observed peaks and those in JCPDS cards. The intermetallic phases were the same at this temperature as those at 723 "K (450 "C, 842"F). However, the oxide phase became more remarkable. The oxide phase in this case was SnO₂, while Sn₃O₄ was the typical oxide at 723 "K (450 "C, 842"F). As the temperature increased, it made the quadravalent tin ion more stable for oxidation and the extent of the oxide layer increased.

Peak No.	2θ in the experiment	2 θ (JCPDS card)	structures
1	26.58	26.610	SnO ₂
2	32.88	33.406	Ni ₃ Sn ₄
3	33.20	33.406	Ni ₃ Sn ₄
4	33.88	33.891	SnO ₂
5	34.00	34.796	Ni ₃ Sn ₂
6	43.50	43.536	Ni ₃ Sn ₂
7	44.36	44.459	Ni ₃ Sn ₂
8	51.80	51.777	SnO_2
9	55.10	55.040	Ni ₃ Sn ₂
10	57.80	57.673	Ni ₃ Sn ₂
11	61.82	61.868	SnO ₂
12	64.78	64.174	Ni ₃ Sn ₄
13	71.32	71.774	Ni ₃ Sn ₄
14	74.54	75.369	Ni ₃ Sn ₄
15	81.10	81.166	Ni ₃ Sn ₂

Table 4 The identification of peaks in Fig.5



From the view point of practical application, oxide formation is not desirable. This can be avoided by three methods as mentioned below. The oxidation will be retarded by a vacuum process or the introduction of a reducing atmosphere like argon gas, hydrogen gas etc. On the other hand, the surface became rough to some extent during the heat treatment, since the diffusion of atoms occurred during the process. Therefore, buff polishing will be required to recover the brightness of specimens. The process will remove the surface oxide films for the practical application.

The basic alloying process of tin and nickel is illustrated schematically in Fig.6. By heating the two stacked single films of tin and nickel on steel, intermetallic compounds between tin and nickel are formed. The types of compounds depend on the treatment temperatures. When the temperature is relatively low, NiSn is more commonly formed. With the increase of temperatures, the unstable compound disappears and thermodynamically stable compounds, N_BSn_4 and N_BSn_2 are formed. NiSn is still found in every case of coelectrodeposition. Therefore, we presume that the compound is produced through an inadequate diffusion process. When the temperature is high enough for the component elements to diffuse

with each other, the thermodynamically stable $N_{i_5}Sn_2$ and $N_{i_5}Sn_4$ are produced. Therefore, the general process for the formation of alloy films like $N_{i_5}Sn_4$ and Ni_3Sn_2 is supposed to occur through the intermediate formation of NiSn.

Fig.7 shows the result for thermal differential analysis on the specimen. All peaks at low temperatures below 400" K (127" C, 260.6" F) related to the vaporization of water. The peaks at about 500" K (227" C, 440.6" F) correspond to the melting of tin. While the base line decreased with the increase of temperature, the formation of intermediate compound, NiSn, and the stable compounds thereafter are presumed to occur till the temperature reached about 1050" K (777" C, 1430.6" F). From the comparison between the peak and the phase diagram shown in Fig.1, we presume it corresponds to the melting of N $_{B}$ Sn₄, and the mixed phases of N $_{B}$ Sn₄ and liquid formed.

Fig.8 shows the hardness profile in the surface layers for specimens heated at different temperatures. The hardness profile for a non heat-treated specimen was shown as a reference in the figure. For non heat-treated specimen, the hardness of surface layers within 20im $(7.87H10^{-4} \text{ inch})$ was very low, since the result reflected the values for single tin or nickel layer. With the heat treatment, the hardness of surface layers increased. It corresponded to the formation of compounds between nickel and tin. Both, at 623 "K (350 "C, 662 "F) and 723 K (450 C, 842 F), the hardness of the inner layers was higher than those at the vicinity of the surfaces, since the latter reflected the hardness of the remaining single tin layer, or the produced thin oxide layer. The Vickers hardness in the inner layers composed of intermetallic compounds between tin and nickel increased with the treatment temperature and reached about 450 at the temperature of 723["]K (450["]C, 842["]F). At the 823["]K (550["]C, 1022["]F), the profile was the same. However, the hardness of the inner surface layers increased remarkably and the maximum value, which found at the distance of 5 im (1.97 H10⁻⁴ inch) from the surface, was over 700. At the higher temperatures, the intermetallic stable compounds were formed and the layers were developed enough to show higher values of hardness.













Fig.9 L-a-b diagram for color.

Fig.9 shows the result of color measurement for the specimens heat treated at different temperatures. The color tones for different heat treated specimens are shown in the L-*a-*b diagram. Compared with the non heat-treated specimen, the brightness of color decreased with heat treatment. It can be attributed partly to the formation of intermetallic compounds, and partly to the surface becoming rough to some extent by the heat treatment. However, it increased with the treatment temperature. It suggests that the formation of oxide films increased the brightness to some extent. The brightness can be recovered by post mechanical treatment like buff polishing etc. As shown in the figure, color tones for heat treatment specimens were based on grey. However, they took on gold to some extent with a positive change of the value in the b direction. As described above, post mechanical treatment to smooth the surfaces will make the color tone clearer and more beautiful.

CONCLUSIONS

We investigated the formation of alloy films between tin and nickel from the stacked layers through heat treatment process. The following results were obtained.

- NiSn was formed at 623 "K (350 °C, 662 °F) mainly, while Ni_bSn₄ and Ni_bSn₂ were more commonly formed at 723 "K (450 °C, 842 °F) and 823 °K (550 °C, 1022 °F). (2)The oxidation of surface layers became remarkable with the increase of heat treatment temperature.
- (3) The hardness of surface layers increased with temperature, and reached a maximum value of 700 (Vickers hardness).
- (4) The brightness of color decreased to some extent due to the surface roughness caused by the diffusion of surface atoms. The color tones were based on grey, and it took on a slight gold color. The color tone will be improved by some proper post treatment like polishing.

REFERENCES

- (1) G.E.Sahin, *Plating & Surface Finishing*, August Issue, p.8(1998)
- (2) M.Jordan, *The Electrodeposition of Tin And Its Alloys*, Eugen G. Leuze Publishers, Saulgau, Germany, 1995, p.122
- (3) ASTM International, *Binary Alloy Phase Diagrams, second edition, plus update version 1.0*, Materials Park Ohio, 1998
- (4) M.Yoshitake & K.Yoshihara, *Surface And Interface Analysis*, **18**, 509(1992)
- (5) M.Yoshitake & K.Yoshhara, *Vacuum*, **51**, 369(1998)
- (6) M.Yoshitake, Y.R.Aprana & K.Yoshihara, J.Vac.Sci.Technol. A 19(4), 1432(2001)
- (7) M.Yoshitake, Y.-R. Aparna & K.Yoshihara, J.Vac.Sci.Technol. A 19(5), 2612(2001)
- (8) D.R.Gabe, J. Iron & Steel Inst., April Issue p.118(1967)
- (9) D.R.Gabe, J.Iron & Steel Inst., May Issue p.1(1967)
- (10) L.R.Beard, D.R.Gabe & L.M.Warner, *Trans.Inst. Met. Fin.* **49**, 63(1971)
- (11) D.W.Ashall, D.J.Burr & J.A.Crossley, J.Iron & Steel Inst., November Issue p.1126(1967)

- (12) H.Takano, H.Kagechika, .yomura & T.Hara, *Proceeding of Third International Tinplate Conference*, London Oct.15th-19th, p.201(1984)
- (13) H.Moriyama, N.Shimizu, T.Fujimoto, Y.Nomura & I.Onoda, *Proceeding of Third International Tinplate Conference*, London Oct.15th-19th, p.214(1984)
- (14) K.Mochizuki, H.Nakakouji, H.Ogata, T.ichida & T.Irie, *Proceeding of Third International Tinplate Conference*, London Oct.15th-19th, p.227(1984)
- (15) H.Kanematsu, T.Kobayashi & T.Oki, Proceeding of AESF Suf/Fin 2000, June 26th-29th, p.75(2000)
- (16) H.Kanematsu, T.Kobayashi & T. Oki, J. Jpn Heat. Treatment Soc., 41, 93(2001)
- (17) H.Kanematsu, T.Kobayashi, T.Oki, J.Jpn, Surface Finishing Soc., 51, 116(2000)
- (18) H.Kanematsu et al, US Patent Application Serial No.09/862, 711(2001
- (19) H.Kanematsu et al, US Patent Application Serial No.09/862,711
- (20) H.Kanematsu et al, Japan Patent Application Serial No. 2000-323631 (2000)
- (21) H.Kanematsu et al, Japan Patent Application Serial No. 2000-377157 (2000)