# Sn-Zn Alloy Films Produced by HSSL And Their Environmental Characteristics

*Hideyuki Kanematsu*[1]*, Kazufumi Murata*[1]*, Akiko Ogawa*[1]*, Yasuyuki Miyano*[2]
*1: Suzuka National College of Technology, 2:Akita University*

Recently it is very often pointed out that cadmium and nickel plating have some problems in terms of environmental friendliness. The alloy film of tin and zinc can be one of the substitutes for some applications. In this paper, the alloy film by HSSL process was produced and the alloying behavior was investigated, by XRD and SEM. As for the environmental characteristics, the dissolution characteristics of the films in aqueous solutions and eco toxicity were investigated. All of these data and the application in the future were discussed from the environmental friendliness, being compared to other plating.

For more information contact:
Professor Hideyuki Kanematsu, Ph.D. FIMF
Dept. MS & E.
Suzuka National College of Technology
Shiroko-cho, Suzuka, Mie 510-0294, Japan
Voice/FAX: +81-59-368-1849
Email: kanemats@mse.suzuka-ct.ac.jp
Web: http://www1.mint.or.jp/~reihidek/

## INTRODUCTION

Nickel Plating has been used extensively, due to its good anti-corrosion and favorable color tone(1). However in recent years, the close relation between the plating and some environmental problems such as dermatitis (Nickel Dermatitis), cancers etc. are pointed out very often(2). One of the recent problems is the application of nickel plating to water outlets. The inner part of the outlets is often plated with nickel and the nickel element dissolves into the tap water to some extent, inevitably. According to WHO's reference regulation standard(3), 0.02mg/L is allowable for potable water. However, it is sometimes difficult to regulate the nickel content in portable water under the limitation. From the viewpoint, the alternative for nickel plating is required. As one of the alternatives, Tin-Zinc alloy plating can be mentioned. In this study, the authors focused on Tin-Zinc Alloy film produced from the stacked single layers of tin and zinc through heat treatment(4)-(8), and the correlation between the surface structures and some film properties such as dissolution characteristics and cell toxicity was discussed.

## EXPERIMENTAL

### *Specimens and bath*

Commercial electrogalvanized steel (substrate: carbon steel JIS SS400) was cut down to 10mm x 10mm coupons by a sheering machine (SHS3x125, Komatsu Co.) The lead wire was attached to a plane of the specimen and the other planes were coated by an organic paint and insulated electrically to be prepared for the following tin-plating process. The bath used for the tin plating was composed of tin sulfate (15g, Wako Pure Chemical Industries Ltd.), sulfuric acid (30g, Wako Pure Chemical Industries Ltd.), cresolsulfonic acid (30g, Yamato Kasei Co.), beta-naphtol (0.3g, Wako Pure Chemical Industries Ltd.) and gelatin (0.6g, Wako Pure Chemical Industries) and the total amount was 300ml.

### *Plating Process*

Tin plating was applied to the electrogalvanized specimens at a certain current density. Current densities used in this study were 50A/dm$^2$, 100A/dm$^2$,

$150 A/dm^2$. The bath temperature was 25 degrees Celsius (deg C) and the plating times were 60s and 120s. By combination of these conditions, 6 types of tin-zinc specimens were prepared in advance to fix the appropriate plating conditions.

### *Heat Treatments*

Stacked single layers specimens of tin and zinc were heat treated in a muffle furnace (Yamato FP31). The heat treatment temperatures were 250 deg C, 350 deg C and 450 deg C. The heat treatment time was one hour. The atmosphere was not regulated and the heat treatment was carried out in an ambient atmosphere.

### *X-ray diffraction analysis (XRD)*

The surface structures of all specimens were investigated by X-ray diffraction analysis. The X-ray diffractometer used in the series of analyses was RINT 2100 (Rigaku Denki Co.). Copper was used as X-ray tube. X-ray voltage was 40kV, X-ray current was 20mA. The diffraction angle was changed from 20 to 100 degrees and the scan rate was 2 degrees / min.

### *Quantitative analyses of surface elements*

Elements in the surface layers of all specimens were analyzed by SEM (Hitachi S-4300) – EDX (Horiba EMAX 7000). The specimens’ surfaces were irradiated by electron beam (acceleration voltage: 20kV) and the characteristic X-rays were analyzed and the elements were identified.

### *Electrochemical measurements*

Polarization behaviors for all specimens were measures mainly by the combination of a potentiostat (Hokuto Denko HA-301) and a function generator (HB-111). The specimen was used as the working electrode, the helical form platinum wire as the counter electrode and silver/silver chloride electrode as the reference electrode. These three electrodes were immersed in the test solution (0.6 mol/l NaCl solution) and the terminals were connected to the potentiostat. The potential was moved at a constant rate (10mV/sec) by the function generator. The potential and current was recorded by a digitized recorder (Hioki 8420) and the polarization curve was made by an application software on PC (Origin Ver.8).

And in addition, the dissolution extent of the surface elements was measured in usual tap water (in Akita City, Akita, Japan) by polarization resistance method. In the latter case, the polarization resistance was recorded at a certain interval for 24 hours. By using the value of measured rest potentials, the specimens were polarized anodically at the scan speed of 1 mV/sec within ±20mV around the rest potential. The change of the current was recorded every second.

## Cytotoxicity test

The specimens were put into a glass beaker, covered by aluminum foil and sterilized by a process of streaming under pressure at 121 deg C for 15 minutes. And then they were put into a sterilized centrifugal tube filled with 5ml MEM culture media containing 5% fetal bovine serum (FBS) in a clean bench and the heat was kept at 37 deg C in 5% $CO_2$ gas.

V79 cells were dispersed into MEM culture media with 5% bovine serum, and the amount of 5ml was disseminated into each of 12 Well Plates, respectively. All of them were cultivated at 37 deg C in 5% $CO_2$ gas for one day. After the 24 hours long cultivation, the culture media was disposed and the new culture media of 1ml dealing with specimens were added into the Well Plates. After the cultivation at 37 deg C in 5% $CO_2$ gas, the V79 cells were stained with Giemsa solution.

## RESULT AND DISCUSSION

### *Electroplating condition & XRD result*s

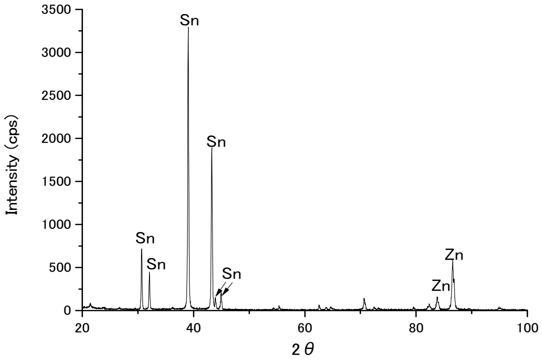

Fig.1 XRD result for the stacked single layer specimen without heat treatment.

The tin plating was produced by all of the plating conditions mentioned in EXPERIMENTAL and the film conditions were checked and compared with each other. Cresolsulfonic acid was absolutely necessary for adhesive film formation. All trials for tin plating indicate that the most appropriate and favorable plating condition was 150A/dm$^2$ for plating current density and 60 seconds for plating time. And the plating films for the following various tests were prepared by using these conditions.

Fig.1 shows the XRD result for the tin plated electrogalvanized specimen without heat treatments. The vertical axis corresponds to X-ray intensities and the horizontal one to diffraction angles as well as those in other XRD results. In Fig.1, all peaks were composed of tin and zinc. Tin was the most remarkable, and the tendency corresponded with the fact that tin was the over layer on zinc one and that the top layer was the most detectable, since X-ray beam was irradiated on the specimens' surfaces. On the other hand, zinc peaks were weak, since the zinc phase was the inner layer under the tin phase. However, they were measured to some extent and the peak intensities were relatively high. The XRD result confirmed that the stacked single layers of tin and zinc were produced on steel specimens.

Fig.2 shows the XRD result for the stacked single layers specimen heat-treated at 250 deg C for one hour. The XRD diagram was also composed of tin and zinc like that in Fig.1. However, the most remarkable peak was not tin, but zinc one. And the X-ray intensities of tin tended to become weak relatively. The tendency suggests that the tin and zinc diffused into another layer mutually, due to the heat treatment and also that the alloying film formation began at this heat treatment temperature.

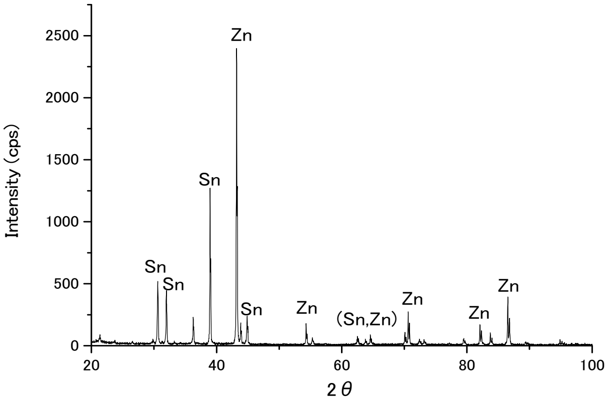

Fig.2 XRD result for stacked single layers specimen heat treat at 250 deg C.

Fig.3 shows the XRD result for the stacked single layers specimen heat treated at 350 deg C for one hour. The peaks were composed of tin, zinc and the solid solution of these elements. The peak intensities for all these phases became low as a whole. It suggests that the fine solid solution

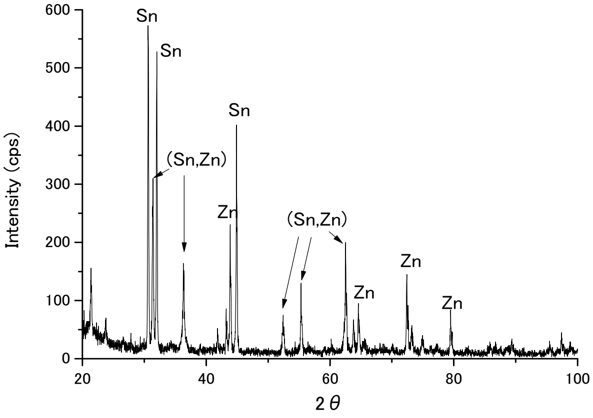

Fig.3 XRD result for stacked single layers specimen heat treated at 350 deg C.

phases of tin and zinc would have been produced. And the intensity of zinc peaks was higher than those of other peaks relatively. The tin and zinc peaks in the figure correspond to the non-reacted phases which were remained as single phases in the surface layers. All of these results in Fig.3 suggest that alloying film formation process proceeded further than the situation in Fig.2. And at the same time, the figure indicates that the surface films were composed of solid solution phases of tin-zinc and those single phases remained without any reactions.

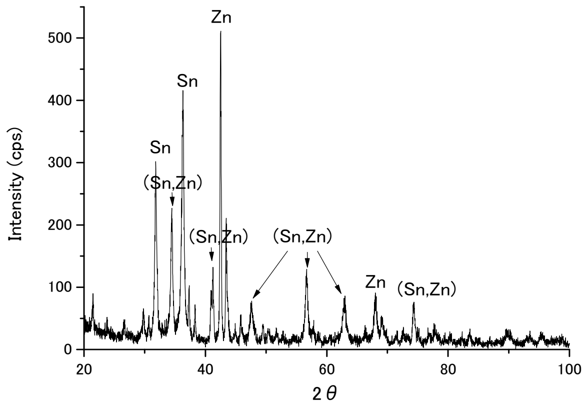

Fig.4 XRD result for stacked single layers specimen heat treated at 450 deg C.

Fig.4 shows the XRD result for the stacked single layers specimen heat treated at 450 deg C for one hour. Also in this figure, the peaks were composed of tin, zinc and the solid solution phase, as well as in Fig.3, and the peak tendency was almost the same with that in Fig.3. However, the peaks for the solid solution phases of tin and zinc became more remarkable than those in Fig.3. It suggests that the thermal diffusion process for alloy film formation proceeded further with the increase of heat treatment temperature.

*Element analysis by SEM-EDX*

Fig.5 shows the results of quantitative element analyses in surface layers of specimens by SEM-EDX. The vertical axis corresponds to the concentration ratio of zinc to tin and the horizontal one to the type of specimens. The numerical values on the vertical axis were the average for the results at many random points in the vicinity of the surfaces. For the specimen without any heat treatments, the ratio was very low and it corresponds with the result and speculation in Fig.1. Since the top layer was tin phase and any thermal diffusion did not occur in this case, the zinc was not found for this specimen seriously. For the specimen heat treated at 250 deg C, the ratio increased and it indicates that the zinc moved from the inner part of the surface layer to the outer one by thermal diffusion. For the specimen heat treated at 350 deg c, the ratio became smaller than that at 250 deg C, even though the ratio was much higher than that without any heat treatment. And for the specimen heat treated at 450 deg C, the ratio was very large and it indicates the clear tendency that the alloying film formation process proceeded with the increase of heat treatment temperature by the zinc diffusion from the inner to the outer surface.

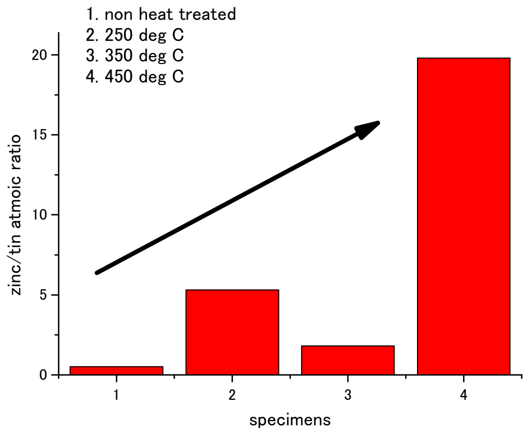

Fig. 5 Zinc/tin atomic ratio measured by SEM-EDX for all specimens.

*Dissolution behavior*

The dissolution behaviors for all specimens were measured mainly by cyclic voltammetry. The potential was scanned from the rest potential (which ranged from -0.95 to -1.05V) to a certain cathodic one (-1.5V) and then scanned back in the anodic direction until the current increased abruptly over the full scale of 10mA. The anodic polarization curves from -1.5V to the final noble end for all specimens were shown in Fig.6, 7, 8 and 9. For all figures, the vertical axis corresponds to the current densities and the horizontal one to the potential versus Ag/AgCl reference electrode.

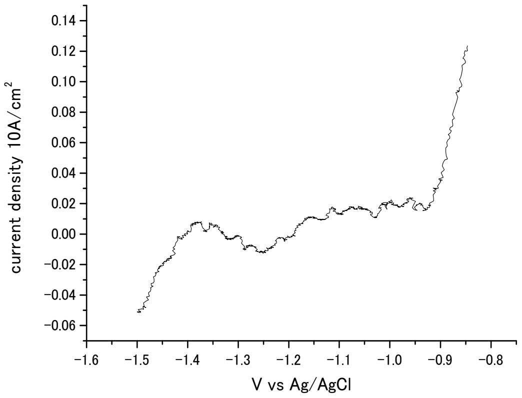

Fig.6 Polarization curve of non heat treated specimen.

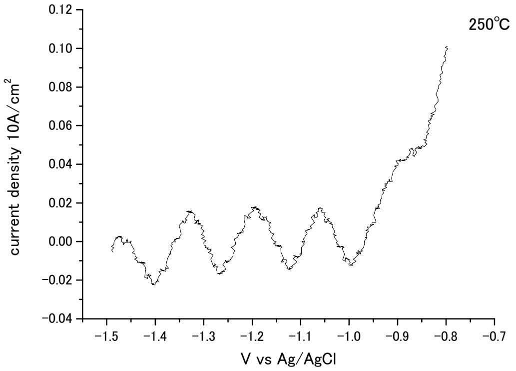

Fig.7 Polarization cuver of the specimen heat treated at 250 deg C.

Fig.6 shows the polarization curve for the specimen without any heat treatments. The steep increase of current density was observed at -0.9V in the figure, which suggests the dissolution of film components. The top of the surface layer in this case was tin. Therefore, the current increase had to include the dissolution of tin layer. However, the potential of initial current increase was much less noble than the equilibrium potential of tin dissolution. Therefore, we assume that the initial current increase was caused by the zinc dissolution. Usually, zinc was covered by the outer tin layer almost perfectly. Therefore, the current increase at about -1.0V which corresponds to the zinc dissolution could not be observed. However, it dissolved at nobler potentials through micro pores and micro detects of the outer tin layer. The initial increase could be explained due to a sort of retardation by the tin coverage effect in this case. However, in the nobler potentials, tin also dissolved and contributed to the increase of the current with the increase of potential.

Fig.7 shows the polarization curve of the specimen heat treated at 250 deg C. In this case, the initial steep increase of current density was observed at -1.0V. It corresponded to the dissolution of zinc which diffused to the vicinity of surface layer from the inner part. At about -0.8V, the small shoulder was found, which corresponded to the dissolution of tin phase.

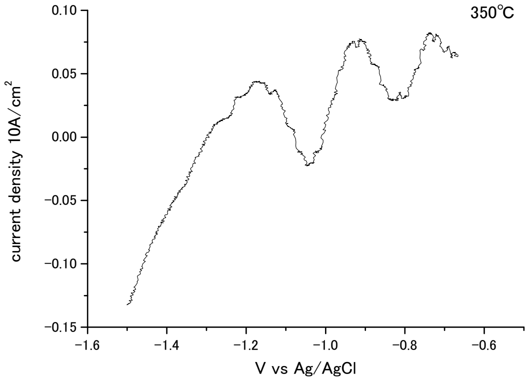

Fig.8 Polarization curve of the specimen heat treated at 350 deg C.

Fig.8 shows the polarization curve of the specimen heat treated at 350 deg C. Also in this case, the steep current increase was found at about -1.0V and the dissolution of surface zinc element was also confirmed. And also in this case, another current increase at about -0.8V was also observed. However, the current was inhibited and it began to decrease at a certain potential with the noble shift of the potential. We assume that the inhibition effect would have been caused by the formation of zinc hydroxide film after the dissolution of zinc phase. Zinc hydroxide was originally a kind of corrosion product. However, the formation inhibited the

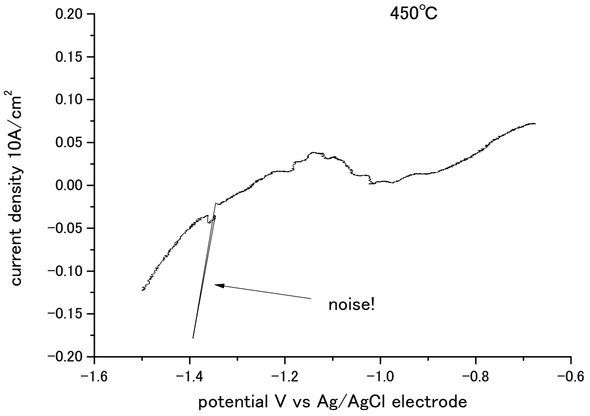

Fig.9 Polarization curve of the specimen heat treated at 450 deg C.

following dissolution of the surface layer due to the barrier effect of the corrosion product. Zinc hydroxide is generally well known as one of zinc corrosion products in neutral aqueous solution. It is sometimes called “white rust”. And actually, the specimen’s surface was covered with a white corrosion product after the anodic polarization. From the viewpoint, we can conclude that the specimen heat treated at 350 deg C have the corrosion resistance to some extent.

Fig.9 shows the polarization curve of the specimen heat treated at 450 deg C. The specimen also showed the two step dissolutions at -1.0V and -0.8V, respectively. However, the dissolution was inhibited by the formation of zinc hydroxide also in this case.

Fig.10 shows the change of polarization resistance for specimens in tap water. When we come to have a close look at the difference among specimens, we could observe that the specimen heat treated at 250 deg C showed the increase of polarization resistance after two days immersion, even though the specimen without any heat treatments did not show such a change. The resistance increase after a certain time passed suggests that the protective corrosion products formed in the time frame to enhance the corrosion resistivity. And it also suggests that the solid solution of tin and zinc accelerated the formation of corrosion product due to its heterogeneous electrochemical characteristic.

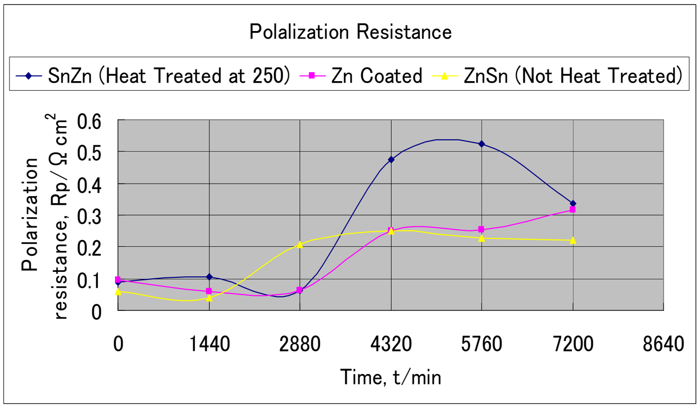

Fig.10 The change of polarization resistance for specimens.

From all of these results, we can conclude that the alloy film produced from stacked single layers of tin and zinc through heat treatment could enhance the corrosion resistance of the substrate steel.

### *Cytotoxicity*

After the cultivation of V79 cells in Well Plates, the specimens showed different characteristics for Giemse stain. When the solution containing V79 cells is stained by Giemse solution, it generally means that the cells are still alive and that the added solution containing the metallic elements can be judged as toxic. For the solution dealing with tin plating, V79 cells continued alive, while they died and did not show any stain for that dealing with zinc plating. The results indicate that tin is non-toxic and also that zinc is toxic. V79 cells in the solutions dealing with various heat treated specimens showed different behaviors for Giemse stain, which corresponded with the alloying formations and zinc diffusion from the inner layer to the outer one.

## CONCLUSIONS

The alloy film formation of tin and zinc on steels was investigated from the stacked single layers through heat treatment. The structures after the treatment was analyzed by XRD and SEM-EDX. And the corrosion characteristics of the surface layer and the cytotoxicity were investigated. The following results were obtained.

(1) When the stacked single layers of tin and zinc was heated to 250 deg C – 450 deg C, tin and zinc single layers reacted each other to form mixed phases on the surface of the specimens.

(2) The surface layers after the heat treatment were composed of the solid solution film of tin-zinc, tin single phase and zinc one as non-reacted phase.

(3) Zinc in the inner layer diffused into the outer layer of tin when the heat was applied.

(4)Due to the formation of solid solution phase, the corrosion resistance in NaCl solution increased.  We presume that the reason could be attributed to the formation of zinc hydroxide as corrosion product of zinc.

(5) Cytotoxity changed with the heat treatment, since the zinc behavior in the vicinity of the surface changed with it.

## REFERENCES

(1) W.H.Safranek: “The Properties of Electrodeposited Metals & Alloys”,2nd ed. AESF, p.253 (1986)

(2) The International Programme on Chemical Safety: Environmental Health Criteria 108, p.383 (1991)

(3) WHO’ Web page: http://www.who.int/water_sanitation_health/dwq/chemicals/nickel/en/

(4) Hideyuki Kanematsu, Hisakazu Ezaki, Naoko Yanagi, Takeo Oki: Proceedings of SFIC Sur/Fin 2005,  June 13-16, 2005, St. Louis, Missouri, USA, p.401-p.411 (2005)

(5) Hideyuki Kanematsu, Hajime Ikigai & Michiko Yoshitake: Journal of Applied Surface Finishing, vol.2(No.1), p.43-p.46

(6) Hideyuki Kanematsu, Hajime Ikigai and Michiko Yoshitake: 2007 SUR/FIN Proceeding, National Society of Surface Finishing, Cleveland, USA, August 13-15, 2007, p.233-242 (2007)

(7) Hideyuki Kanematsu, Aiko Nakao, Michiko Yoshitake: 2007 SUR/FIN Proceedings, National Society of Surface Finishing, Cleveland, USA, August 13-15, 2007, p.253-p.261 (2007)

(8) Hideyuki Kanematsu, Aiko Nakao and Michiko Yoshitake: Journal of Applied Surface Finishing, Vol.2(No.4), p.308-p.311 (2007)