Corrosion Characteristics of Alloy Films Produced By HSSL Process

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Sn-Ni alloy film has been investigated as a substitute for Chromium plating. Any process relating to it has utilized only alloy electro-deposition, however, even though it was very hard to find the best deposition condition. On the other hand, we have developed a new process for alloy film formation where alloy films can be produced from the stacked single layers through heat treatment. In this study, we investigated the corrosion characteristics for different Sn-Ni films produced by the new process. The corrosion test was done by cyclic voltammetry, mainly. The results for Sn-Ni alloy films were compared with other conventional plating films (such as chromium plating etc).

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INTRODUCTION

Environment-friendly engineering and technology is required nowadays, and in the plating field, various processes are going to come under review(1). Many environment protection laws and codes like ELVs Directive (Directive 2000/53/EC on the end of life vehicles) will be much stricter for platers and surface finishers in the future(2). Thus, conventional environment harmful metals for plating such as lead, cadmium, or hexavalent chromium will be partially or fully prohibited. However, since these harmful elements are very useful and have a high performance, useful substitutes should be urgently found and established. Alloy plating is one of the many substitute processes proposed so far.

Particularly for chromium plating as well as nickel-cobalt alloy, nickel-tin alloy are substitutes(3),(4). Conventionally, alloy films have been made by alloy deposition from aqueous solutions electrochemically. However, we proposed forming these alloy films by the Heating Stacked Single Layers Process (HSSL)(5)-(14). In this experiment, we investigated the corrosion characteristic of nickel-tin film produced by HSSL process and the results were compared with other conventional high anti-corrosive films, using cyclic voltammetry.

HSSL PROCESS

As already mentioned above, alloy plating has utilized co-electrodeposition of the components constituting ally films for its production. Alloy electrodeposition is useful process for the production of different alloy films. However, it sometimes requires a certain combination of chemicals, to make the simultaneous electrodeposition possible, and these may be very harmful for the environment. In addition, the produced films may be unstable thermodynamically, since non-equilibrium phases can be often produced by co-electrodeposition. It may lead to some changes of the products' properties during services. From this background, we proposed a new process called HSSL process, composed of two main steps. The first is a series of deposition processes in aqueous solutions where the multilayers are produced, and the second is heat treatment. Fig.1 shows the schematic illustration of this process, Fig.2 illustrates the conventional electrodeposition schematically, and table 1 shows the comparison between HSSL and the conventional processes. In the HSSL process, element A and B are produced sequentially by a two-step electrodeposition. The stacked single layers are heat treated to produce an alloy film composed of element A and B. Compared with the conventional process in which the deposition occurs simultaneously, HSSL is more complex because of its many steps. However, HSSL doesn't depend on chemicals for the

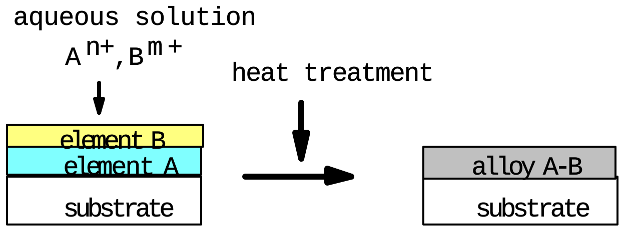

Fig.1 Principle of HSSL process

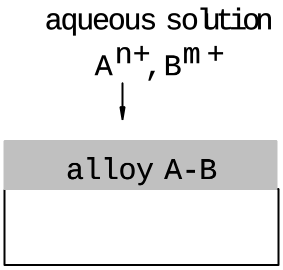

Fig.2 Conventional alloy electrodeposition

production of alloy films, but on materials factors such as heat treatment times and temperatures driving diffusion phenomena between stacked single layers, thus it is much more convenient and easy to use. We have proposed Sn-Ni alloy film as a substitute for chromium plating and Sn-Zn alloy film as a substitute for cadmium plating by HSSL process so far. In this paper, we focused on the former. We confirmed that the color tone of the alloy films is dark gold and that the maximum Vickers hardness was about 800. However, the corrosion characteristics have not been investigated so far, thus, we measured them electrochemically in this paper.

Table 1 Comparison between HSSL and conventional alloying deposition

	HSSL	Conventional process
merits	1. Since the alloying occurs through heat treatment, environment-friendly chemicals can be selected. 2. Produced films are stable thermodynamically.	1. Alloying can occur through a single step process. 2. Characteristics of alloy films can be controlled by electrochemical factors.
demerits	1. Processes become complicated.	1. Chemicals are restricted. 2. Produced films are often unstable thermodynamically.

EXPERIMENTAL

Stacked single layers of tin and nickel were produced on steel specimens by Hatsumec Co. (Kuwana, Mie Pref. Japan) and used in this experiment. The film thickness of each layer was exactly 10 micrometer (3.94 10^{-4} inch). The specimens were heat treated at 623K (350C, 662F) and 823K (550C, 1022F) for three hours. In addition to the two kinds of HSSL specimens, a chromium plated steel specimen, zinc-nickel plated steel specimens with chromate coating and without chromate coating, tin-zinc plated steel specimens with and without chromate coating, and tin-zinc plated steel specimens with and without chromate coating, were used as reference.

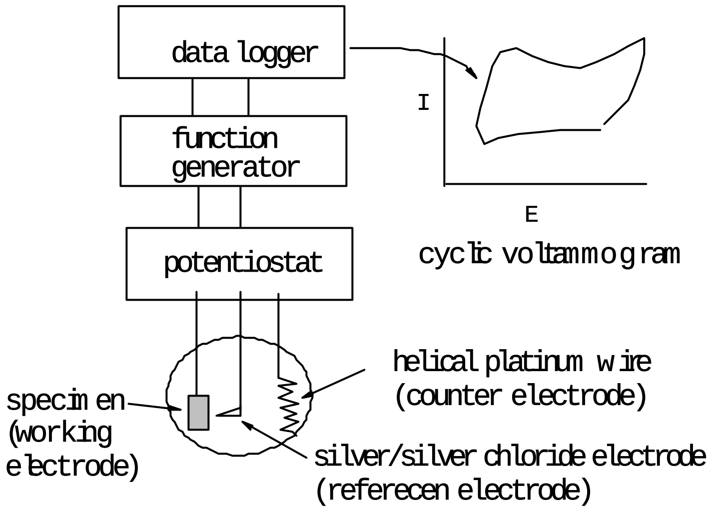

Fig.3 Schematic diagram of experimental appratus

Corrosion characteristics were measured and evaluated, using cyclic voltammetry. The procedure for the measurement was carried out as follows. Small Sheets (10mm x 10mm, thickness 0.6mm; 39.4in x 39.4in, thickness 0.024in) were cut from the larger specimens. All of them were connected by a lead wire and all surfaces of each specimen except for one used as an electrode were coated with epoxy resins and subjected to electrochemical measurements. Fig.3 shows the block diagram of the experimental apparatus used in the present investigation. Specimens were used as the working electrode. Platinum in a helical form was used as the counter electrode with silver/silver chloride (Ag/AgCl/3.3kmol m^{-3} KCl) as the reference electrode. (All potentials in the present paper are described on the basis of the reference electrode.) The cell was constituted by the three electrodes connected to a potentiostat (Hokuto Denko HA303) and cyclic voltammograms were measured. Sodium chloride solutions were used at 0.6kmol/m^3 as the test solution and were not deaerated. The temperature of the solutions was maintained at 298K (25C, 77F) during the measurements. The potentials of these specimens were scanned with a function generator (Hokuto Denko HB)

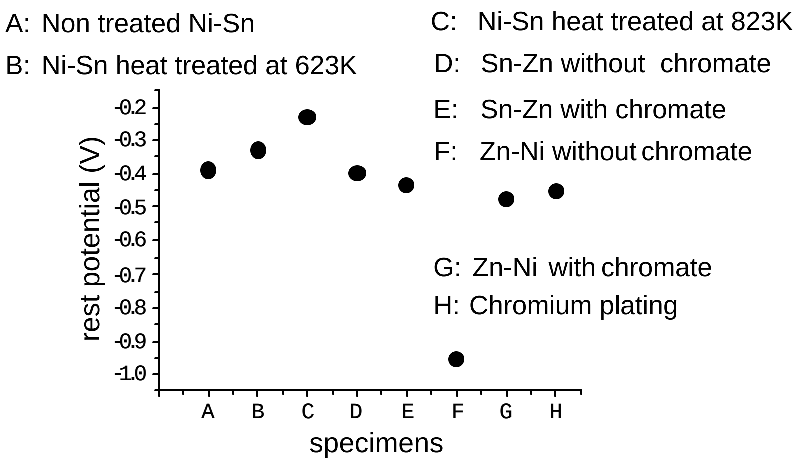

Fig.4 Rest potentials of specimens used in this experiment

connected to the potentiostat. Scan rate was kept at 10mV/sec. The procedure of cyclic voltammetry was as follows. Firstly, the rest potentials were measured at 1.2ks after immersion. Then the potential of the specimens was scanned at a constant rate from the rest potentials to the hydrogen evolution potential (-1.2ks) cathodically to eliminate the surface oxide films formed in the air, and then scanned again anodically. The current and potential data were recorded by a data logger (Hioki 8051) and the current-potential curves were made using an application software (Origin ver.7) on personal computers.

RESULTS AND DISCUSSION

Fig.4 shows the rest potentials of all specimens used for this experiment. The rest potential of the Ni-Sn plated specimen without heat treating (spec.A) was about –0.4V. It moved in the noble direction with heat treatment. That of the Ni-Sn plated specimen heat treated at 623K (350C, 662F) (spec.B) was –0.33V, while that heated at 823K (550C, 1022F) (spec.C) was –0.23V. In our previous studies, we confirmed that some intermetallic phases between nickel and tin, such as Ni_3Sn_4, Ni_3Sn_2 and Ni_3Sn were produced through the HSSL process. Therefore, these intermetallic layers between nickel and tin had higher noble rest potentials inherently and the formation of these layers made them move in the noble direction. The rest potentials of tin-zinc plated specimens both with and without chromate coating (spec.D & E) were about –0.4V. Since these films were composed mostly of tin, it reflected on the rest potential of the specimens. The rest potential of zinc-nickel plated steel specimen without chromate coating (spec. F) was the least noble. The surface film of the specimen was composed mostly of zinc and the nickel content was very low according to SEM-EDX analysis. Therefore, the rest potential was very close to that of pure zinc film. However, the rest potential for the chromate coated zinc-nickel film (spec.G) was much nobler than the non chromate specimen. The rest potential for the chromium plated specimen (spec.H) was –0.45V and very close to other chromate coated specimens.

Fig.5 shows a part of cyclic voltammograms for the Ni-Sn plated specimen without heat treatment. The curve was the result when the potential was scanned from –1.2V to 0V. Three peaks were found in the diagram. The peak at –0.9V corresponds to the dissolution reaction of the top tin layer, the broad current peak from –0.6V to –0.4V corresponds to the dissolution of nickel layer, and the current increase at –0.4V corresponds to the anodic dissolution of substrate iron. Stacked single layers of tin and nickel dissolved separately at their own characteristic potentials. Fig.6

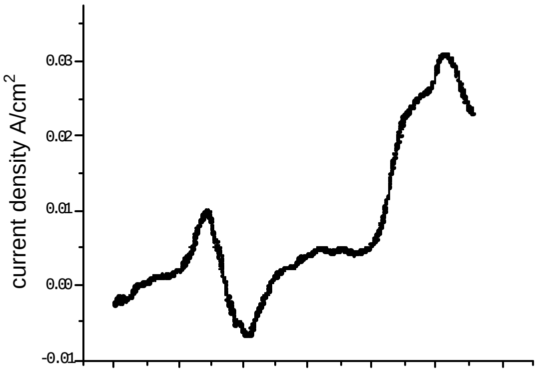

Fig.5 a part of cyclic voltammogram for Ni-Sn plated specimen without heat treatment.

shows a part of CV for Ni-Sn plated film heat treated at 623K (350C, 662F). It indicates that no current peaks were found in this diagram and that the current at all potentials were very low. As mentioned above, several intermetallic compounds like Ni_3Sn_2, Ni_3Sn_4 and Ni_3Sn were produced on the surface through heat treatment. Since these intermetallic compounds have higher corrosion resistance, the specimen showed low current densities. Fig.7 shows a part of CV for Ni-Sn plated specimen heat treated at 823K (550C, 1022F).

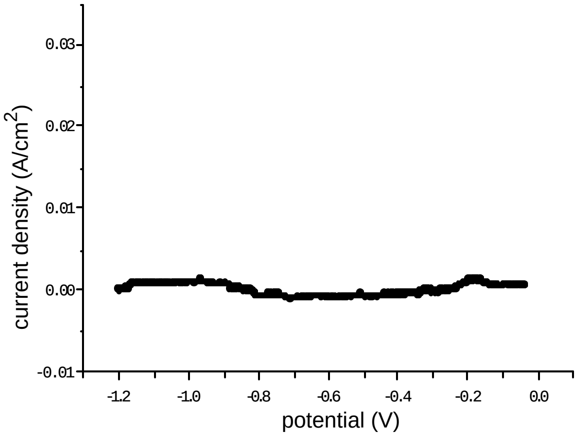

Fig.6 A part of cyclic voltammogram for Ni-Sn plated specimen heat treated at 623K

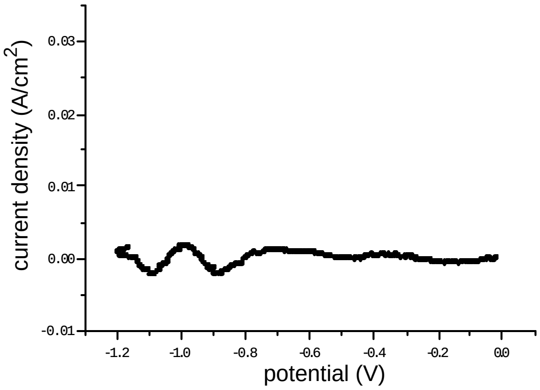

Fig.7 A part of cyclic voltammogram for Ni-Sn plated specimen heat treated at 823K.

Also, for this specimen, the current density was very low in all potential ranges, as well as that in Fig.6. We can conclude that corrosion characteristics increased due to the formation of intermetallic compounds. However, the current densities were more unstable in Fig.6 rather than in Fig.7. It suggests that the surface layers produced at 823K (550C, 1022F) were more corrosive, even though they were relatively anti-corrosive. It can be attributed to the fact that the surface layer produced at higher temperatures is rough at the microscopic level and unstable from the viewpoint of corrosion protection. However, the surface films in Fig.7 were much more stable against corrosion in NaCl solution than the non-treated Ni-Sn plated specimen.

Alloying improved corrosion resistance of stacked single layers for the Ni-Sn plated specimen, as shown in Fig.5-7. It has been originally investigated as a substitute for chromium plating. Therefore, it is very important to compare the corrosion behavior with that of the chromium plated specimen. Fig.8 shows a part of the CV for the chromium plated specimen (spec.H). This figure shows that the chromium plated specimen was very stable and anti-corrosive in the potential range from –1.2V to –0.4V. From that viewpoint, chromium plated specimens have high anti-corrosiveness, which is one of the beneficial characteristics for chromium plating. However, the current density began to increase at –

0.4V and this indicates that the plating film was not stable in the noble potential region from the viewpoint of corrosion protection. Compared with the corrosion behavior for heat treated Ni-Sn specimens, the latter was higher anti-corrosive and it indicates that Ni-Sn alloy film formed by the HSSL process can be a good alternative for chromium plating.

We compared the corrosion characteristics of Ni-Sn alloy film by HSSL with several commercial anti-corrosive plating. Fig.9 shows CV of tin-zinc alloyed film without chromate coating (spec.D), and Fig.10 shows that of the same specimen with chromate coating (spec.E). Fig.9 shows that the Sn-Zn alloy film without chromate coating was stable and anti-corrosive in the potential range between –1.2V and –0.3V. However, the current increased at –0.3V which suggests that the plated film was corrosive in the potential region nobler than –0.3V. SEM-EDX analysis confirmed that tin dominated the film composition. However, the corrosion characteristics of the alloy film of tin and zinc improved more than that of the tin film stacked on nickel layer shown in Fig. 5. From this viewpoint, the Sn-Zn alloy film has very good anti-corrosion

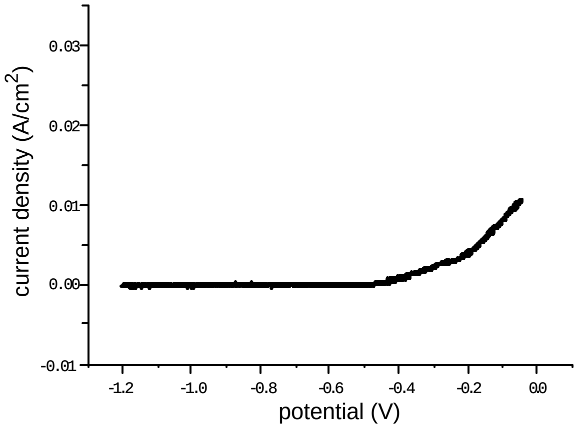

Fig.8 A part of cyclic voltammogram for chromium plated specimen.

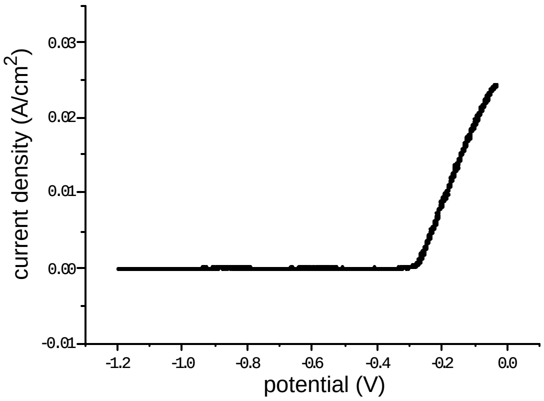

Fig.9 A part of cyclic voltammogram of Sn-Zn plated specimen without chromate coating.

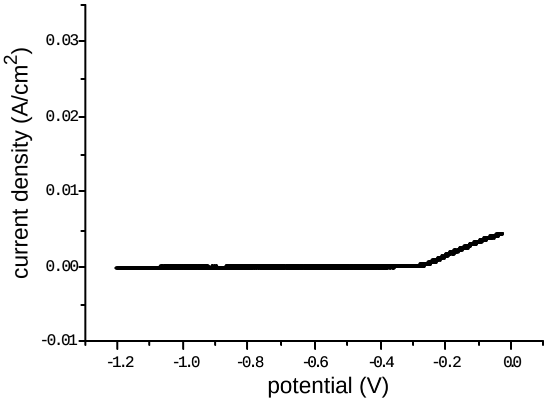

Fig.10 A part of cyclic voltammogram of Sn-Zn plated specimen with chromate coating,

characteristics. However, a comparison between Fig.6, 7 and 9 suggests that the alloy film of nickel and tin formed by the HSSL process has better anti-corrosive characteristics. The chromate coated Sn-Zn film improved the anti-corrosiveness much more as shown in Fig.10. Even though the current increase was observed at –0.3V, the current has been suppressed to a relatively low value due to chromate coating.

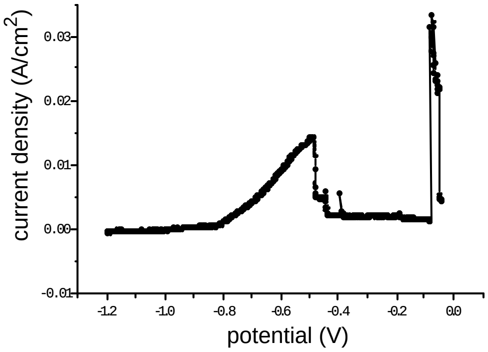

Fig.11 A part of cyclic voltammogram of Zn-Ni plated specimen without chromate coating.

Fig.11 and Fig.12 show parts of cyclic voltammograms for Zn-Ni plated specimens, another anti-corrosive plating. The result for the Zn-Ni plated specimen without chromate coating (spec.F) showed that the current increased at about –0.8V. According to SEM-EDX analysis, the alloy film was composed mostly of zinc and the nickel content is very low (several percent). Since the dissolution potential of zinc is relatively negative (-0.9V to –1.0V), the specimen dissolved at a relatively negative potential of –0.8V. However, the potential was nobler than that of zinc film and it can be attributed to the alloying between zinc and nickel. Another current increase was found at –0.1V, which was caused by the anodic dissolutions of both steel substrate and the oxygen evolution. Chromate coating of the Zn-Ni plated specimen (spec.G) also improved corrosion characteristic as shown in Fig.12. Any current peaks were not observed and it indicates that chromate coating worked well for corrosion prevention.

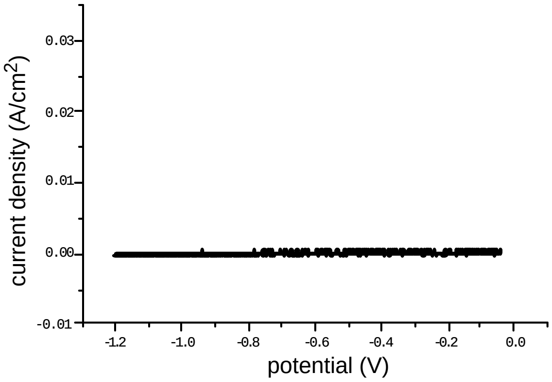

Fig.12 A part of cyclic voltammogram of Zn-Ni plated specimen wtih chromate coating.

All of these results and the comparison between Ni-Sn alloy films produced by the HSSL process and other anti-corrosive plating films indicate that Ni-Sn alloy films by HSSL process have good corrosion resistance against chloride containing environments and that the films were comparative not only to chromium plated film, but also to anti-corrosive zinc plating with chromate coating. Chromate coating is very useful and effective for anti-corrosiveness. However, the production of hexavalent chromium can conflict with various regulations and codes like ELVD (End of Life Vehicles Directive in Europe) in the future.

Unfortunately, the self healing capability is lacking for Ni-Sn alloy plating. However, the intrinsic high anti-corrosiveness of intermetallic compound films between nickel and tin can compliment it with high environmental-friendly production.

CONCLUSIONS

The corrosion characteristics for Ni-Sn alloy films produced by the Heating Stacked Single Layers (HSSL) process were investigated, using cyclic voltammetry in NaCl solution. The Corrosion characteristics for chromium plated steels and several other zinc plated specimens with and without chromate coating were compared to those for Ni-Sn plated steels formed by the HSSL process and the following results were obtained.

(1) Ni-Sn alloy films produced by heating single stacked tin and nickel layers at 623K (350C, 662F) and 823K (550C, 1022F) improved corrosion resistance of the stacked single layers.
(2) Ni-Sn alloy films produced by the HSSL process has higher anti-corrosiveness than chromium plating film.
(3) Ni-Sn alloy films produced by the HSSL process has higher anti-corrosiveness than several anti-corrosive zinc plated alloy films.
(4) The anti-corrosion characteristics of Ni-Sn alloy films produced by the HSSL process were comparative to that of zinc alloy plated steels with chromate coating.

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