Alloying of Stacked Nickel/Zinc Films Through Heat Treatment

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Abstract
Environmental Regulation has become strict year by year and the substitutes for some harmful elements are required urgently in various areas. Alloy plating is one of the candidates as substitute. Nickel-Zinc Alloy Film has been well known for high corrosion resistance. However, the conventional alloy plating requires a certain combination of chemicals and it may lead to another environmental problems such as effluent. Therefore, we investigated another production process for the alloy film through the combination of heat treatment and multi-step plating (HSSL Process). The possibility of alloying was examined by X-ray analysis and SEM-EDX.

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1. INTRODUCTION

Environmental problems have affected the industrial movement recently. The use of some useful elements for anti-corrosive plating such as lead, chromium and cadmium have been regulated more ore less and the substitutes are now required urgently. For the purpose, alloy plating has attracted much attention. However, the chemicals used for the process are often unique combinations of some special ones which make plural elements possible to electrodeposit simultaneously and in many cases, those special chemicals are environment-harmful such as cyanides etc. And in addition, the process often requires delicate and high-tech elaboration. Therefore, the authors have proposed HSSL (Heating Stacked Single Layers) process to produce alloy films[(1)-(5)]. In this unique process, Single phase layers stacked on the materials surfaces are heated to produce alloy films. In this paper, we focused on the Nickel-Zinc alloy films and investigated if the HSSL process could be applied to the alloy film formation.

2. EXPERIMENTAL

2.1 Specimens

Carbon steel (JIS SS400) was used for the substrate. At first, Nickel was electrodeposited on it. The bath for the nickel plating was composed of Nickel Sulfate (240g/L), Nickel Chloride (45g/L) and Boric Acid (30g/L). The specimen was plated at the current density of $1A/dm^2$ in three minutes. Then zinc was deposited electrochemically in the zinc chloride bath (Zinc Chloride 70g/L, Potassium Chloride 45g/L and Boric Acid 30g/L) at the current density of $1A/dm^2$ in three minutes. Specimens having these two stacked single layers were cut into small pieces (10mm x 10mm). These specimens were heat treated in an electric furnace (Yamato Muffle furnace, FP31). The treatment temperatures were 350, 400 and 450 degrees Celsius and the specimens were heated at a certain temperature of them in 1hr, 2hrs or 3hrs. The atmosphere was not regulated specially.

2.2 Analyses

The surface hardness was measured, using Micro-Vickers hardness testing machine (Akashi MVK-E). The load was 100gf. The structure of surface was confirmed by X-ray analysis (Rigaku RINT2100). The target was copper. X-ray voltage and current were 40kV and 20mA, respectively. The diffraction angles measured in these experiments ranged from 30 to 100 degrees at the scan rate of 2 degrees per minute. The cross sections of surface layers were observed also by SEM (Scanning Electron Microscope, Hitachi S-4300)-EDX(Horiba EMAX-7000). In advance, the specimens were embedded into epoxy resin and polished mechanically for SEM observation. The acceleration voltage was 20kV and the current was 1 x 10^{-8}A. Table 1 shows the notations of the specimens and their experimental conditions.

Table 1 Specimens used for this experiment.

	0 hrs	1hr	2hrs	3hrs
Non-heat treatment	#1			
350 degrees Celsius		#2	#3	#4
400 degrees Celsius		#5	#6	#7
450 degrees Celsius		#8	#9	#10

3. RESULTS AND DISCUSSION

Originally, the specimens having two stacked single layers of zinc and nickel had relatively high glossiness. After the heat treatments, the glossiness decreased more or less. The decrease of the glossiness depended on the heat treatment temperatures and times. Concretely speaking, the glossiness decreased with increases of temperatures and times. Since the diffusion reaction of components lead to the concavo-convex surfaces on microscopic level, the glossiness decreased with the heat treatment. At 450 degrees Celsius, the surface color was turned to white because of the zinc oxide formation.

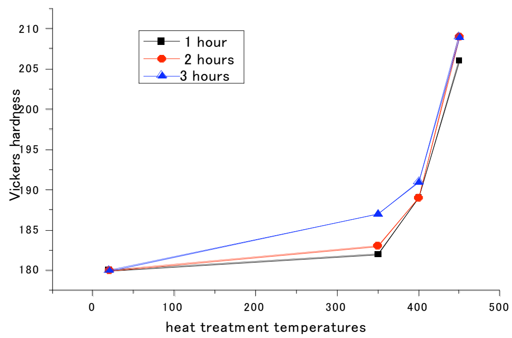

Fig. Vickers hardenss for various specimens.

Vickers hardness was measured by a Micro-Vickers Hardness testing machine. The results were shown in Fig.1. At any heat treatment temperatures, the hardness increased with the temperature, since the solid solution between nickel and zinc was formed in the surface layers. When the temperature was increased to 450 degrees Celsius, the increase of hardness was more remarkable. It suggests that an intermetallic compound was formed at the temperature. For the treatment time, the hardness had the tendency to become higher with the prolonged time. It suggests that the alloy film formation made progress with time.

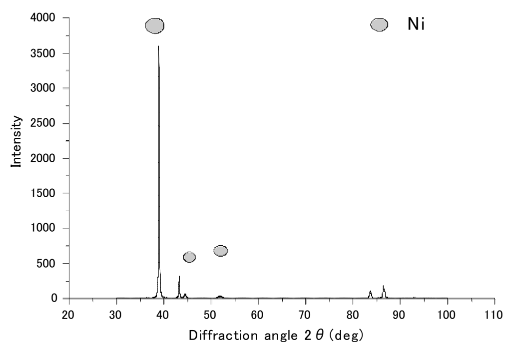

Fig.2 XRD result for non-heat treated specimen.

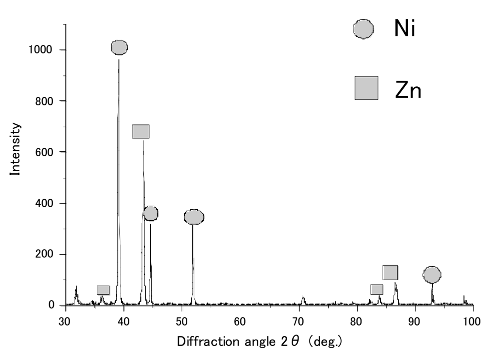

Fig.3 XRD result for the specimen heat treated at 350 degrees Celsius

Fig.2, 3, 4 and 5 show the X-ray results for various specimens. Fig.2 corresponds to the XRD result for non-heat treatment specimen(#1). In Fig.2, nickel peak only was observed, even though zinc was produced on the nickel under-layer. It suggests that the thickness of the upper zinc layer was very small.

Fig.3 shows the XRD result for the specimen heat treated at 350 degrees Celsius in 3 hours. For these figures, both nickel and zinc peaks were observed. Before the heat treatment, nickel peak only was observed. However, both zinc and nickel peaks were observed after the heat treatment at 350 degrees Celsius. The reason could be attributed to the formation of the solid solution film where zinc was dispersed and dissolved in nickel layer.

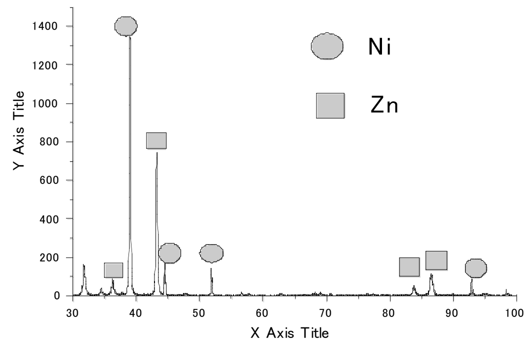

Fig.4 XRD result for the specimen heat treated at 400 degrees Celsius.

Fig. 4 shows the XRD result for the specimen heat treated at 400 degrees Celsius in 1 hour. Also in this figure, both elements' peaks were observed. However, Ni_2O_3 and ZnO_2 were produced in 2hrs and 3 hrs, since nickel and zinc phases were oxidized, respectively.

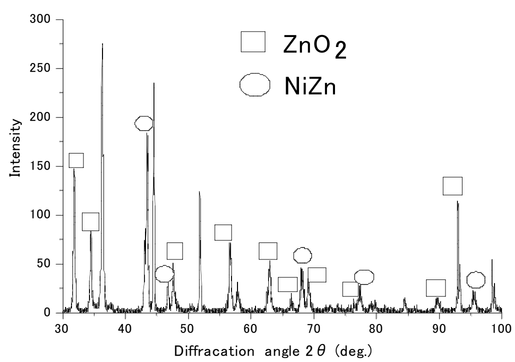

Fig.5 XRD result for the specimen heat treated at 450 degrees Celsius

Fig.5 shows the XRD result for the specimen heat treat at 450 degrees Celsius in 1 hour. This figure indicates that the intermetallic compound, NiZn, was observed. And the zinc oxide was also observed. Since the temperature was over the melting point of zinc, the zinc layer was melted. Then the solid nickel diffused into liquid zinc phase very rapidly to form the intermetallic compound. However, the top of liquid zinc layer was oxidized to some extent and zinc oxide was formed. Table 2 shows the produced phases for various experimental conditions.

Table 2 Produced phases observed by XRD in various heat treatment cases.

	1 hr	2hrs	3hrs
350 degrees Celsius	Ni Zn	Ni Zn	Ni Zn
400 degrees Celsius	Ni Zn	Ni_2O_3 ZnO_2 Zn	Ni_2O_3 ZnO_2 Zn
450 degrees Celsius	NiZn ZnO_2	NiZn ZnO_2	NiZn ZnO_2

The cross sections of surface layers for all specimens were observed and analyzed by SEM-EDX. For the non-heat treated specimen, SEM images show the surface layer was composed of three layers, iron, nickel and zinc phases. However, the thickness of zinc layer was very small and the truth corresponds to the result by XRD shown in Fig.2. The SEM image of the specimen heat treated at 350 degrees Celsius in 1 hour indicates that the nickel diffused in the surface area and enlarged its phase. For the specimen heated at 450 degrees Celsius, the SEM-EDX element analysis showed the nickel image was overlapped with zinc one. All of these results indicate that nickel-zinc alloy films were formed on the steel surfaces by thermal diffusion process.

4. CONDLUSIONS

Nickel and zinc were produced layer by layer on steel surfaces. Then they were heated at various temperatures in a certain time. The surface structures were identified by X-ray diffraction analysis and SEM-EDX. Then the hardness in the surface layer was measured by Micro-Vickers hardness testing machine for all of specimens. The following results were obtained.

(1) X-ray analysis and SEM-EDX results indicate that the alloy films between zinc and nickel could be produced on steel surfaces by HSSL process. Below the melting point of zinc, solid solution films were formed and the intermetallic compound film was formed over the melting point of zinc.

(2) Over the 400 degrees Celsius, the oxides of nickel and zinc were formed, respectively.

(3) The surface hardness increased with heat treatment temperatures. Below the melting point of zinc, the reason could be attributed to the formation of solid solution film between zinc and nickel. Over the melting point of zinc, the hardness could be explained by the formation of intermetallic compound, NiZn.

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