Non-reactive Stacked Surface Layers and Their Heat Treatment Behavior - The Application to Nickel Plating

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Abstract

The Heating of Stacked Single Layers Process (HSSL Process) has many potential practical applications. The process has been investigated so far to find some suitable substitutes for environmentally harmful alloy films, such as chromium, cadmium plating etc. In most cases, the alloy systems which could form intermetallic compounds were chosen to be investigated. However, in this study, we selected the couple elements which could not form any compounds, silver and nickel, to produce stacked single layers on steel specimens. Silver was plated on steel firstly, and then Nickel was. Finally, the heat was applied to the specimens at different temperatures. The surface layers were investigated by X-Ray Diffraction and XPS. The practical application of the phenomenon measured in these experiments to nickel plating was discussed.

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INTRODUCTION

The Heating of Stacked Single Layers Process (HSSL Process[(1)-(7)]) has many potential practical applications. The process has been investigated so far to find some suitable substitutes for environmentally harmful alloy films, such as chromium, cadmium plating etc. In most cases, the alloy systems which could form intermetallic compounds were chosen to be investigated. However, in this study, we selected the couple elements which could not form any compounds, silver and nickel, to produce stacked single layers on steel specimens. When heat would be applied to such a system, what would happen at all? Would silver diffuse into nickel layer or into iron substrate? In this study, HSSL process was applied to nickel/silver stacked layers. For the purpose, the stacked single layers of nickel and silver were formed firstly and then heat was applied to the specimens. And the surface layers changed by heat treatments were observed by XRD and XPS.

EXPERIMENTAL

A commercial silver plated steel specimen (Japan Industrial Standard SS400, the thickness of silver film was 5 micrometers.) was cut into tiny oblong sheets of 10mm x 10mm by a sheering machine (SHS3X125, Komatsu Co.). These specimens were plated with nickel in the following bath. The bath composition was 100g nickel sulfate ($NiSO_4$-$6H_2O$), 15g nickel chloride ($NiCl_2$-$6H_2O$) and 10g boric acid (H_3BO_3), and the total amount of the bath solution was 300mL. The specimens were immersed into the bath at 40 degrees Centigrade and plated with nickel under the current density of $0.2A/dm^2$, by a direct current source (PA36-3A, Kenwood Co.).

Plated specimens were heat treated in an electric furnace (Muffle Furnace FP31, Yamato Co.) in 2 hours. The atmosphere was not regulated. The heat treatment temperatures were 200, 300, 400 and 500 degrees Centigrade. After the heat treatment, the specimens were cooled in the air.

The surface color tone was measured by a colorimeter (Color Reader CR-13, Konica-Minolta). The color tones of the specimens' surfaces based on L-a-b standard were measured for specimens before and after the heat treatments.

The measurement of surface structures was carried out by an X-ray Diffraction Analyses (RINT 2100, Rigaku Co.). Copper was used as electrode. X-ray voltage was 40kV and the current 20mA. The diffraction angle ranged from 20 to 100 degrees and the scan rate was 2 degrees per minutes.

The element profiles in the vicinity of surfaces were measured by X-ray Photoelectron Spectroscopy (XPS). The XPS measurements were carried out using a VG ESCALAB 250 spectrometer (Thermo-Fisher Electron Co.) employing monochromatic X-ray AlK radiation. The applied power was operated at 15kV and

200W. The base pressure of the analysis chamber was less than 10^{-8} Pa. The overview spectra were taken between 0 and 1000eV with an energy step of 1.0eV, while the detailed spectra of the peaks of interest were recorded with an energy step of 0.1eV. Depth profile analysis was carried out using an AR ion gun with 3kV.

RESULTS AND DISCUSSION

Surface Color Tone

The surface color tone for the heat treated specimens was measured by the colorimeter. L values correspond to the surface brightness. "a" values correspond to the extent of redness in the positive direction, while it does to that of blueness in the negative direction. On the other hand, "b" values correspond to the extent of yellowness in the positive direction, while it does to that of greenness in the negative direction. The results indicate that all heat treated specimens decreased L values, which means that the surfaces became irregular on microscopic level through the thermal diffusion process. "a" and "b" values also decreased after the heat treatment. However, the decreases of "a" and "b" were not so remarkable. As a result of heat treatments, the surface color tone became matt and blackish.

XRD Results

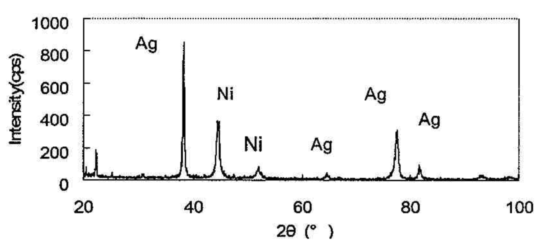

Fig.1 XRD results for non treated spec.

XRD results were shown in Fig.1 - 5. For all these figures, the abscissa axis corresponds to diffraction angle and the longitudinal axis to x-ray intensity. Fig.1 shows the result for the nickel-silver surface layers specimen before heat treatment. The peaks were composed of nickel and silver. They suggest that the non-heat treated specimen had the two single stacked layers of silver and nickel on the surface. Even though the upper layer was nickel, the corresponded peaks were not so strong. It suggests that the amount of nickel plating was not so large.

Fig.2 shows the XRD result for the specimen heat treated at 200 degrees Centigrade. The peaks were also composed of silver and nickel like the result in Fig.1. However, the peak ratio of silver to nickel increased with the heat treatment temperature. It suggests that these atoms moved through heat treatment without the formation of compounds.

Fig.3 shows the result for the specimen heat treated at 300 degrees Centigrade.

In this figure, the peak for the compounds of iron and nickel was observed, even though peaks for silver and nickel were still observed. It suggests that the single layers were consumed to form the intermetallic compound of nickel and iron and that the specimen had three phases in the surface layers, silver, nickel and $FeNi_3$.

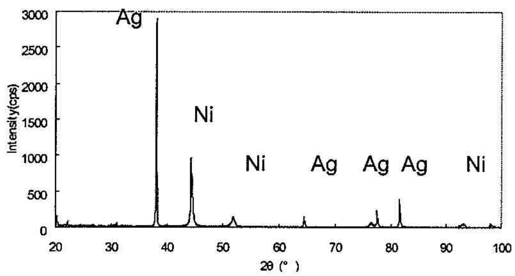

Fig.2 XRD results for the spec. treated at 200C.

Fig.4 shows the XRD result for the specimen heat treated at 400 degrees Centigrade. The peaks were also composed of silver, nickel and the intermetallic compound of iron and nickel. And the peak of the latter became more remarkable, which suggests the increase of intermetallic compound with the temperature. The intensity ratio of silver phase to other ones decreased relatively. It suggests that these three elements, silver, nickel and iron, moved each other through heat treatment in the surface layers.

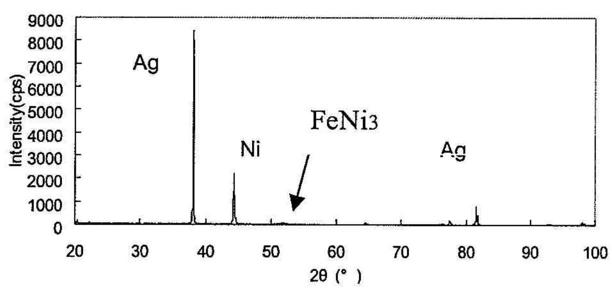

Fig.3 XRD result for the spec. treated at 300C.

Fig.5 shows the XRD result for the specimen heat treated at 500 degrees Centigrade. The tendency for the peak constitution in this figure was almost the same with that in Fig.4. However, the relative intensity of the peak for the intermetallic compound of iron and nickel increased more. It suggests that the formation reaction through thermal diffusion for the intermetallic compound proceeded with the heat treatment temperature.

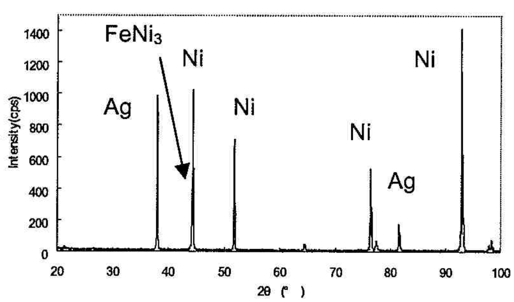

Fig.4 XRD result for the spec. treated at 400C

These XRD results suggest that silver, nickel and iron diffused each other in the surface layers. We carried out the measurements to confirm elements' profiles in the surface layers, by using XPS. The results were shown in Fig.6, 7 and 8. For all these figures, the abscissa axes were sputtering

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times and the longitudinal axes were atomic concentrations.

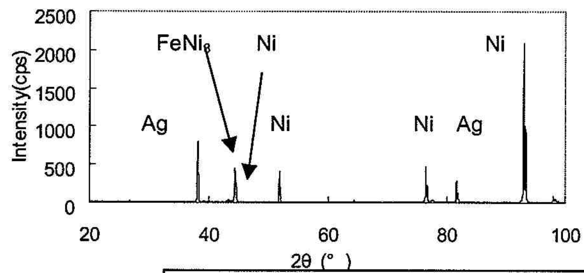

Fig.5 XRD result for spec. treated at 500C

Fig.6 shows the XPS result for the stacked single layers specimen before heat treatment. Nickel content was relatively high in the range of sputtering time, while silver content was uniformly low, even though the latter began to increase at the

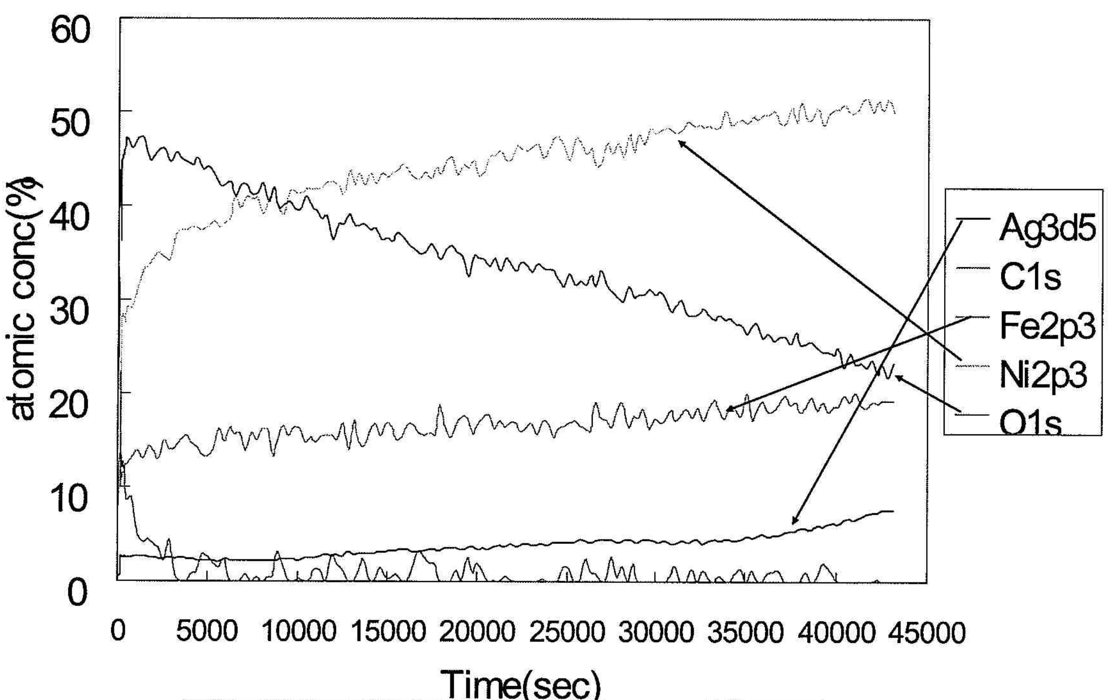

Fig.6 XPS result for non-treated spec.

sputtering time of forty thousands seconds. It suggests that this sputtering range corresponds to the nickel single layer on the silver one. In the surface layer, iron, the substrate element, was also recognized to some extent. The iron could be mixed into the surface layers to some extent during the plating processes. Oxygen was observed at a relatively higher level (about 50%). At the outer surface, oxygen absorbed very strongly. However, it diffused into the inner parts of the specimen through grain boundaries. The concentration decreased with the depth.

Fig.7 shows the XPS result for the specimen heat treated at 300 degrees

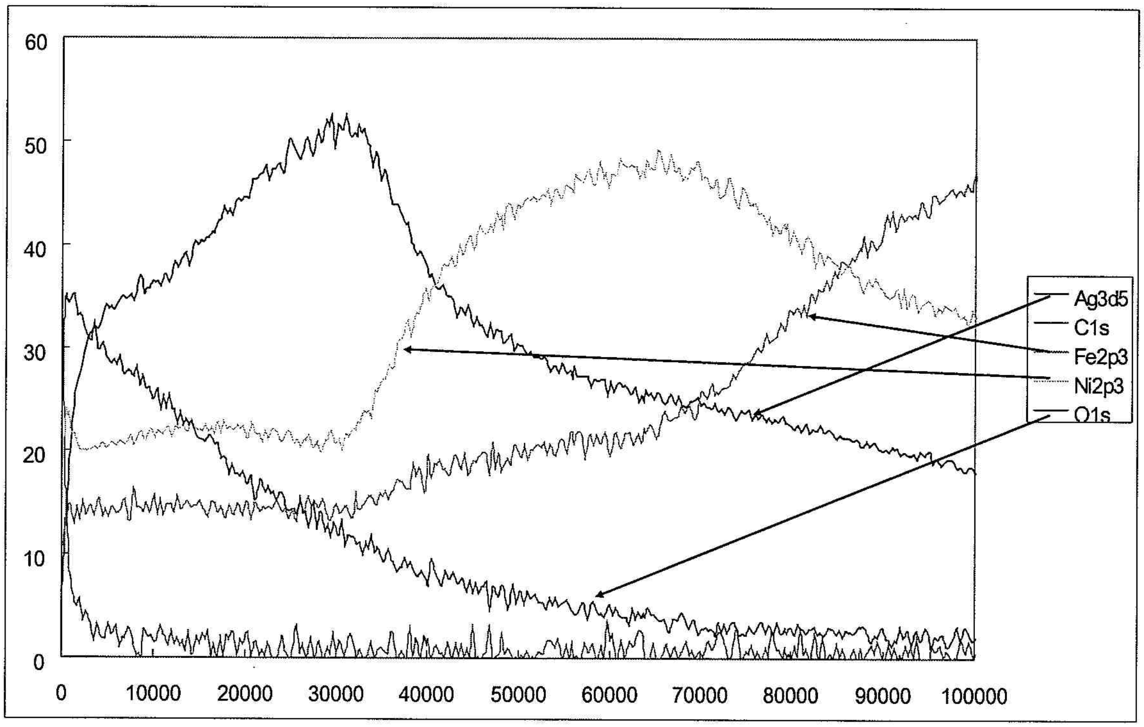

Fig.7 XPS result for spec. treated at 300C.

Centigrade. Oxygen was found at the outer surface also in this case. However, the concentration decreased gradually with the depth. Relatively large amounts of silver could be observed in the range from ten thousands seconds to forty thousand seconds. Due to the heat applied to the specimen, silver diffused from the inner layer to the surface through nickel layer. Since silver does not form any compounds with nickel, it seemed to exist as a single element in the nickel layer. On the other hand, the concentration of iron increased in the range of 35,000 seconds and higher. In the range, large amounts of nickel were also found a lot. As shown in Fig.3, both elements formed the intermetallic compound of iron and nickel in this area.

Fig.8 shows the XPS result for the specimen heat treated at 500 degrees Centigrade. Large amounts of iron and nickel were found in the surface layer. It suggests the intermetallic compound of iron and nickel formed in the area. Iron diffused through the silver layer by heating. It was also found that silver atoms diffused toward the surface through the nickel layer.

From all these results, we can presume how the atoms constituting surface layers in this experiment moved by thermal diffusion. The stacked single layers composed of nickel and silver on steels are formed before heat treatment. When heat is applied

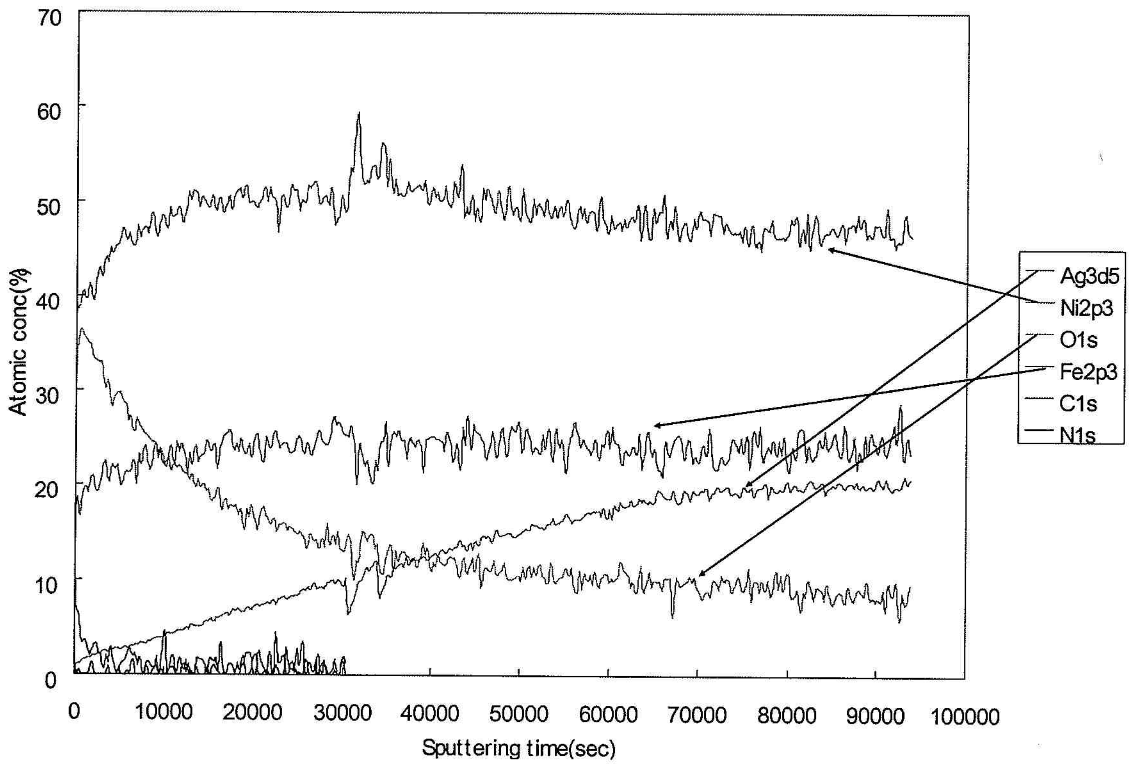

Fig.8 XPS result for spec. treated at 500C.

to the specimen, mutual diffusions occur among the constituents. Iron atoms also move toward surface, being attracted by nickel and oxygen. Since it is hard for silver and nickel to react and solve each other or to form intermetallic compounds, silver tends to diffuse through nickel layer and may reach the top of the surface. The phenomena may be utilized to cover nickel plating in the future, since it can enhance the antibacterial property or can protect nickel dissolution for the purpose of environmental protection. From the practical viewpoint, the diffusion control for these surface films would be interesting.

CONCLUSIONS

Commercial tin plating steels were plated by nickel. Then the stacked single layers specimen was heated to 200-500 degrees Centigrade and the surfaces were analyzed and identified by X-ray Diffraction Analysis. The following results were obtained.

(1) The stacked single layers of silver and nickel on iron substrate existed up to 200 degrees Centigrade.

(2) From 300 to 500 degrees Centigrade, iron diffused into nickel layer to form an

intermetallic compound of nickel and iron, $FeNi_3$.

(3) The surface color tone became matt and the glossiness decreased through the thermal treatment.

(4) The surface phase control may lead to various future practical applications.

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