Effect of Electrolysis Condition on Internal Stress and Hardness of Ni-W Electrodeposits

Soo Young Kang$^{1*}$ and Woon Suk Hwang$^2$

$^1$Department of Metallurgical & Material Engineering, Inha Technical College, Incheon - 402-752, Korea; sykang@inhatc.ac.kr
$^2$School of Materials Science and Engineering, Inha University, Incheon - 402-751, Korea

Abstract
Chromium plating has widely used as a surface treatment method, which has high wear resistance, hardness, and corrosion resistance. There are restrictions on the hard chromium plating to cause environmental pollution. The need to develop a wet plating method to replace this situation is being raised. Ni-W alloy plating has been reported to exhibit high hardness, wear resistance, excellent corrosion resistance and high-temperature stability, such as catching a Chrome plating by a wet plating method to replace. For the precipitation mechanism and the plating solution of this Ni-W alloy plating research, it has long been carried out by many researchers. Ni-W alloy plating has recognized as Induced Co-deposition alloy. It reported that Ni-W alloy plating is amorphous and shows a tendency to decrease of the crystal grains as the W content is increased in the coating layer, the hardness increases due to the decrease of the crystal. In this study, mechanical property of Ni-W electrodeposits in various manufacturing condition such as temperature and current density was investigate to understand the effect of electrolysis temperature and current density on internal stress and Hardness. The overvoltage strength and thermal strength explained the results.

Keywords: Ni-W Alloy Plating, Mechanical Property, Overvoltage Strength, Thermal Strength

1. Introduction

Alloy plating plates with a metal or non-metal of two or more. At the same time the coating on the cathode side in the electrolytic solution. The potential of the coating must be equal to the two kinds of metallic cations at the cathode surface which is coated. In the case of the small difference in the standard electrode potential, it is possible to plate. In the case of the big difference in the standard electrode potential, after making a metal ion complex to regulate the activity and over-voltage of the ion plating, it is possible to plate.

Chromium plating has widely used as a surface treatment method, which has high wear resistance, hardness, and corrosion resistance. There are restrictions on the hard chromium plating to cause environmental pollution. The need to develop a wet plating method to replace this situation is being raised. Ni-W alloy plating has been reported to exhibit high hardness, wear resistance, excellent corrosion resistance and high-temperature stability, such as catching a Chrome plating by a wet plating method to replace. For the precipitation mechanism and the plating solution of this Ni-W alloy plating research, it has long been carried out by many researchers. Ni-W alloy plating has recognized as Induced Co-deposition alloy. It reported that Ni-W alloy plating is amorphous and shows a tendency to decrease of the crystal grains as the W content is increased in the coating layer, the hardness increases due to the decrease of the crystal. When alloy plating forms a solid solution, the free energy decreases. The Co-deposited potential of the tungsten moves in the noble direction$^{1-8}$.

2. Experimental Method

2.1 Plating Condition
Table 1 shows the plating bath composition and plating conditions used in this experiment. The first-class
reagent used for plating solution. Respectively, as a source of nickel and tungsten was used NiSO$_4$.6H$_2$O and Na$_2$WO$_4$.2H$_2$O. Citric acid used as the complex agent.

| Table 1. Bath Composition |
|---------------------------|
| Na$_2$WO$_4$.2H$_2$O       | 0.20 M          |
| NiSO$_4$.6H$_2$O           | 0.20 M          |
| C$_6$H$_8$O$_7$.H$_2$O     | 0.41 M          |

2.2 Preparation of Test Piece

The anode was used to produce an insoluble anode of platinum with $5 \times 9$ cm$^2$. The cathode was used as 99.9% pure copper plate was cut to a size of $2 \times 2$ cm$^2$. As a pretreatment before plating, it was mirror-polished to 1μm diamond paste. The specimens were degreased in an ultrasonic wave for 5 minutes alkaline degreasing solution. The specimens were washed with water, and then 60°C 10wt% H$_2$SO$_4$ solution was treated with 5 seconds. The electrolytic cell of acrylic with the size of 20 cm $\times$ 10 cm $\times$ 10 cm was used. The distance between the cathode and the anode was 10 cm.

2.3 Analysis

Deposit stress analyzer was used to measure the internal stress of the plated layer. Deposit stress test specimen with Be copper is the full length of 14 cm $\times$ 1.5 cm, and the structure of a “П” shape, as shown in Figure 1 (b). After measuring the distance of the specimen, internal stress is calculated by the following equation.

$$S = 5.94 \times U \times K / T$$

$S$(kg/mm$^2$) is a stress, $U$ is a total number of gage, $K$ is a correction factor, and $T$(μm) is an electroplating thickness on the copper specimen.

SEM with Hitachi S-4300SE measured the surface morphology. EDX with Hitachi S-4300SE analyzed W content of the coating layer. For the study of the crystal structure changes in the alloy plating, XRD analysis with Phillips PW3040 was carried out by the plating conditions. Microvikers hardness tester with Mitutoyo MVK-E3 measured the hardness of the coating.

3. Experimental Results

3.1 Internal Stress by the Electrolysis Condition

3.1.1 Effect of the Current Density

Figure 2 shows the internal stress with the current density. As the current density increases, the internal stress rises. The stress in 0.3A/dm$^2$ and 70°C is 9 kg/mm$^2$, 11.39 kg/mm$^2$ in 0.5A/dm$^2$ and 16.39 kg/mm$^2$ in 0.9A/dm$^2$. As the current density increases, the overvoltage in the cathode increases. As the over voltage in the cathode increases, the strength of electro deposit increases.

The lattice constant of pure Cui is 3.61Å. The lattice constant of pure Ni is 3.52Å. When nickel plates over the copper specimen, the specimen is bent toward the small lattice constant. Therefore, the specimen is bent towards the nickel.

As the current density increase, the strength of electro deposit increases, the bent degree increases. Therefore as the current density increases, the internal stress increases.

3.1.2 Effect of the Temperature

Figure 3 shows the internal stress with the temperature. As the temperature increases, the internal stress decreases. The internal stress in 60°C and 0.7A/dm$^2$ is 23.79 kg/mm$^2$, 14.59 kg/mm$^2$ in 70°C and 89 kg/mm$^2$ in 80°C. As the temperature increase, the overvoltage in the cathode decreases. As the overvoltage in the cathode decreases, the strength of electro deposit decreases.

Figure 2. Internal Stress at Various Current Densities.

Figure 3. Internal Stress at Various Temperatures.
As Section 3.1, it can be explained by the same logic. As the temperature increases, the overvoltage in the cathode decreases, the strength of electro deposit decreases, the bent degree toward Ni decreases.

The expansion coefficient of pure Cu is $1.71 \times 10^{-5}$. The lattice constant of pure Ni is $1.30 \times 10^{-5}$. The lattice constant of pure Ni is $0.45 \times 10^{-5}$. When nickel plates over the copper specimen, the specimen is bent toward Cu of the large expansion coefficient. If the plating temperature is high, a larger thermal strength occurs, the bent degree toward Cu increases, the bent degree toward Ni decreases.

Therefore as the temperature increases, the bent degree toward Ni from over voltage strength and thermal strength decrease, the internal stress decreases.

3.2 Hardness by the Electrolysis Condition

3.2.1 Effect of the Current Density

Figure 4 shows the hardness with the current density. As the current density increases, the hardness rises. The hardness in 0.3 A/dm$^2$ and 60°C is 345VHN, 500VHN in 0.5 A/dm$^2$ and 560VHN in 0.7 A/dm$^2$. As the current density increases, the overvoltage in the cathode increases. As the overvoltage in the cathode increases, the strength and hardness of electro deposit increases.

3.2.2 Effect of the Temperature

Figure 5 shows the hardness with the temperature. As the temperature increases, the hardness is nearly the same. The hardness in 60°C and 0.7 A/dm$^2$ is 268VHN, 510VHN in 70°C and 515VHN in 80°C.

As the temperature increases, the overvoltage in the cathode decreases. As the overvoltage in the cathode decreases, the hardness decreases. As the overvoltage in the cathode decreases, the strength and hardness of electro deposit decreases. However, it is different from the result.

It may explain the reason as follows. The expansion coefficient of pure Cu is $1.71 \times 10^{-5}$. The lattice constant of pure Ni is $1.30 \times 10^{-5}$. The lattice constant of pure Ni is $0.45 \times 10^{-5}$. When nickel plates over the copper specimen at the high plating temperature, a larger thermal strength occurs. As the temperature increases, the strength from the overvoltage in the cathode decreases, but thermal strength increases. Therefore, the strength and hardness of electro deposit is nearly the same.

3.3 W Content by the Electrolysis Condition

3.3.1 Effect of the Current Density

Figure 6 shows the W content with the current density. As the current density increases, the W content rises.

Figure 3. Internal stress at various temperatures.

Figure 4. Vicker’s Hardness at Various Current Densities.

Figure 5. Vicker’s hardness at various temperatures.

Figure 6. W Content at Various Current Densities.
The W content in 0.3 A/dm$^2$ and 70°C is 21wt%, 22wt% in 0.5 A/dm$^2$ and 27wt% in 0.9 A/dm$^2$. In general, if the overvoltage in the cathode rises, the less noble metal W is plated more. As the current density increases, the overvoltage in the cathode increases. As the overvoltage in the cathode increases, the W content increases.

### 3.3.2 Effect of the Temperature

Figure 7 shows the hardness with the temperature. As the temperature increases, the W content decreases. The W content in 60°C and 0.7 A/dm$^2$ is 27.8wt%, 27.6wt% in 70°C and 25.5wt% in 80°C. As the temperature increases, the overvoltage increases. As the overvoltage increases, the less noble metal W decreases.

![Figure 7. W content at various temperatures.](image)

### 3.4 Surface Morphology

Figure 8 shows the observations of the surface of the current density are shown in. As the current density increases, the surface roughness decreases.

![Figure 8. Surface Morphology of Ni-W alloy deposited at (a) 0.5 A/dm$^2$ and (b) 0.7 A/dm$^2$.](image)

### 4. Conclusion

The impact of the current density and temperature in the plating solution on internal stress, temperature and W content is investigated.

The lattice constant of pure Cu is 3.61Å. The lattice constant of pure Ni is 3.52Å. When nickel plates over the copper specimen, the specimen is bent toward the small lattice constant. Therefore, the specimen is bent towards the nickel. As the current density increases, the strength of electro deposit increases, the bent degree increases. Therefore as the current density increases, the internal stress increases.

The expansion coefficient of pure Cu is $1.71 \times 10^{-5}$. The lattice constant of pure Ni is $1.30 \times 10^{-5}$. The lattice constant of pure Ni is $0.45 \times 10^{-5}$. When nickel plates over the copper specimen, the specimen is bent toward Cu of the large expansion coefficient. As the temperature increases, the bent degree toward Ni from overvoltage strength and thermal strength decrease, the internal stress decreases.

As the current density increase, the overvoltage in the cathode increases. As the overvoltage in the cathode increases, the strength and hardness of electrodeposit increases.

As the temperature increases, the strength from the overvoltage in the cathode decreases, but thermal strength increases. Therefore, the strength and hardness of electrodeposit is nearly same.

### 5. References

1. Younes O, Gileadi E. Electroplating of high tungsten content Ni/W Alloys. Electrochemical and Solid-State Letters. 2000; 3(12):543–5.
2. Ahmad J, Asami K, Takeuchi A, Louguine DV, Inoue A. High strength Ni-Fe-W and Ni-Fe-W-P alloys produced by electrodeposition. Materials Transactions. 2003; 44(10):1942 –7.
3. Jeong G, Lee CK. Electrolysis for NiW functional alloy plating. J Kor Inst Surf Eng. 2011; 44(1):1–6.
4. Mizushima I, Tang PT, Hansen HN, Somers MAJ. Residual stress in Ni–W electrodeposits. Electrochimica Acta. 2006; 51(27):6128–34.
5. Casciano PNS, Benevides RL, Lima-Neto Pd, Correia AN. Corrosion resistance of electrodeposited Ni-Mo-W coatings. Int J Electrochem Sci. 2014; 9:4413 –28.
6. Matsui I, Takigawa Y, Yoko D, Kato T, Uesugi T, Higashi K. Strategy for electrodeposition of highly ductile bulk nanocrystalline metals with a face-centered cubic structure. Materials Transactions. 2014; 55(12):1859–66.
7. Alimadani H, Ahmadi M, Ahmadi M, Aliofkhazraei M, Younes R. Corrosion properties of electrodeposited nanocrystalline and amorphous patterned Ni-W alloy. Materials and Design. 2003; 30(4):1356–61.
8. Pramod Kumar U, Kennady CJ. Electrodeposition of Ni-W alloy from citrate electrolyte containing anisaldehyde as inhibitor. Int J Res Chem Environ. 2014; 4(4):184–91.