Abstract: Chromium plating has excellent corrosion resistance and is widely used in industry. However, it also has a high environmental load. As an alternative, electric Ni-W plating is attracting attention. However, it is not widely used because the stress is high and the film is prone to cracks. Furthermore, although it is necessary to thicken the film to improve the corrosion resistance, there are also problems that the current efficiency is low and the plating time is long. Therefore, we investigate a film with high corrosion resistance by using the jet-flow plating method that enables plating at a high current density. Our results show that the jet-flow plating enables plating of 50 $\mu$m, and high corrosion resistance is obtained by randomly generating fine cracks in the film at 20 A·dm$^{-2}$. We also found that the stress changed depending on the current density and shape of the crack also changed.

Keywords: electro Ni-W plating; jet-flow device; high current density; corrosion resistance; micro cracks

1. Introduction

In general, chromium plating has excellent properties, such as corrosion resistance, acid resistance, and high hardness. It is widely used in modern industries, such as parts, engines, and dies, taking advantage of its hardness and wear resistance [1,2]. However, the environmental load of hexavalent chromium used for chrome plating is high and may become unusable, due to environmental regulations [3–6].

Alternative research on chromium plating has been widely conducted, Ni-W is attracting attention in addition to WC film formation by sputtering, and trivalent chrome plating [7–9]. Tungsten is a metal with high hardness and high wear resistance [10]. While it does not precipitate as a plating film by itself, it has the property of induced co-deposit with iron groups, such as nickel [11]. It has already been reported that Ni-W plating has high wear resistance and hardness [12,13]. However, Ni-W plating film has many problems, such as cracks easily, low current efficiency, and high internal stress [14,15], and has not been widely put into practical use. Even if the corrosion resistance of the Ni-W plating film is high, it is necessary to be careful because corrosion factors, such as gas and plating solution that enter from cracks, corrode the base of the plating film and deteriorate the performance of the film.

We investigated the relationship between the structure of the Ni-W plating film and corrosion resistance. As a means for improving the corrosion resistance of the film, there are methods, such as multi-layering the films having different structures, increasing the W content, and combining nanoparticles [16–18]. However, considering the long-term reliability of the product, thickening the film is one of the most effective means. On the other hand, it takes a long time to make a thick film and can be one of the barriers to industrialization [19]. Although the speed of electroplating can be achieved by increasing the current density, in the conventional plating equipment, the supply of metal ions to the cathode may be delayed, and abnormal precipitation may occur [20]. We have succeeded
in producing a good plating film even at 50 A·dm$^{-2}$ in electrolytic copper plating using the jet-flow electroplating device that can supply stable metal ions even under high current density [21]. We tried to thicken the Ni-W plating using this device and evaluated its corrosion resistance.

2. Materials and Methods

2.1. Plating Conditions

Table 1 shows the basic composition and conditions of the plating bath. Nickel sulfate and sodium tungstate were used as metal salts, and triammonium citrate was used as a complexing agent [22]. All chemicals are special grade chemicals. The concentration of the complexing agent was 0.8 mol·dm$^{-3}$, which was equivalent to the total number of moles of the metal salt, and the bath pH was adjusted to 6.0 with dilute sulfuric acid and an aqueous solution of sodium hydroxide. The temperature of the plating bath is 40 °C. Platinum-coated titanium was used for the anode. A copper plate (Halcel plate, Yamamoto-MS) was used as the test substrate, and after adjusting the plating area to 10 mm × 20 mm, the protective sheet on the effective surface was peeled off, and plating was performed immediately.

Table 1. Plating bath composition and conditions.

| Plating bath composition | Ni$_2$SO$_4$·6H$_2$O | 0.4 mol·dm$^{-3}$ |
|--------------------------|----------------------|-----------------|
|                          | NaWO$_4$·2H$_2$O      | 0.4 mol·dm$^{-3}$ |
|                          | (NH$_4$)$_2$C$_6$H$_5$O | 0.8 mol·dm$^{-3}$ |
| Operating condition      | Substrate            | Cu              |
|                          | Plating area         | 10 mm × 20 mm   |
|                          | pH                   | 6.0             |
|                          | Temperature          | 40 °C           |

2.2. Normal Plating and JET-Flow Plating

Experiments were carried out by the normal plating and the jet-flow plating. For the normal plating, a 500 mL plating bath was placed in a 500 mL beaker, and stirred with a magnetic stirrer. For the jet-flow plating, we used the equipment (Yamamoto-MS) shown in Figure 1.

![Figure 1. Schematic diagram of the jet-flow plating equipment. The magnified view is a schematic view of the diffusion layer. The strong jet makes the diffusion layer thin and enables plating under high current densities.](image)

The diffusion limit current (faradaic current density) $i$ (A·cm$^{-2}$) is given as Equation (1).

$$i = zFDC_o/\delta_N$$  (1)
where $z$ is the electron valence, $F$ is the Faraday constant, $D_o$ is the diffusion coefficient (cm$^2$·s$^{-1}$) of the plating bath (reactant Ox), $C_o$ is the concentration of the plating bath offshore (mol·dm$^{-3}$), and $δ_N$ are the thickness of the Nernst diffusion layer [23].

That is, since it is proportional to the plating bath concentration and inversely proportional to the thickness of the diffusion layer, it is important to thin the diffusion layer. This device sets the surface to be plated downward and injects the plating solution from below. The structure can constantly supply a new plating solution to the reaction interface. It effectively thins the diffusion layer and has succeeded in plating with a current density of 50 A·dm$^{-2}$ in electrolytic copper plating [21]. In this study, the jet-flow plating was performed with a liquid flow of 7 dm$^3$·min$^{-1}$.

2.3. Evaluation of Plating Film

2.3.1. Alloy Composition Analysis

The film composition was determined by ICP (ICPW-9820, Shimadzu Corporation, Kyoto, Japan). After dissolving the 2 µm plated film with aqua regia, the alloy composition of Ni and W was analyzed and determined at an exposure time of 30 s, observation wavelengths of 207.911 nm for Ni, and 231.604 nm for W.

2.3.2. Current Density

The weight difference between the substrates before and after plating was measured with the electronic scale (GR-202, AND, Tokyo, Japan), and the film thickness was calculated from the alloy composition of Section 2.3.1. The current efficiency was calculated by comparing the obtained film thickness with the calculated 100% electrodeposition. Plating was applied three times at each current density, and the value of the average film thickness was used.

2.3.3. Corrosion Resistance Test

Chromium plating for functionality is plated at 5 to 500 µm depending on the application and purpose. Although the thicker the film thickness, the better the corrosion resistance is expected, it is generally used in industry at 30 to 50 µm [24]. Therefore, in this study, the evaluation was performed at 50 µm. The corrosion resistance of the 50 µm film was tested according to Annex 1 of JIS H8620. Nitric acid was placed on the bottom of the desiccator, and a sample masked with tape other than the plated surface was left at 24 °C for 24 h in that atmosphere. Then, the degree of corrosion was visually observed. The case when there was no change, when partial corrosion was observed, and when corrosion occurred on the entire surface, it was judged as A, B, and C, respectively.

2.3.4. Observation of Plating Film Surface and Cross Section

The 50 µm plated film was observed with a nano-search microscope (OLS4500, Olympus, Tokyo, Japan) 2000×. For cross section view, polished with a cross section polisher (SM09010, JEOL Ltd., Tokyo, Japan) for 10 h, and then the cross section was observed using FE-SEM (JSM-7000F, JEOL Ltd., Tokyo, Japan) at the acceleration voltage of 5 kV.

2.3.5. Number of Cracks in the Plating Film

The number of cracks on the surface of the film was counted by the following method. A straight line of 130 µm was arbitrarily drawn in the field of view observed with a nano-search microscope (OLS4500, Olympus, Tokyo, Japan) 2000×, cracks intersecting the line were counted, and converted to the number of intersections per 1 mm. The number of fields of view was 2, and cracks were counted with three lines in each field of view, and the average value was adopted [15]. Figure 2 shows an example of counting cracks.
the line were counted, and converted to the number of intersections per 1 mm. The number of cracks per 1 mm is reflected in the result.

2.3.6. The Internal Stress in the Normal Plating

The film stress of normal plating was obtained by plating 1 µm on the plating internal stress measurement test piece (here in after referred to as a test strip, Specialty Testing, and Development Company). The test strip is a 100 µm thick copper alloy C-1940 (Cu–2.4 Fe–1.0 Zn; mass%), and the open legs are masked on different sides and open according to the degree of leg opening. When the plated surface was opened inward, it was judged as the compressive stress, and when the masked surface was opened inward, it was judged as the tensile stress [25,26].

3. Results and Discussion

3.1. Alloy Composition Analysis

Figure 3 shows the tungsten content in the plating film when the current density is changed by eight levels from 5 to 50 A·dm⁻² in the normal plating and the jet-flow plating. As a result, no correlation was observed between normal plating and the jet-flow plating, and the composition of the Ni-W plating film remained within 10 to 25 wt% as W.

Figure 2. An example of counting cracks. Draw a straight line in the field of view and count the cracks that intersect that line. In this example, there are three cracks in the field of view. One side of this field of view corresponds to 130 µm, and the number of cracks converted to the number of cracks per 1mm is reflected in the result.

(a) Normal plating (b) Jet-flow plating

Figure 3. Relationship between current density and W content in deposited film on (a) the normal plating and (b) the jet-flow plating.
No significant relationship between the current density and the alloy composition has been reported [12], and no clear effect was observed on the alloy composition even when the jet plating apparatus used in this study was used. Although the ratio of tungsten in the plating film depends on the composition of the plating bath and the pH, it is assumed that the ratio of the alloy is not affected because the current density and the plating method do not affect the eutectoid and potential of tungsten.

3.2. Thickening of the Plating Film

Figure 4 shows the visual appearance of the 5 A·dm\(^{-2}\), 20 µm plated film by the normal plating and the jet-flow plating. The film peeled because of internal stress on the normal plating; however, no peeling on the jet-flow plating was observed visually. In addition, when plating was performed with a current density of 5 to 50 A·dm\(^{-2}\), all of the normal plating peeled off to various degrees. On the other hand, in the jet-flow plating, there was no film peeling under all conditions, and a thickness of 50 µm was possible. It is assumed that this is related to the time required for the hydrogen gas generated by the plating reaction to separate from the substrate surface. In the normal plating, hydrogen gas tends to stay on the reaction surface, and the growth of the plating film at the gas-adhered portion is hindered. As a result, the plating growth became non-uniform, which is considered to have led to film peeling. On the other hand, in the jet-flow plating, it is considered that even if hydrogen gas is generated, the gas is quickly released by the jet-flow, and a uniform plating surface can be formed.

![Figure 4](image_url)

(a) Normal plating  
(b) Jet-Flow plating

**Figure 4.** Visually images of the plating film surface (20 µm) obtained from (a) normal plating and (b) jet-flow plating (taken by digital camera). While the plating film was peeled off in the normal plating, plating was possible in the jet-flow plating.

3.3. Current Efficiency in the Jet-Flow Plating

With the normal plating, cracks and film peeling occurred at 5 µm or less; therefore, current efficiency could not be measured. Figure 5 shows the current efficiency of 50 µm film by the jet-flow plating. The current efficiency at 20 to 50 A·dm\(^{-2}\) was higher than the current efficiency at 5 to 15 A·dm\(^{-2}\), and the current density tended not to change significantly at a current density of 20 A·dm\(^{-2}\) or higher. It is assumed to be because the amount of hydrogen gas generated increases at high current densities, which further promotes gas release from the reaction surface. It took only 13 min to deposit 50 µm with a current density of 50 A·dm\(^{-2}\).

Below 20 A·dm\(^{-2}\), the lower the current density, the lower the current efficiency tends to be.
Figure 5. Relationship between current density and current efficiency.

3.4. Relationship between Corrosion Resistance, Number of Cracks, and Stress

Table 2 shows the corrosion resistance test results of the film plated with 50 µm by the jet-flow plating. As a result, it was found that there is a difference in corrosion resistance depending on the current density. At 20 A·dm$^{-2}$, no patina derived from copper, which is the substrate, is observed. It shows excellent corrosion resistance. In the other samples, patina occurred in part or in whole. Even in the sample in which patina was observed, the Ni-W film itself was not dissolved when washed with deionized water and dried, and the appearance was close to that before the corrosion resistance test. Although the corrosion resistance of Ni-W can withstand an environment of 24 h under a nitric acid atmosphere, it is assumed that the substrate corrosion occurred, due to film defects.

Table 2. Each current density and its corrosion resistance on jet-flow plating (50 µm). “A” had the highest corrosion resistance, and no patina derived from copper, which is the base material, was found. In “B”, patina is generated on a part of the board. In “C”, patina occurred on the entire surface.

| Current density (A·dm$^{-2}$) | 5   | 10  | 15  | 20  | 25  | 30  | 40  | 50  |
|-------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Corrosion level (-)           | C   | C   | B   | A   | B   | C   | C   | C   |

Figure 6 shows the surface and the cross section of the film plated with 5, 20, and 50 A·dm$^{-2}$ at 50 µm. From the surface, it was found that in 5 A·dm$^{-2}$, there were many smooth parts, and cracks were linearly formed. On the other hand, at 20 and 50 A·dm$^{-2}$, the surface was uneven, and cracks were also generated along with the unevenness. At high current densities, it is assumed that the amount of gas generated per unit time is large, and the film grows before the gas is completely removed from the reaction surface, therefore the surface had become uneven.

From the cross section, in both 5 and 50 A·dm$^{-2}$, large cracks penetrating the substrate surface were observed. On the other hand, at 20 A·dm$^{-2}$, it was observed that fine cracks were randomly formed. It is assumed that the random fine cracks disperse the origin of corrosion, therefore high corrosion resistance was obtained [27,28]. As shown in Figure 3, since there is no difference in the tungsten content (about 15 wt %) depending on the current density, it can be judged that there is no correlation between the crack-morphologies and the tungsten content.
Figure 6. Surface view by nano-search microscope (above) and cross section view by FE-SEM (below). In both 5 and 50 A·dm⁻², large cracks penetrating the substrate surface were observed. On the other hand, at 20 A·dm⁻², it was observed that fine cracks were randomly formed. (a) Surface 5 A·dm⁻², (b) Surface 20 A·dm⁻², (c) Surface 50 A·dm⁻², (d) Cross section 5 A·dm⁻², (e) Cross section 20 A·dm⁻², (f) Cross section 50 A·dm⁻².

Figure 7 shows the results of the number of cracks obtained by averaging three lines for each of the two fields of view.

![Number of cracks vs. current density](image)

Figure 7. Relationship between current density and number of cracks. The number of cracks was maximum at 20–25 A·dm⁻².

As a result, the number of cracks generated on the surface was maximum at 20–25 A·dm⁻², and then tended to decrease. From the results in Table 2, it was found that 15 to 25 A·dm⁻², which showed good corrosion resistance, had more surface fine cracks than the conditions with low corrosion resistance. It is assumed that many surface fine cracks suppressed the generation of large cracks reaching the substrate.
As a result, the number of cracks generated on the surface was maximum at 20–25 A·dm$^{-2}$, which had many fine cracks in Figure 7, was high. Due to the high stress, many fine cracks were formed at the initial stage of film formation, and the cracks randomly occurred. Therefore, it is assumed that large cracks penetrating the substrate were avoided, due to the film thickening [29]. On the other hand, if the film stress is low, cracks do not generate at the initial stage, and the large cracks generate after the film becomes thick; therefore, it is assumed that the cracks penetrate the substrate.

![Figure 8. Relationship between current density and film stress in the normal plating. The stress tended to be high in the vicinity of 20–25 A·dm$^{-2}$, where the number of cracks was large in jet plating.](image)

4. Conclusions

As a result of performing electric Ni-W plating by the normal plating and the jet-flow plating, the following was found:

1. In the normal plating, when 20 µm plating was performed in the current density range of 5 to 50 A·dm$^{-2}$, film peeling occurred in all cases. On the other hand, the jet-flow plating did not cause film peeling, and a film formation of 50 µm was possible.
2. When the corrosion resistance was tested in the range of 5 to 50 A·dm$^{-2}$, the fine cracks were randomly generated at 20 A·dm$^{-2}$, showing the excellent corrosion resistance.
3. When the stress of normal plating was measured, it was all tensile stress. The higher the current density, the higher the stress. However, at 25 A·dm$^{-2}$ and above, it decreases as the current density increased. This had a correlation with the number of the surface fine cracks in the film plated with 50 µm by the jet-flow plating. It was found that the higher the stress, the finer the cracks on the surface of the plating film, the larger the number, and the more randomly generated, which is a factor for improving the corrosion resistance.

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