Corrosion Behavior of Chromium Nitride Films Produced by Reactive Ion Plating in Sulfuric Acid Solution

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Chromium nitride films of various composition were deposited on glass substrates by r.f. reactive ion plating, and the deposition rate, along with the structure and the corrosion resistance of the films were investigated: At a constant nitrogen pressure the deposition rate increases, but the nitrogen content of the nitride film tends to decrease with an increase in the electron beam current used for evaporating chromium. X-ray diffraction shows that the film is a solid-solution of Cr and N (α -Cr) at a current of 100 mA, a mixture of Cr_2N and CrN at 60 mA, and a single phase of CrN at 10 ~ 50 mA. Decrease in the current leads to a transformation in the film structure: a structured film changes to a nearly amorphous, dense film with a smooth surface, and there is a great improvement in the corrosion resistance. The Cr and α -Cr film are rapidly corroded in $1 \text{ kmol} \cdot \text{m}^{-3} \text{H}_2\text{SO}_4$ at 373 K, while the single phase of CrN hardly corrodes at all. In a mixture of Cr_2N and CrN, Cr_2N is selectively corroded, and the amount of dissolved chromium is about two orders of magnitude larger than that for the single phase of CrN. The films deposited with a low electron beam current are bent due to the difference in thermal expansion between the film and substrate, and some of the films peel off during the corrosion test.

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I. Introduction

The transition metal nitrides such as titanium nitride and chromium nitride are expected to have new applications as corrosion resistant materials, because they are chemically stable. The present authors have investigated the corrosion behavior of titanium nitride powder synthesized from titanium hydride and found that corrosion was apparently inhibited in $1 \text{ kmol} \cdot \text{m}^{-3} \text{H}_2\text{SO}_4$ at 373 K when the nitrogen content was more than 40 at%⁽¹⁾⁻⁽³⁾. On the other hand, a mixture of ($\text{Cr}_2\text{N} + \text{CrN}$) containing 33 at% nitrogen or more shows improved corrosion resistance, although a mixture of (α -Cr + Cr_2N) and the single phase Cr_2N are rapidly attacked⁽⁴⁾⁽⁵⁾. This data suggests that the single phase CrN should have a high corrosion resistance. However, it is very difficult to obtain the single phase of the higher nitride, CrN, by the conventional procedure, high temperature nitriding. This phenomenon is attributed to the following causes. The single phase of CrN could not be produced at low temperatures. Even if CrN is temporarily formed during the reaction process, it dissociates into Cr_2N due to thermodynamic instability above 1323 K⁽⁶⁾. However, a modern procedure using a plasma reaction makes it possible to produce this compound by adjusting the constituents of the plasma, namely the ratio of chromium to nitrogen. Knotek *et al.*⁽⁷⁾ reported that the various kind of phases, Cr, Cr_2N and CrN, were deposited with replicable results.

The purpose of the present study is to evaluate the corrosion behavior of various chromium nitrides, including the single phase of CrN, against the non-oxidizing acids. For this purpose, chromium nitride films were produced by reactive ion plating. The reasons for choosing reactive ion plating as the processing are that the temperature of the substrate is comparatively low and the films deposited have high quality. However, few studies have been made on the production of chromium nitride by this method⁽⁸⁾⁽⁹⁾, and been published on the corrosion behavior of the film. In this paper, we report on the influence of the plating condition on the deposition rate and the structural features of chromium nitrides and the relationship between the structure and corrosion behavior in sulfuric acid solutions.

II. Experimental

1. Production of chromium nitride films

Chromium nitride films of various compositions were produced on glass substrates using an r.f. ion plating apparatus (JEOL Ltd., LC-8P type). A schematic diagram of the apparatus is shown in Fig. 1. The superiority of the apparatus over the conventional d.c. method is that plasma can be steadily generated even at a low gas pressure⁽¹⁰⁾, and there are certain advantages to the apparatus, such as improvement of the film quality and depression of the substrate temperature⁽¹¹⁾⁽¹²⁾. Ion plating was carried out according to the following procedures. (1) After evacuation by a diffusion pump to a pressure of less than $4.00 \times 10^{-3} \text{ Pa}$, argon gas was fed into the reaction

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Fig. 1 Apparatus for reactive ion plating. A: substrate, B: high frequency induction coil, C: shutter, D: electron beam, E: diffusion pump, F: heater, G: thermocouple, H: insulator, I: D. C. source, J: Ar gas inlet, K: high frequency induction source, L: N₂ gas inlet.

chamber to a pressure of 5.33×10^{-2} Pa. The surfaces of the substrates were cleaned by argon sputtering for about 600 s prior to plating. (2) The chamber was evacuated again. High purity nitrogen (99.9995 vol%) as a reactive gas was fed through a fine-control variable valve to a pressure of 1.07×10^{-1} Pa. The nitrogen plasma was generated by a high frequency source of 800 W. (3) High purity chromium (99.94 mass%) in the crucible is evaporated by an electron beam under a constant accelerated voltage of 10 kV. The current of the electron beam was varied from 10 to 100 mA depending on the composition of the films. (4) The stainless substrate holder was negatively biased by 1.0 kV, and subsequently the shutter was opened. Plating was continued until a film thickness of about $1 \mu\text{m}$ was obtained. The temperature of the substrates and the pressure of the chamber were monitored during the plating. The product films were slowly cooled to room temperature in a vacuum. The thickness of the films was measured exactly by an interference microscope. The surface of the films was examined with a scanning electron microscope (SEM), and the crystalline phase was identified by X-ray diffraction (XRD).

2. Potential/current density curve measurement and corrosion test

Potential/current density curves of the product films were measured by a potentiodynamic method in deaerated $1 \text{ kmol} \cdot \text{m}^{-3}$ H₂SO₄ at 313 K. A lead wire was attached to the film with silver paste and epoxy resin, and the specimen was coated with silicone resin except for an area of 100 mm^2 to make it the working electrode. The counter electrode consisted of a platinum sheet and the reference was a silver/silver chloride/ $3.33 \text{ kmol} \cdot \text{m}^{-3}$ KCl. After immersing the specimen electrode in the solution for about 1.8 ks, the measurement was carried out at a scan

rate of $2 \times 10^{-4} \text{ V} \cdot \text{s}^{-1}$.

In order to evaluate the corrosion resistance of the nitride films, the sample electrodes were prepared as mentioned above and a corrosion test was performed in $1 \text{ kmol} \cdot \text{m}^{-3}$ H₂SO₄ at 373 K. The electrodes were immersed in a $500 \times 10^{-6} \text{ m}^3$ test solution in a flask with a water-cooled condenser for 14.4 ks and the potentials were continuously monitored. Part of the solution was collected at regular intervals to determine the amount of dissolved chromium by the ICP mass spectrometer. The electrode potentials were measured using a reference electrode maintained at room temperature, and the potentials include liquid junction potential, attributed to the difference in temperature. Since the viscosity of sulfuric acid is high and the mass spectrum of ⁵²Cr overlaps that of ³⁴S¹⁸O, which is the isotope of a component of sulfuric acid, sulfuric acid in the solution was replaced with nitric acid to serve for analysis. Moreover, similar test runs were conducted under other sulfuric acid concentrations of 0.1 and $10 \text{ kmol} \cdot \text{m}^{-3}$, in order to clarify the influence of acid concentration on corrosion behavior of the product films.

III. Results and Discussion

1. Effect of plating conditions on properties of chromium nitride films

Figure 2 shows the deposition rate of chromium nitride film and N₂ gas pressure of a reaction chamber as a function of electron beam current for evaporating chromium. The deposition rate is small, about $5 \times 10^{-11} \text{ m} \cdot \text{s}^{-1}$ below 40 mA. However, the rate markedly changes at 40 mA and increases in proportion to the current. On the other hand, N₂ gas pressure gradually decreases with an increase in the current. Increasing the electron beam current implies a rise in the evaporation rate of chromium. Moreover, a drastic change in the pressure was observed when the shutter was opened, so as to introduce the evaporated chromium into the nitrogen plasma. Thus, we presume that the evaporated chromium reacted chemically and electronically in nitrogen plasma to decrease the density of gas molecules in the reaction chamber.

Figure 3 shows scanning electron micrographs of chromium and chromium nitride films produced by reactive ion plating. All these films have lustrous, silver surfaces, and it is difficult to find a difference in tone due to the plating condition with the naked eye. However, observation by scanning electron microscope makes it clear that the surface of the chromium nitride film (B) is rougher than that of the chromium metal film (A). The former was produced in N₂ gas and later in Ar gas at the same electron beam current of 100 mA. According to the surface morphology model of sputter deposition film put forward by Thornton⁽¹³⁾⁽¹⁴⁾, the difference in morphology reflects the melting point of the constitution phase. On the other hand, as the electron beam current becomes lower, the surface tends to be smoother and more dense in the chromium nitride films produced in N₂ gas. For these films, a longer plating time was required for the

Fig. 2 Deposition rate of chromium nitride film and N_2 gas pressure of reaction chamber as a function of electron beam current for chromium evaporation.

same thickness of about $1 \mu\text{m}$ formed in the lower current. Moreover, the temperature of the substrate gradually increased as time passed. The final temperature of the substrate for the chromium nitride film (C) produced at 30 mA of an electron beam current was 50 K higher than that of film (B) at 100 mA. Therefore, increase in the substrate temperature largely affects the surface to become smoother and more dense at a lower electron current beam.

Figure 4 shows the X-ray diffraction patterns of chromium and chromium nitride films produced at various electron beam currents. The film produced at an electron beam current of 100 mA in N_2 gas is recognized as α -Cr containing small amount of nitrogen. Compared with the metallic chromium film produced in Ar gas, the Cr peaks slightly shift to the lower angle. Since the strongest peak of cubic CrN is found with the diffraction lines of hexagonal Cr_2N , the film is identified as a mixture of ($\text{Cr}_2\text{N} + \text{CrN}$) at 60 mA. When the electron beam current decreases to 50 mA, only a diffraction line of CrN (200) remains; namely, the lines of Cr_2N disappear. This line becomes broader and its intensity markedly decreases

Fig. 3 SEM photographs of chromium and chromium nitride films; chromium film (A) was produced at electron beam current of 100 mA in Ar gas, and chromium nitride film (B) and (C) were produced at 100 mA and 30 mA in N_2 gas, respectively.

with a decrease in the electron beam current.

Under plating conditions described above, the higher chromium nitride tended to be formed at a lower electron beam current, and a film of the single phase CrN could be produced at 50 mA or less. This is attributed to the change in the evaporation rate of chromium. The rise in the electron beam current increases the evaporation rate of chromium from the water-cooled crucible. Under the constant pressure of nitrogen gas, the yield rate of nitrogen plasma is constant. Therefore, the rise in current in-

Fig. 4 X-ray diffraction patterns of chromium and chromium nitride films produced at various electron beam currents.

creases the production rate of film, which relates to the total amount of chromium and nitrogen deposited. The nitrogen content of the film must be decreased contrary to the production rate, because the ratio of nitrogen to chromium decreases with the current. In other words, the decrease in current results in the production of film with high nitrogen content. It also leads to a transformation in the film structure; a structured film changes to a nearly amorphous, dense film with a smooth surface. This change is probably caused by the decrease in the evaporation rate of chromium in addition to the rise in the substrate temperature. The former reduces the number of plating particles to promote refinement of the crystal grain.

We observed that the lower the current we used in the preparation of the film, the greater the bending of the substrate. The bending results when the sample is cooled to room temperature from the plating temperature and is caused by stress due to the difference in thermal expansion between the film and the substrate. Therefore, it is presumed that films produced with a low electron beam current, whose temperature is high during the plating,

have a greater compression stress inside.

2. Corrosion behavior of chromium nitride films in sulfuric acid solution

Figure 5 shows the anodic polarization curves of chromium and chromium nitride films in deaerated $1 \text{ kmol} \cdot \text{m}^{-3} \text{ H}_2\text{SO}_4$ at 313 K. The anodic polarization curve of α -Cr film is similar to that of Cr film. The former was produced in nitrogen plasma and the latter in argon plasma at the same electron beam current of 100 mA. Those films begin to dissolve at about -0.62 V and the dissolution current densities rapidly increase with potential to reach the maximum value, $300 \sim 400 \text{ A} \cdot \text{m}^{-2}$ at about -0.5 V . On the other hand, both $(\text{Cr}_2\text{N} + \text{CrN})$ mixture film and CrN film do not show active dissolution and the corrosion potentials are noble, -0.40 and -0.32 V , respectively. Moreover, the anodic current densities are $5 \sim 9 \times 10^{-2} \text{ A} \cdot \text{m}^{-2}$ at $+0.4 \text{ V}$ vs. Ag/AgCl and are smaller than 1/10 of the passive current densities of the Cr film and the α -Cr film (about $1 \text{ A} \cdot \text{m}^{-2}$).

Figure 6 shows the change in the corrosion potential, and Fig. 7 shows the change in the amount of dissolved chromium with time for chromium and chromium nitride films in $1 \text{ kmol} \cdot \text{m}^{-3} \text{ H}_2\text{SO}_4$ at 373 K. The corrosion potential of the Cr film is about $+0.4 \text{ V}$ immediately after immersion and it decreases with vibration to reach -0.2 V at 3.6 ks. The potential is stable for 7 ks, then it drops to -0.7 V in a few seconds. The amount of dissolved chromium rapidly increases to almost 10^{-5} kg at the drop in potential. A similar change is observed in the case of the α -Cr film; i.e., the corrosion potential suddenly drops from about -0.2 V to -0.7 V at 11.4 ks and the dissolved chromium rises to the 10^{-6} kg level. As men-

Fig. 5 Anodic polarization curves of chromium and chromium nitride films in deaerated $1 \text{ kmol} \cdot \text{m}^{-3} \text{ H}_2\text{SO}_4$ at 313 K.

Fig. 6 Change in corrosion potential with time for chromium and chromium nitride films in $1 \text{ kmol} \cdot \text{m}^{-3} \text{H}_2\text{SO}_4$ at 373 K.

Fig. 7 Change in amount of dissolved chromium with time for chromium and chromium nitride films in $1 \text{ kmol} \cdot \text{m}^{-3} \text{H}_2\text{SO}_4$ at 373 K.

tioned above, these films tend to dissolve unexpectedly and the reaction is finished in a short time. However, the induction period of the films before corrosion is about 10 times as long as the HIP chromium. Therefore, we presume that chromium film produced by reactive ion plating is more active than HIP chromium and that the surface reacts with air to form a protective oxide layer. On the other hand, the corrosion potential of a $(\text{Cr}_2\text{N} + \text{CrN})$ mixture that was -0.2 V immediately after immersion

decreases to -0.32 V at 3.6 ks and a minute amount of dissolved chromium is detected. The amount rises to $1.7 \times 10^{-6} \text{ kg}$ at 14.4 ks. However, in all the cases when the chromium nitride films are identified as the single phase of CrN, the corrosion potential is higher than -0.2 V and the amount of dissolved chromium is inhibited to the low level, $10^{-9} \sim 5 \times 10^{-8} \text{ kg}$.

Figure 8 shows the amount of dissolved chromium from chromium nitride films in $1 \text{ kmol} \cdot \text{m}^{-3} \text{H}_2\text{SO}_4$ at 373 K for 14.4 ks as a function of electron beam current for chromium evaporation. The amounts of dissolved chromium from the Cr film and the α -Cr film are not more than 10^{-5} kg . For the thicker films, this amount would increase in several orders of magnitude with the increase in the thickness. There is a significant decrease, about 1/50, in the amount of dissolved chromium between the electron beam current of 50 and 60 mA. This result corresponds to the fact that the structure changes from the $(\text{Cr}_2\text{N} + \text{CrN})$ mixture to the CrN single phase. In the case of the CrN, the lower electron beam current, the lower amount of chromium is dissolved. So, the chromium nitride films that were produced at the lower electron beam current have higher corrosion resistance and the current has a major influence on the corrosion resistance of the films. By the way, the amount of dissolved chromium from the CrN film is depressed extremely low, $1 \sim 5 \times 10^{-8} \text{ kg}$. According to the author's study, even if chromium was kept at a potential of $+0.4 \text{ V}$ to passivation, the amount of dissolved chromium reached $8 \times 10^{-8} \text{ kg}$ for 14.4 ks in deaerated $1 \text{ kmol} \cdot \text{m}^{-3} \text{H}_2\text{SO}_4$ at 313 K. After consideration of the difference in corrosion temperature, it led us to conclude that the corrosion resistance of CrN film is superior to that of

Fig. 8 Amount of dissolved chromium from chromium nitride films in $1 \text{ kmol} \cdot \text{m}^{-3} \text{H}_2\text{SO}_4$ at 373 K for 14.4 ks as a function of electron beam current for chromium evaporation.

the passive chromium.

In the case of titanium nitride, the ($\text{Ti}_2\text{N} + \text{TiN}$) mixture was found to be inferior in corrosion resistance to the single phase of TiN, whose nitrogen content is 40 at% or more. The lower resistance of the mixture is attributed to selective corrosion of the lower nitride, $\text{Ti}_2\text{N}^{(2)(3)}$. So, the possibility of preferential attack on the Cr_2N was investigated; that is, the ($\text{Cr}_2\text{N} + \text{CrN}$) mixture was corroded for 57.6 ks and the film was re-examined by the X-ray diffraction method after the corrosion test (cf. Fig. 9). When the corrosion time is longer, the diffraction intensity of the Cr_2N is more remarkably decayed than that of the CrN. For example, the strongest line, Cr_2N (111), is continuously decayed; the intensity of 500 cps before corrosion to 348 cps at 57.6 ks. On the other hand, the intensity of the strongest line, CrN (200), is a minimum, 460 cps at 28.8 ks, but it tends to increase slightly after that. Therefore, we conclude that the preferential attack onto the lower nitride, Cr_2N , progresses like titanium nitrides.

Figure 10 gives the change in the amount of dissolved chromium with time for the CrN and the ($\text{Cr}_2\text{N} + \text{CrN}$) film in 0.1, 1 and 10 $\text{kmol} \cdot \text{m}^{-3}$ H_2SO_4 at 373 K. In the case of the ($\text{Cr}_2\text{N} + \text{CrN}$) mixture, the amount of dissolved chromium is extremely low, 1.6×10^{-8} kg in 0.1 $\text{kmol} \cdot \text{m}^{-3}$, but it increases to about hundred times in 1 $\text{kmol} \cdot \text{m}^{-3}$ H_2SO_4 . The amount of dissolved chromium from the single phase CrN produced by an electron beam current of 30 mA is inhibited below 8×10^{-8} kg in even 10 $\text{kmol} \cdot \text{m}^{-3}$ H_2SO_4 , although it tends to increase with the concentration of sulfuric acid. Accordingly, the usefulness of the CrN film as a corrosion resistant material is confirmed at higher sulfuric acid concentrations.

As mentioned earlier, if the chromium nitride film is adopted for a corrosion resistant material, the film is required to be the single phase of CrN. From the viewpoint of chemical stability, it is quite possible for this nitride film to inhibit corrosion at successive levels in a high-temperature and concentrated sulfuric acid. However, peeling of the film was found for some of the specimens, therefore, a further improvement in soundness of the film is necessary. The peeling is attributed to the presence of internal stress. When a part of the film surface is damaged, the stress concentration occurs at this part and the film is fractured. Consequently, a device to cancel the difference in thermal expansion between the film and the substrate is necessary for the film to be put to practical use.

IV. Conclusion

Chromium nitride films were produced by reactive ion plating, and the deposition rate, along with the structure and the corrosion resistance of the films against sulfuric acid solution were investigated. The main results are summarized as follows.

(1) The deposition rate increases, but the nitrogen content of the nitride film tends to decrease with an increase in the current of an electron beam for evaporating

Fig. 9 X-ray diffraction patterns of ($\text{Cr}_2\text{N} + \text{CrN}$) film and the residues after corrosion test; the test was carried out in 1 $\text{kmol} \cdot \text{m}^{-3}$ H_2SO_4 at 373 K for 28.8 and 57.6 ks.

Fig. 10 Change in amount of dissolved chromium with time for CrN and ($\text{Cr}_2\text{N} + \text{CrN}$) films in 0.1, 1 and 10 $\text{kmol} \cdot \text{m}^{-3}$ H_2SO_4 at 373 K.

chromium at a constant nitrogen pressure. X-ray diffraction shows that the film is a solid-solution of Cr and N (α -Cr) at a current of 100 mA, a mixture of Cr_2N and CrN at 60 mA, and a single phase of CrN at 10–50 mA.

(2) Decrease in the current leads to a transformation in the film structure; a structured film changes to a nearly

amorphous, dense film with a smooth surface. However, films deposited with a low electron beam current are bent due to the difference in the thermal expansion between the film and substrate, and some of them peel off during corrosion testing.

(3) The Cr and α -Cr film are rapidly corroded in 1 kmol·m⁻³ H₂SO₄ at 373 K, while the film of single phase CrN hardly corrodes. The corrosion resistance of the CrN is superior to that of the passive chromium. On the mixture of Cr₂N and CrN, the Cr₂N is selectively corroded and the amount of dissolved chromium is about two orders of magnitude larger than that of the single phase CrN.

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