Hydrogen Dissolution and Structural Changes in Electrodeposited Cr Films*1

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Effects of hydrogen on the structure of electrodeposited Cr films have been investigated by combining X-ray diffraction and thermal desorption spectroscopy, systematically varying the plating conditions. A large amount of hydrogen was dissolved at high current densities in a Cr-rich bath at low temperatures, and caused structural changes from bcc to hcp and fcc hydrides with increasing hydrogen concentrations. Hydrogen dissolved in regular interstitial sites in the hcp and fcc hydrides desorbed at \( \sim 100 \) °C, but its certain fraction remained as bubbles and desorbed at \( > 800 \) °C leaving dimples on the surface.

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1. Introduction

The dissolution of hydrogen is known to occur in some metals in the process of electrodeposition from aqueous solutions, and induce various changes in the properties of the film, including the crystal structure, the grain size, the internal stress, among others.1–4 Recently, it has come to be recognized, as the electroplating has become more widely used in many different industries, that the presence of hydrogen in electrodeposited metals sometimes induce deteriorating effects and limits the reliability of the products. In order to solve these problems, understanding the basic properties of hydrogen in electrodeposited metals is indispensable.

The purpose of this paper is therefore to characterize the state of existence of hydrogen dissolved in the process of electrodeposition of metals, and investigate its effects on the structure of the film. For this purpose, Cr is one of the best choices because there is ample evidence that its electrodeposition is strongly affected by hydrogen: The current efficiency is low due to evolution of hydrogen; internal stresses probably built up by forced dissolution of hydrogen are so large as to initiate cracks, different crystal structures appear under different hydrogen deposition conditions, etc.5,6 Among them the most prominent is the structural change, namely that the hcp and fcc structures appear during electrodeposition and revert to the ordinary bcc structure in relatively short times after recovery to ambient conditions.7–12 Many different factors are known to affect these changes, including e.g. the composition (additives included) of the electrolyte,8,9 the temperature and structure of the substrate, application of pulsed currents,10 but no decisive factors have been identified yet. We anticipate that the decisive factor here is the dissolution of hydrogen. One of the reasons for this conjecture is that we observed the appearance of hcp and fcc structures in our recent high hydrogen pressure experiments on Cr, and identified these phases as Cr–H alloys of high hydrogen concentrations (H/Cr \( \sim 1 \)).13 The phase diagram obtained from the high-pressure experiment is reproduced in Fig. 1 for later reference.

The heat treatment under high hydrogen pressures and electrodeposition at certain cathodic overpotentials are thermodynamically equivalent in that both produce environments of high hydrogen chemical potentials. A relation between the chemical potential of gaseous hydrogen and the cathodic overpotential is shown in Fig. 2. The overpotential is measured from the standard hydrogen electrode (SHE), i.e. the potential of hydrogen electrode at \( 10^5 \) Pa (1 atm) and \( 25 \) °C. It can be seen that overpotentials usually encountered in electrodeposition correspond to gaseous pressures of a few GPa. Thus we expect the overpotential applied in the electrodeposition to have the same effect and induce similar structural changes as in high-pressure experiments.

In the present experiment, we adopted simplest possible conditions for the electrodeposition, using a mixture of chromic acid and sulfuric acid for the electrolyte and amorphous Ni–P alloy for the substrate, and in this way

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tried to isolate the effect of dissolved hydrogen by comparison with high-pressure experiments.

2. Experimental Method

The electrolytes of two different compositions were adopted: Bath A; ordinary Sergent solution (CrO$_3$ 250 kg/m$^3$ (2.5 mol/L) + H$_2$SO$_4$ 2.5 kg/m$^3$ (0.025 mol/L)) and Bath B; a more concentrated solution (CrO$_3$ 1000 kg/m$^3$ (10 mol/L) + H$_2$SO$_4$ 3.0 kg/m$^3$ (0.031 mol/L)). The bath was constantly stirred by a magnetic stirrer, and its temperature was set at every $\pm 1$°C to within $\pm 1$°C between 3 and 65°C. For the anode a Pt plate of 20 × 20 mm in size was used, and for the cathode a polycrystalline Cu plate electrodeposited with Ni–30 at% P amorphous film (200 nm thick) was used. The structure of the Ni–P film being amorphous was confirmed by electron diffraction. The use of the amorphous film for the substrate obviates possible effects of epitaxial growth. The deposition was made on the area of 10 × 10 mm of the substrate, at different current densities, e.g. 1000, 3000, and 5000 A/m$^2$. The corresponding overpotential, not easily measurable, is expected to increase roughly in proportion to the current density.

The structure of the deposited film was determined by XRD (McScience, MX Labo2). The surface morphology was observed by SEM (JEOL, JSM-6100), and the cross section of the film by SIM (Scanning Ion Microscope) after polishing by the focused ion beam (FIB) technique. For the analysis of hydrogen in the film, thermal desorption spectroscopy (TDS) was measured after removing the substrate by nitric acid. The sample was placed in a quartz tube, evacuated to 2.7 × 10$^{-4}$ Pa, and the gas evolution in the course of heating to 1000°C was measured at a rate of 1/12 K/s (5°C/min).

3. Experimental Results and Discussion

3.1 Relation between the deposition condition and the structure of the film

Figure 3 shows the XRD patterns of the films observed after deposition at different bath temperatures; Fig. 3(a) for Bath A and Fig. 3(b) for Bath B. In both cases, the current density was fixed at 3000 A/m$^2$ to facilitate comparison. In Bath A, the structure was always bcc, whereas in Bath B, the structure changed from fcc at the lowest temperature 3°C, to hcp + bcc above 25°C.

Figure 4 shows the XRD patterns observed after deposi-
tion in Bath B at 3°C, at three different current densities. The structure was hcp at the lowest current density (1000 A/m²), and changed to fcc at higher current densities (3000, 5000 A/m²). In fact, the films grown at high current densities exhibited only one diffraction line, to be assigned either to fcc(111) or hcp(002), showing that these close-packed planes were grown in parallel to the substrate surface. Thus, in order to identify the structure, the XRD was re-measured on a sample prepared by crashing the film of Case (b) (3°C, 3000 A/m²). The result, reproduced in Fig. 5, shows unambiguously that the film consisted solely of the fcc phase without any admixture of other phases.

Figure 6 shows the structure of the film grown in Bath B as a function of bath temperature and current density. The bcc structure is most stable at high temperatures and low current densities, which gives way to hcp and subsequently to fcc at lower temperatures and higher current densities. Films grown in Bath A always assumed the bcc structure.

The thermal desorption of hydrogen was measured for all these films, for investigating the possible relation between the state of hydrogen and the crystal structure. Figure 7 shows the correlation between the total amount of desorbed hydrogen and the structure of the films. The amount of hydrogen desorbed on heating to 1000°C is the lowest in the bcc phase (x = 0.3 ± 0.3), and appreciably higher in hcp (x = 1.0 ± 0.4) and fcc (x = 1.3 ± 0.2). These results indicate that the dissolution of hydrogen is a primary cause of the observed structural changes of the deposited Cr film. The situation is very similar to what was observed in high-pressure experiments.13)

Thermal desorption spectra measured on samples of the three different structures are shown in Figs. 8(a)–(c). Note that the vertical scale of Case (a) is magnified by 100 times. For interpreting the results, it is useful to remember the TDS
data on samples prepared by heat treatments at high hydrogen pressures. There, sharp peaks observed at \( \sim 100^\circ C \) in the hcp and fcc structures were identified as the desorption of hydrogen on regular interstitial sites, a broad peak at \( \sim 200^\circ C \) in the bcc structure as desorption from Vac-H clusters, and a gradual desorption above \( \sim 800^\circ C \) as decomposition of \( H_2 \) bubbles.\(^{13}\) Similar thermal desorption spectra were observed in electrodeposited Cu and Ni.\(^{16}\) Noting that H atoms on regular interstitial sites and in Vac-H clusters may partially condense into bubbles before being desorbed, we roughly identify the total amount of hydrogen initially present in as deposited film with the amount of hydrogen desorbed to 1000°C.

These results of TDS experiments indicate that the dissolution of hydrogen stabilizes the structure in the order bcc \( \rightarrow \) hcp \( \rightarrow \) fcc. This general systematics is exactly what was observed in high-pressure experiments.\(^{13}\)

### 3.2 Temporal variation of the structure of deposited films

Figure 1 shows that the hcp and fcc structures formed under high hydrogen pressures are unstable under ambient conditions, and indeed these structures were found to undergo gradual reversion to the bcc structure.

The temporal variation of the structure of a deposited film was examined by XRD, with the result shown in Fig. 9. At room temperature, a film initially of the fcc structure gradually decomposed, and eventually became the bcc structure after several months. With this structural change, a thermal desorption spectrum was also found to change, as shown in Fig. 10. The two spectra differ only in the disappearance of the 100°C peak after ageing; they look very similar above 100°C. This is understandable because, in the course of TDS measurement of the originally fcc film, the structure should have changed to bcc after 100°C desorption. (In comparison to Fig. 8, a background increasing with increasing temperature is noticeable in Fig. 10. This is because the latter experiments were performed on samples of much smaller quantity, and therefore affected by a small gas evolution from the spectrometer. This background contribution has been properly subtracted in evaluating the hydrogen contents inscribed.)
3.3 Volume changes accompanying structural changes

The lattice parameter of bcc, hcp and fcc structures, derived from Figs. 3(a), 4(a) and 4(c), respectively, are compiled in Table 1, together with the atomic volume (volume per formula unit CrHₓ) calculated therefrom. The expansion of the atomic volume, $(0.24/\text{C}^{60})/\text{C}^{103}/\text{nm}^3$, in going from bcc to hcp/fcc structures is believed to be caused by dissolution of hydrogen. Comparison with H-induced volumes in various transition metals suggests that the observed lattice expansion corresponds roughly to the stoichiometric composition $x \approx 1$. This is based on the premises that the solubility in the bcc phase is negligibly small, and the reference volume of the three structures are nearly the same, the facts based on our previous high-pressure experiments\(^\text{13}\) and first-principles calculations.\(^\text{17}\)

### Table 1

<table>
<thead>
<tr>
<th>Structure</th>
<th>Lattice parameter</th>
<th>Atomic volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc</td>
<td>$a = 0.288 \text{ nm}$</td>
<td>$11.9 \times 10^{-3} \text{ nm}^3$</td>
</tr>
<tr>
<td>hcp</td>
<td>$a = 0.272 \text{ nm}$</td>
<td>$14.4 \times 10^{-3} \text{ nm}^3$</td>
</tr>
<tr>
<td></td>
<td>$c = 0.444 \text{ nm}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c/a = 1.63$</td>
<td></td>
</tr>
<tr>
<td>fcc</td>
<td>$a = 0.386 \text{ nm}$</td>
<td>$14.2 \times 10^{-3} \text{ nm}^3$</td>
</tr>
</tbody>
</table>

Let us examine the implication of this H-induced volume expansion for the morphology of the film during hydrogen desorption. Figure 11 shows the surface of the films having the fcc structure, compared with the surface after reversion to bcc by hydrogen desorption. For a film prepared at a low current density (a), the surface remained smooth, showing that the lattice contraction took place uniformly. For films prepared at higher current densities (b) and (c), on the other hand, many dimples were observed, showing that a part of hydrogen formed bubbles before being desorbed.

![Fig. 10](image1.png)

![Fig. 11](image2.png)
4. Summary and Conclusion

Chromium films were prepared under various conditions of electrodeposition, and a correlation between the crystal structure and the state of dissolved hydrogen was examined in detail by XRD and TDS. An increasingly larger amount of hydrogen was incorporated in the films in a more Cr-rich solution at higher current densities and lower temperatures, and with this increase of hydrogen concentration the structure changed in the order \( \text{bcc} \rightarrow \text{hcp} \rightarrow \text{fcc} \). This correlation between the crystal structure and hydrogen concentration is consistent with the result of high pressure experiment, another method to produce high chemical potentials of hydrogen.

REFERENCES


Fig. 12 Cross sectional SEM images of Cr films electrodeposited in Bath B at 3°C and 3000 A/m² (Case (b) of Fig. 4); (A) as deposited, and (B) after heat treatment at 800°C for 900 s. The structure changed from fcc to bcc during the heat treatment. Arrows indicate small voids of \( \sim 50 \) nm in diameter formed by the heat treatment.