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Hard chromium plating on cold swaged Cr-Mo steel using rotating cylinder electrode

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Hard chromium plating is widely used owing to its good wear and corrosion resistance. This plating technology has been practiced and well developed for many decades [1, 2]. Since reduction of hydrogen ions occurs at electrode surface during chromium plating, the current efficiency for the plating is normally under 25% [1]. However, Hoare [3] shows that rapid flow of the electrolyte over the cathode surface is essential for high-speed chromium plating due to the reduction of the diffusion path in a diffusion-controlled electrode reaction. Plating by using rotating disc electrode (RDE) method is useful to study this effect.

Cross-section microstructure of the plated hard chromium was studied with optical microscope and scanning electron microscope (SEM) [4, 5]. The results showed that the grain size of as-plated chromium was so fine that the grain size cannot be estimated, and only the grains after annealing can be observed. Pina [5] showed that a fiber texture existed with $\langle 111 \rangle$ axis perpendicular to the chromium deposit surface by using X-ray diffraction method. The interface microstructure between Cr-Mo steel and chromium deposit has not been studied yet. Especially, little work has been done on the current efficiency and TEM-cross section microstructure of chromium plating using rotating cylinder electrode (RCE), by which a uniform mass transport over all of the electrode surface can be obtained. In this letter the aspects mentioned above are reported using RCE specimens.

Cold swaged Cr-Mo steel was the chosen specimen with its chemical composition shown in Table I. The cylinder specimen dimension was 16 mm $\varphi \times 5$ mm with an exposing plating area of 2.51 cm^2. Platinized-Ti mesh with dimension of 25×35 mm was used as anode. All chromium plating was performed in a conventional bath containing 250 g/l of CrO_3 and 2.5 g/l of H_2SO_4 at 50 °C. Cathodic current densities applied were 30, 40, 50 and 60 A/dm^2, respectively. Rotating speed of RCE was controlled in the range of 5–1000 rpm.

Before electroplating, the RCE specimens were anodically polarized with current density of 40 A/dm^2 at 200 rpm for 30 s. The current efficiency was evaluated with three RCE specimens after a constant applied cathodic charge of 1.33 A h under same plating condition. The weight increment of chromium plating was measured and compared with theoretical weight increment according to Faraday's law. After plating, the RCE specimen was rinsed in acetone, dried with hot air, then prepared for current efficiency evaluation; TEM-cross section specimens were prepared as mentioned elsewhere [6] and their microstructure examined.

The current efficiency of applied cathodic current density with respect to logarithmic rotating speed of RCE is shown in Fig. 1. The results show that all current efficiency increases with the increasing of cathodic current density, suggesting that higher electric field tends

TABLE I Chemical composition of Cr-Mo steel

element	Cr	Mo	C	Mn	V	Si	S	P
wt %	1.2	1.1	0.22	0.4	0.3	0.4	<0.035	<0.035

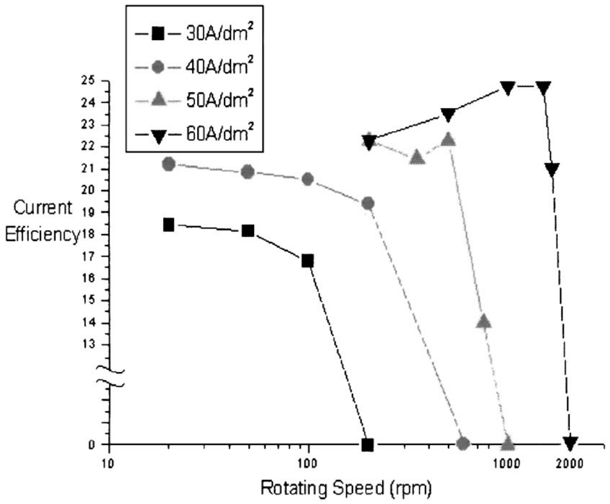


Figure 1 The relation between current efficiency and rotating speed of RCE.

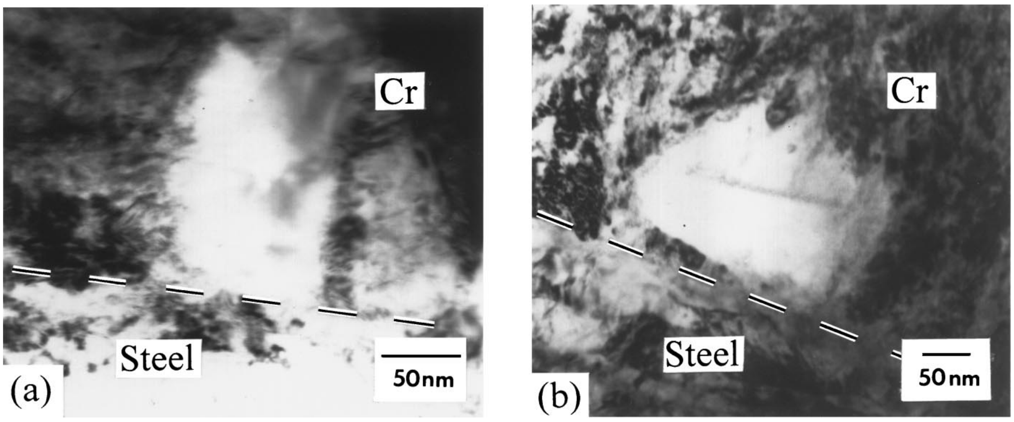


Figure 2 TEM - cross sectional microstructure of interface between Cr-Mo steel and plated chromium under (a) 30 A/dm^2, 100 rpm (b) 50 A/dm^2, 350 rpm.

to increase chromium ion reduction reaction despite that all current efficiencies are still very low. The current efficiency decreases with the increasing of rotating speed at lower cathodic current densities of 30 and 40 A/dm^2. On the contrary, the current efficiency increases with increasing of rotating speed at 60 A/dm^2. It is interesting to find that the current efficiency exhibits a reversing point at 350 rpm when plating at 50 A/dm^2.

More importantly, no chromium deposition is detected when plating at 30 A/dm^2 at speeds higher than 200 rpm, neither are found for plating at 40 A/dm^2 higher than 500 rpm, at 50 A/dm^2 higher than 1000 rpm and at 60 A/dm^2 higher than 2000 rpm, respectively (Fig. 1). Under above conditions hydrogen bubbles vigorously on RCE's surface. The above phenomena can possibly be explained as follows; the initial uprising tendency at 60 A/dm^2 in Fig. 1, which is contrary to the downward tendencies at 30 A/dm^2 and 40 A/dm^2, perhaps is caused by the strong electric field enhanced by the more efficient mass transport of chromium ion (Cr^{+6}) with increasing speed. However, in all cases, hydrogen ion (H^+) reduction reaction consists of three steps: H^+ catches electron to form the hydrogen atom, the reduced hydrogen atoms diffuse on steel surface combining to from H_2 molecule, which then leaves the steel surface. The generally acknowledged rate-controlling step is H_2 molecules being driven away the steel surface and this step would obviously occur more readily at higher rotating speed. Thus, as speed increases to certain value, H^+ reduction reaction would preclude Cr^{+6} reduction reaction, leading to nil current efficiency. The enhanced competition between H^+ and Cr^{+6} reduction reactions at higher current density would thus result in higher nil-current-efficiency rotating speed.

Fig. 2 shows the interface microstructure between Cr-Mo steel and chromium deposit. The plating conditions were at 30 A/dm^2, 100 rpm and 50 A/dm^2, 350 rpm, respectively. According to grain size and dislocation density shown, two kinds of the deposit grain are detected adjacent to the interface as shown in dashed line. Equiaxed grains, about 200 nm in size, with low dislocation density nucleate on the surface of the steel. These grains are much larger than the adjacent fine grains ($\sim$20 nm). The very fine grains are also found in the outer layer of the deposit and the grains assume lath shape with dimensions about 50 nm $\times$ 20 nm (Fig. 3b). The result of SAD pattern of these fine grains is also shown in Fig. 3, in which diffracted $g\langle 110\rangle$ points in reciprocal space for those fine grains do not present a ring but a straked pattern. That is, the grains are oriented in preferred direction and have a textured structure.

A detailed interfacial cross-section TEM-microstructure for chromium deposited at 60 A/dm^2 and 1000 rpm is shown in Fig. 4. The same results of interfacial grain nucleation as observed in lower

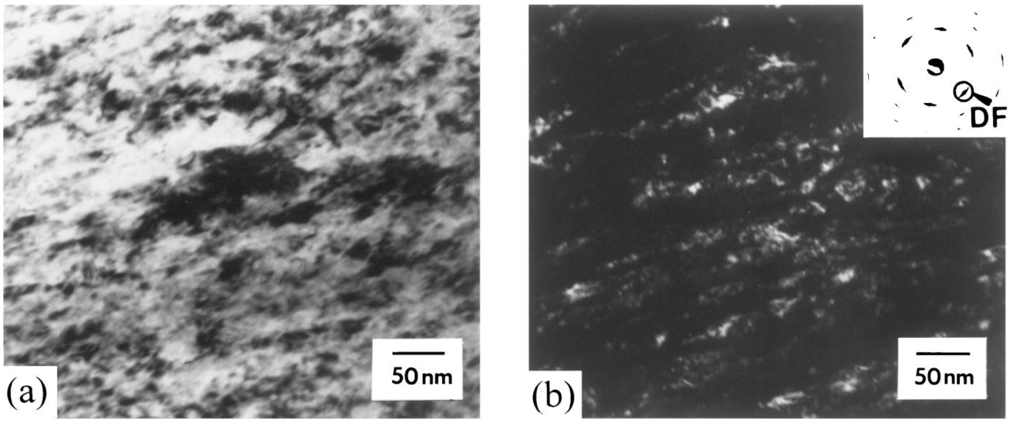
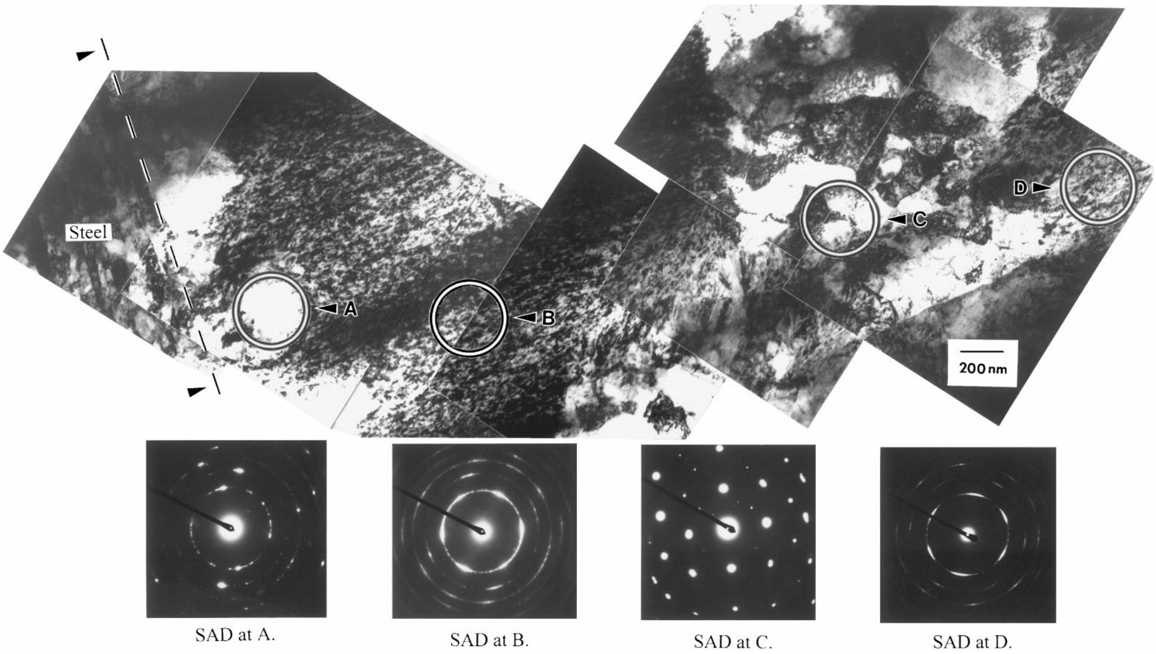


Figure 3 TEM - cross sectional outer layer of chromium deposit, showing very fine grain size and textured structure (50 A/dm^2, 350 rpm) (a) bright, (b) dark field images.



SAD at A. SAD at B. SAD at C. SAD at D.

Figure 4 Detailed TEM - cross section microstructure of the interface between Cr-Mo steel and chromium deposit (60 A/dm^2, 1000 rpm).

current densities plating (Fig. 2) are obtained, there are larger equiaxed grains nearby circle A and very fine grains in lath shape nearby circles B and D (Fig. 4). However, dissimilar to Fig. 3, in a region near interface shown around circle C in Fig. 4, some equiaxed grains with sizes about 150 nm are observed. From the results of SAD patterns shown in Fig. 4, these equiaxed grains have no preferred orientation and grow aggregately forming about 500 nm band adjacent to the very fine grain region. But following these equiaxed grains region a textured fine grains region (nearby circle D in Fig. 4) are observed again. The growth mechanism and its effect on the mechanical properties of this fascinating deposit microstructure certainly deserve further study and the work is in progress.

In conclusion, effects of current density and rotating speed on hard chromium plating on steel are studied using RCE specimen; chromium/steel interfacial TEM-microstructure are investigated. The mechanism of competition between reductions of Cr^{+6} ion and H^+ ion due to current density and rotating speed can be explained and utilized to rationalize current efficiency result. The interfacial TEM-microstructure of chromium/steel shows interesting nanoscale grain sizes, although large size difference and textured structure still exist among grains in various regions. Further study in this aspect is in progress.

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