Corrosion and wear characteristics of pulse-plated chromium deposits

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Corrosion and wear characteristics of pulse-plated chromium deposits obtained from a self-regulating high speed (SRHS) bath have been studied as a function of pulse current parameters such as duty cycle, average current density and pulse period. The chromium deposits obtained at duty cycles of 100 (direct current) to 60% were composed of a hemispherical nodular growth with a body centred cubic (bcc) lattice while those obtained at 20% duty cycle were composed of a needle-like structure containing a mixture of bcc lattice and hexagonal hydride. Corrosion rate, wear loss of chromium deposits and occluded hydrogen content in the deposits decreased up to 60% duty cycle, and then increased with further decrease in duty cycle to 20%. A two-stage variation of corrosion and wear properties with decreasing duty cycle is discussed in terms of crack density and the crystal structure of chromium deposits.

1. Introduction

Electrodeposited chromium is used in decorative coating, die-marking and other engineering purposes for protection against corrosion and wear. Recently, the possibility of using a pulse current (PC) has been investigated to modify the properties of chromium deposits [1–8]. Sutter [1] reported that pulse-plated chromium of thinner deposits showed a better resistance to corrosion and good hardness than conventional direct current (d.c.) coating. Malinin et al. [2] maintained that the use of PC increased the current efficiency by 15 to 25% and made it possible to obtain bright deposits while having practically no effect on the absolute hydrogen content in the deposits.

However, several authors [3, 4] maintained that the current efficiency of PC chromium plating was lower than that of d.c. plating, and PC formed a deposit with a high hydrogen content due to the formation of chromium hydride. This discrepancy seems to arise from the fact that the effects of the range of PC parameters on the current efficiency of chromium plating and the crystal structure of chromium deposits are not considered discretely. Moreover, the scientific basis of pulsed electrodeposition and the effects of PC on the properties of the deposits have not yet been fully established.

The present work is concerned with the current efficiency, crystal structure, surface morphology, occluded hydrogen content, corrosion rate and wear loss of pulse-plated chromium deposits as a function of the PC parameters such as duty cycle, average current density and pulse period from a self-regulating high speed (SRHS) bath. The optimum electrolytic conditions have been established in the light of the crystal structure–properties relationship.

2. Experimental procedure

All specimens were electrodeposited from an SRHS bath containing reagent grade 250 g/l CrO_3, 4.0 g/l Na_2SiF_6 and 2.0 g/l $SrSO_4$. The mild steel specimen used as a rectangular cathode was 2 cm × 3 cm in area, and 0.1 cm thick, ground mechanically with 1000 grit silicon carbide paper, and then activated with a 5 min dip in concentrated H_2SO_4 solution, followed by rinsing in acetone and distilled water. The soluble anode of a 3.5 cm × 3.5 cm Pb–5% Sn plate was located in parallel with a cathode with 5 cm inter-electrode distance in the plating bath. In order to eliminate the uneven current distribution around the edge region of cathode, only a central square portion of 4 cm² of the cathode was exposed and the remaining area was coated with epoxy resin.

The PC was provided with Pulsir 1210RP(LWD Scientific minipulsir), which controls peak cathodic current between zero and a constant value. The electrodeposition was conducted at duty cycles of 100 (d.c.) to 20%, average PC densities of 0.6 to 1 A cm⁻², and pulse periods of 1 and 10 msec. The pulse period is defined as the sum of on-time and off-time of a rectangular current. The duty cycle is the percentage of on-time within a pulse period, 100% duty cycle means d.c. plating. No agitation was used in order to accentuate the effect of PC during electrodeposition. All the experiments were performed over 2 h at a constant temperature of 50 ± 1° C.

The cathodic current efficiency was measured using a gravimetric method with an analytic balance with an accuracy of 0.1 mg. The waveforms of applied PC and resulting cathodic overpotential were determined with an oscilloscope using a saturated calomel electrode (SCE) as reference. The potential of the

working electrode was determined by the final value just before the current was cut off. The measured overpotential includes resistance over potential (*IR*-drop) so that *IR*-drop is subtracted from total overpotential [9].

The amount of hydrogen absorbed into the chromium deposits during electrodeposition was measured by the electrochemical method [10]. In the present measurement of hydrogen extraction, only the detection side, anodic compartment, was employed. To prevent extraneous anodic reaction on the detection side, a homogeneous coating of palladium was produced before conducting chromium plating on another side of the specimen. The detection area for hydrogen extraction was 0.8 cm² and circular in shape.

Hydrogen flux was measured electrochemically from the detection side, maintaining this side of the specimen at an anodic potential of 200 mV versus standard hydrogen electrode (SHE) in a 0.1 N NaOH solution with a potentiostat at $19° \pm 2°C$. The extraction current required to keep the anodic potential constant was recorded by a sensitive strip chart recorder. The amount of hydrogen absorbed into the chromium deposits was estimated from the area under the hydrogen extraction current–time curves [10]. In this study the extraction time was limited to 24 h for convenience.

The presence of microcracks in the pulse-plated chromium deposits was confirmed by optical microscopy after etching in 10% H_2SO_4 at 90° C for 10 sec. The corrosion rate was determined by measuring the weight loss of the deposits after immersing in a solution of one part 32% HCl to one part distilled water at 30° C for 10 min.

Knoop microhardness of the pulse-plated chromium deposits was measured at 50 g load. Wear tests were carried out using a pin-on-disc type machine [11] for a duration of 30 min, at a sliding velocity of 14.3 m min⁻¹ and an applied load of 19.6 N. The wear pin, a cylindrical rod 3 cm long and 0.8 cm diameter, was a mild steel coated with sintered diamond paste.

After conducting the pulse-plating, the structure and morphology of the chromium deposits were also examined with an X-ray diffractometer and a scanning electron microscope (SEM), respectively.

3. Results

Figure 1 shows the variation of the current efficiency as a function of duty cycle at a pulse period of 1 msec for different average current densities. The current efficiency of the chromium plating decreased with decreasing duty cycle, irrespective of average current density. The same result was obtained at the pulse period of 10 msec, which is inconsistent with that of Chin and Zhang [3]. Because the cathodic reaction during chromium plating involves both the reduction reactions of chromium and of hydrogen ions, the decrease in current efficiency with decreasing duty cycle means an increase in the hydrogen evolution rate. PC is considered to behave as a depolarizer for the reduction of chromium ions.

The cathodic overpotential increased with decreasing duty cycle and accordingly the peak current increased
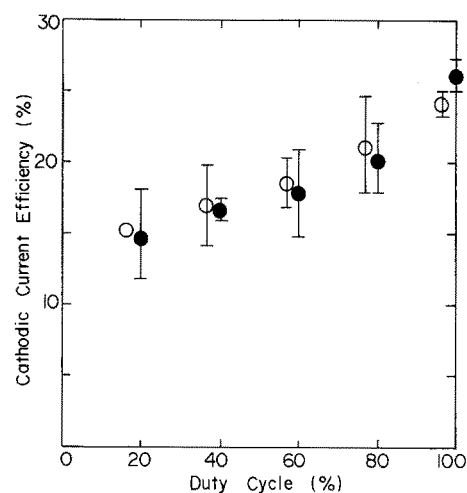

Figure 1 Cathodic current efficiency during pulsed electrodeposition of chromium plotted against duty cycle for various average current densities and a pulse period of 10 msec. (O) 0.6 A cm⁻²; (●) 1 A cm⁻².

in the current-on time. X-ray diffraction patterns are shown in Fig. 2 for the chromium deposits obtained under different duty cycles at an average current density of 1 A cm⁻² and a pulse period of 1 msec. The deposits obtained at duty cycles between 100 and 60% in Figs 2a and b showed typical body centred cubic (bcc) chromium peaks. However, unknown extra peaks, neither chromium oxide nor base metal peaks, were observed from the deposits obtained at the 20% duty cycle as in Fig. 2c. By decomposing completely the chromium deposits made at the 20% duty cycle through heating at 450° C for 10 min, metallic chromium changed to bcc lattice only as shown in Fig. 2d. From these facts we infer that the hexagonal lattice is formed due to the chromium hydride in the regime of duty cycles between 40 and 20%, as typically shown in Fig. 2c. Thus, the chromium deposit has either a bcc or a hexagonal lattice, depending on the conditions of electrodeposition as reported by previous workers [8, 12–14].

Figs 3a to e show that the crack density on the chromium deposits decreased markedly with decreasing
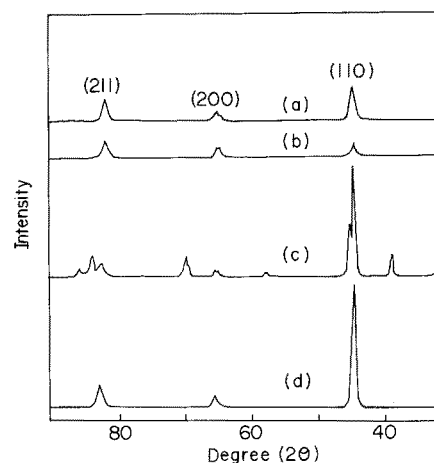

Figure 2 X-ray diffraction patterns of chromium deposits as a function of duty cycle: (a) 100% (d.c.), (b) 60%, (c) 20%, plated at an average current density of 1 A cm⁻² and a pulse period of 1 msec, and (d) 20%, plated at an average current density of 1 A cm⁻² and a pulse period of 1 msec, followed by heat-treating at 450° C for 10 min.
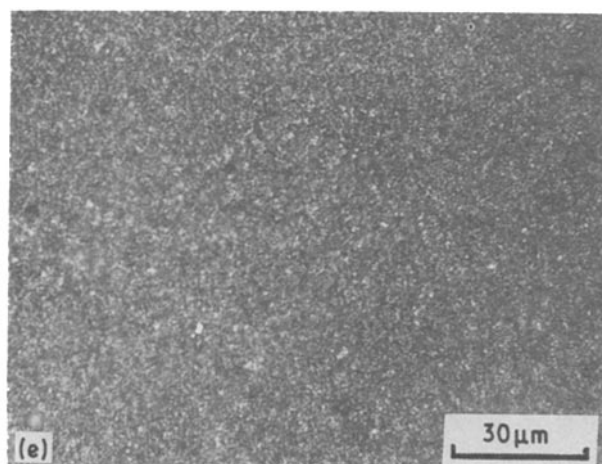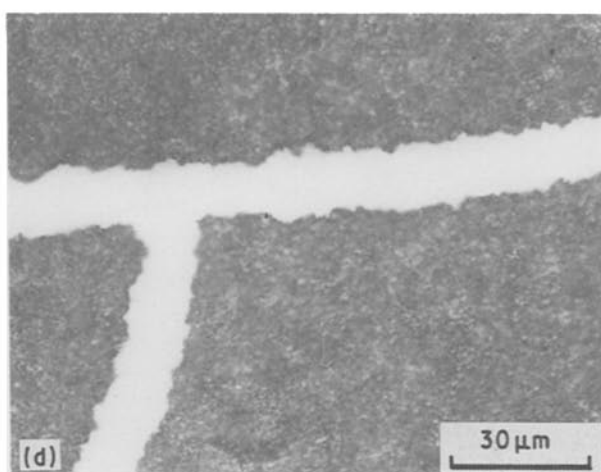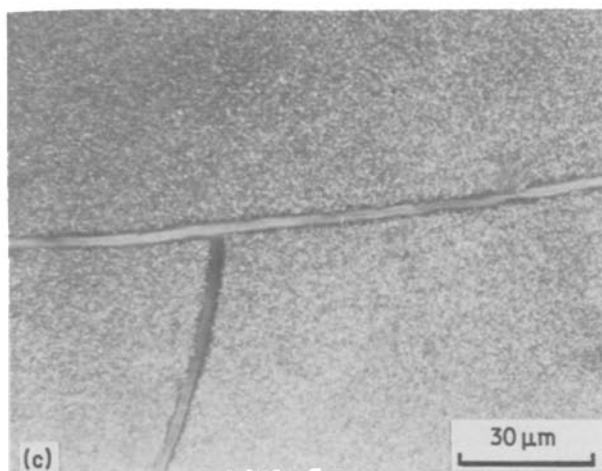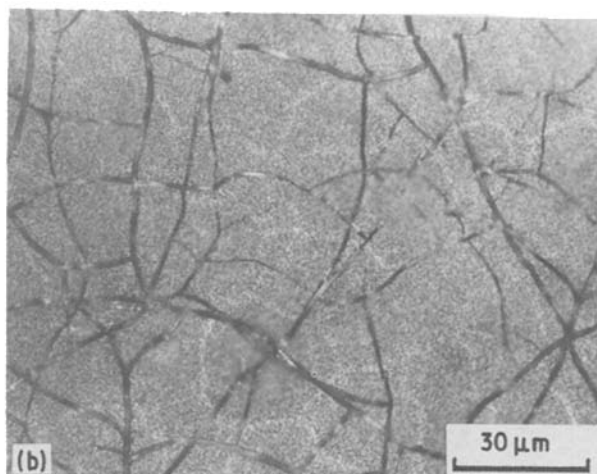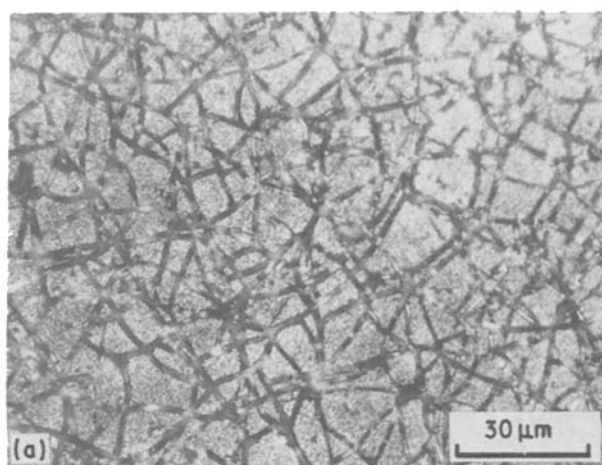
Figure 3 Surface cracks of chromium deposits as a function of duty cycle: (a) 100% (d.c.), (b) 80%, (c) 60%, (d) 40%, and (e) 20% for plating at an average current density of $1 A cm^{-2}$ and a pulse period of 1 msec.

duty cycle. Crack-free chromium deposits, in Fig. 3e, were obtained at duty cycles less than 40%.

Figs 4a to e show surface morphology of the chromium deposited at an average current density of $1 A cm^{-2}$ and a pulse period of 1 msec with varying duty cycle. The morphology changed from hemispherical nodular type to needle-like type as the duty cycle decreased from d.c. plating to 20% duty cycle.

The variation of hydrogen extraction current in the chromium deposited at an average current density of $0.6 A cm^{-2}$ and a pulse period of 1 msec, is plotted against extraction time if Fig. 5 as a function of duty cycle. The hydrogen content in the deposits showed a minimum value at the 60% duty cycle.

Fig. 6 shows the corrosion rate of the chromium deposits in 30% HCl solution plotted against duty cycle, at an average current density of $1 A cm^{-2}$ and pulse periods of 1 and 10 msec. The corrosion rate of chromium deposits decreased up to 60% duty cycle, then increased as the duty cycle decreased, regardless of pulse periods.

The variation of the Knoop microhardness and wear loss of chromium deposits with duty cycle, at an average current density of $1 A cm^{-2}$ and a pulse period of 1 msec, are shown in Fig. 7. The chromium deposits obtained with PC showed relatively lower hardness values than that with d.c.; however, the hardness was relatively constant within experimental scatter. Wear loss of chromium deposits showed a minimum value at the 60% duty cycle. Thus, it is suggested that the optimum electrolytic condition for chromium plating is 60% duty cycle in view of the hydrogen content, corrosion rate and wear loss.

4. Discussion
4.1. Effect of PC on the crystal structure and morphology of chromium deposits
The b c c structure of chromium deposits is highly distorted, mainly due to the incorporation of foreign substances within the deposited film. As hydrogen
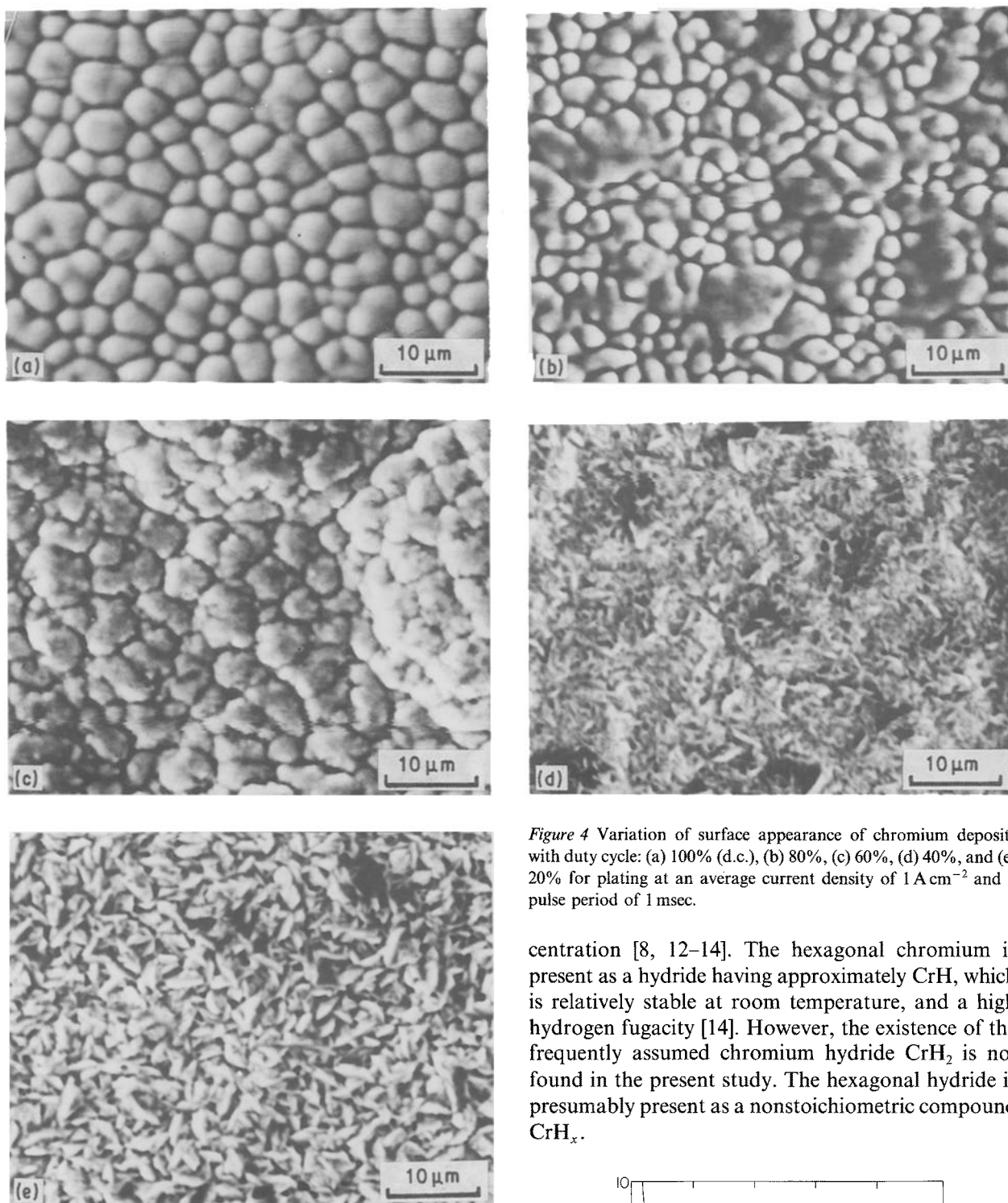
Figure 4 Variation of surface appearance of chromium deposits with duty cycle: (a) 100% (d.c.), (b) 80%, (c) 60%, (d) 40%, and (e) 20% for plating at an average current density of $1 \, A \, cm^{-2}$ and a pulse period of 1 msec.

centration [8, 12–14]. The hexagonal chromium is present as a hydride having approximately CrH, which is relatively stable at room temperature, and a high hydrogen fugacity [14]. However, the existence of the frequently assumed chromium hydride CrH_2 is not found in the present study. The hexagonal hydride is presumably present as a nonstoichiometric compound CrH_x.

absorption in the deposits increases further, the bcc structure becomes unstable at room temperature and high hydrogen fugacity, changing to the hexagonal form having a higher hydrogen content than the bcc chromium deposit. Thus, hydrogen is present in bcc deposits as a supersaturated solid solution, while that in the hexagonal deposits is present as a chemically bonded hydride. The bcc structure developed between 100 and 60%, and the hexagonal structure between 40 and 20%, are attributable to the low and high hydrogen fugacities, respectively.

The hydride formation occurs mainly under specific electrodeposition conditions, such as low plating temperature, high current density, high chromic acid con-
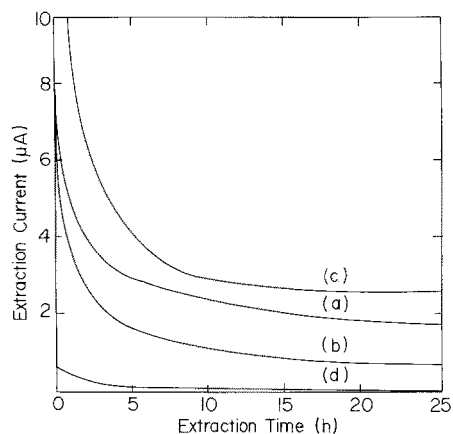

Figure 5 Hydrogen extraction current plotted against extraction time as a function of duty cycle for plating at an average current density of $0.6 \, A \, cm^{-2}$ and a pulse period of 1 msec: (a) 100% (d.c.), (b) 60%, (c) 20%, and (d) 0% (no chromium plating), exposed area: $2.54 \, cm^2$.
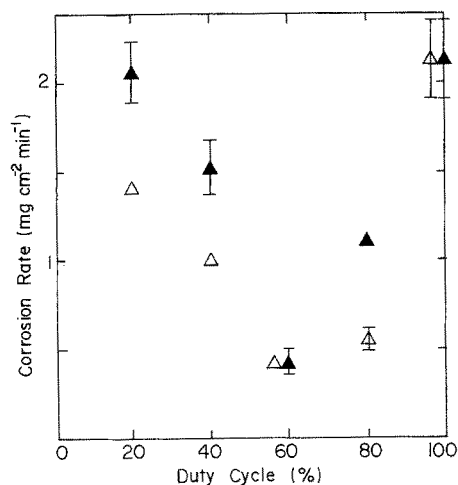
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Figure 6 Corrosion rate of chromium deposits in an HCl solution (32% HCl + distilled water, 1:1) plotted against duty cycle, deposited at an average current density of $1 \, A \, cm^{-2}$ and pulse periods of 1 and 10 msec. ($\triangle$) 1 msec; ($\blacktriangle$) 10 msec.

Because the hydride deposit will have undergone a decrease in hydrogen fugacity and become thermodynamically unstable, the electrodeposited chromium hydride CrH_x formed during the plating at 100 to 60% duty cycles decomposes and shrinks into chromium metal and hydrogen upon deposition. Volume reduction of some 15% occurs as a result of this conversion [15] and very high internal stress develops in the chromium deposits. Because the adhesion of the chromium on its substrate is extremely high, the shrinkage occurs parallel to the substrate, producing many fine cracks along the chromium layers within the d.c.-plated deposits, as shown in Fig. 3a.

The electrolytic nucleation rate is determined by an exponential function of cathodic overpotential [16]. D.c. with low overpotential causes the grain growth of a typical hemispherical nodular type as shown in Fig. 4a.

As the duty cycle decreased from 100 to 60%, the high overpotential associated with the high PC density increases the nucleation rate greatly, thus a smoother and finer electrodeposit was obtained. The grain thus developed into hemispherical nodular deposits with fine secondary growths as shown in Fig. 4c. This result
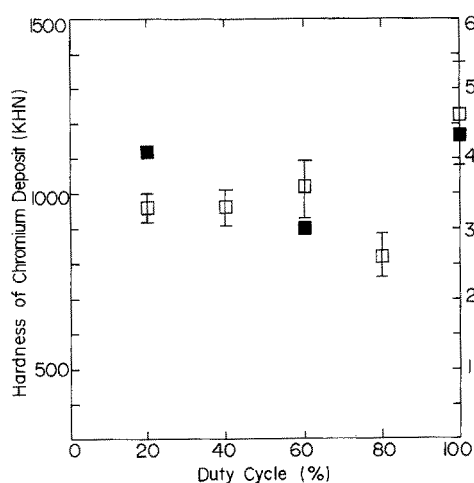

Figure 7 Hardness and wear loss of chromium deposits plotted against duty cycle for plating at an average current density of $1 \, A \, cm^{-2}$ and a pulse period of 1 msec. ($\square$) hardness; ($\blacksquare$) wear loss.

may be attributed to the capability of PC to enhance the mass transport process, rate of nucleation, and kinetics of electrodeposition. Chin [17] proposed a current–potential relationship in PC electrolysis on the basis of mass transfer theory. PC produces a pulsating diffusion layer wherein the concentrations of the ionic species fluctuate periodically with time near the electrode surface reducing the effective thickness of the Nernst diffusion layer. An instantaneous PC density of one to two orders of magnitude greater than the steady-state limiting current density of d.c. can be used without depleting the metal ions at the electrode surface [17]. For this reason, PC can be used in the electroplating to improve the properties of electrodeposits.

However, rough needle-like deposits with a high hydrogen content were formed at duty cycles lower than 40% in spite of such a high overpotential. Therefore, the other characteristic feature of PC electrolysis must influence the current-off period during which the adsorption and desorption phenomena, as well as recrystallization of the deposits, occur as suggested by Ibl [18]. The needle-like morphology containing chromium hydride resulted from adsorption of excess hydrogen and oxygen at the 20% duty cycle.

4.2. Effect of PC on the hydrogen content and crack density in deposits

The surface of chromium deposits has a tendency to absorb oxygen during the long current-off period. However, it also has a tendency to increase the hydrogen evolution rate due to higher cathodic overpotential during the short current-on period in the range of lower duty cycles of PC plating. These tendencies cause the blockade of hydrogen liberation on the pulse-plating at lower duty cycles. This condition is believed to cause crack-free chromium deposits, as shown in Fig. 3e.

However, absorbed hydrogen may be desorbed during the current-off period in the PC electrolysis, thus the amount of hydrogen absorbed decreases with decreasing duty cycles from 100 to 60%, as shown in Figs 5a and b. The result is in accord with that obtained from palladium electrodeposition [9, 19]. Thus, it is important to note that the current-on periods should be set so as not to exceed the time necessary to deposit chromium hydride. Furthermore, the current-off periods should be initially programmed to allow sufficient time to decompose the chromium hydride into b c c chromium and escaping hydrogen in the form of molecular gaseous hydrogen. Therefore, these PC plating conditions yielded a chromium deposit containing less absorbed hydrogen than that obtained by d.c. electrolysis.

4.3. Effect of PC on the corrosion rate and wear loss

Chromium hydride is a thermodynamically unstable phase at room temperature and low hydrogen fugacity, and may be more soluble in acidic solution than is b c c chromium deposit. Generally, chemical attack on the chromium deposits originates from the cracks in the deposits. Therefore, the corrosion rate may be reduced

by decreasing the crack density on these deposits. Thus, the decrease in corrosion rate with decreasing duty cycles from 100 to 60%, is attributed to reduced crack density. However, an increase in corrosion rate with further decrease in the duty cycles from 60 to 20% is ascribed to the formation of chromium hydride, where cracks were hardly observed on the chromium deposits obtained in this regime of duty cycles.

The hardness of the deposit is regarded as a direct indication of its wear loss; however, it should be noted that not only the hardness, but also the ductility and crack density in chromium deposits are determining factors for the wear loss [20]. It is realized from the worn surface of the chromium deposits, in Fig. 8, that a crack network, generated mainly during electro-deposition as a result of the accumulation of internal stress on the chromium deposits, is apparent, which is a typical feature in conventional d.c. chromium deposits. Most of the cracks initiated at pre-cracks formed during the d.c.-plating, propagated by wear process in the transverse direction to the wear direction. The initiation and propagation of wear cracks resulted in a greater increase of wear loss.

Decrease in the wear loss with decreasing duty cycles from 100 to 60% is ascribed to both a decrease in crack density and an increase in ductility caused by the presence of fine-grained deposits. However, the increase of wear loss at duty cycles less than 60% is probably attributable to the presence of brittle chromium hydride in the deposits, although those chromium deposits show a crack-free morphology. Thus, the minimum wear loss of the chromium deposits at the 60% duty cycle was due to reduced crack density.

5. Conclusions

Pulse-plating of chromium has been conducted in the SRHS bath as a function of duty cycle to investigate the effects of PC on the crystal structure, morphology, corrosion and wear characteristics of chromium deposits. The results are summarized as follows.

1. The crystal structure and morphology of chromium deposits were changed markedly by PC. As the duty cycle decreased from 100 to 60%, the chromium deposits changed from a hemispherical nodular appearance in d.c. plating to smooth and fine secondary growths with b c c structure. The chromium deposits obtained at a duty cycle less than 40% exhibited a needle-like structure composed of mixtures of b c c lattice and hexagonal hydride. The most important factors determining crystal structure and morphology are cathodic overpotential, adsorption or desorption of impurities such as hydrogen and oxygen during the current-off period.

2. The crack density in the chromium deposits decreased with decreasing duty cycle up to 60%. Crack-free chromium deposits with a higher hydrogen content were obtained by further decreasing the duty cycles from 40 to 20%. The hydrogen content of deposits decreased to the minimum value at 60% duty cycle due to the competing effects of hydrogen in the desorption from the metal surface during the current-off period and in the decomposition of chromium hydride.

Figure 8 Optical micrograph of worn chromium deposits, d.c. plated at the current density of $1\,A\,cm^{-2}$.

3. The corrosion rate and wear loss decreased with decreasing duty cycles from 100 to 60%, and then increased with further decrease in duty cycles from 60 to 20%. The first-stage decrease and second-stage increase in corrosion rate and wear loss are ascribed to crack density and the formation of chromium hydride phase CrH_x, respectively.

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