Microcracks in Hard Chromium Electrodeposits

By A.R. Jones

Microcracking in thick chromium deposits varies over a broad range depending on plating bath composition. Observations during electroplating indicated that microcracking occurred periodically with copious evolution of hydrogen gas. A correlation between microcrack density and microhardness was established, but no correlation was found between microcrack density and appearance, using data derived from four different baths.

ard chromium is a term used to describe chromium electrodeposits thicker than about 2.5 µm (0.1 roil). In this paper, the term microcrack refers to a crack that does not extend from the basis metal to the surface of the deposit; the term "micro" does not imply a high crack count. A macrocrack extends throughout the entire thickness of the chromium deposit, from the substrate to the surface.

Microcracks are networks of cracks visible with the aid of magnification, after development, and are desirable in hard chromium deposits. Microcracks form during deposition when the tensile stress exceeds the cohesive strength of the chromium. As chromium thickness increases, tensile stress increases until microracking occurs, which relieves stress in the deposit. At a thickness of about 125 μ m (5 mils) internal stress reaches a constant value. ¹² Deposits free of microcracks are not as hard as microcracked chromium. Deposits thicker than about 10 μ m (0.4 mil) electrodeposited from a "crack-free" process tend to form macrocracks, and may not be mechanically sound.

The pattern of interconnecting microcracks in Fig. 1 has about 900 cracks/cm (2200 cracks/in.). Before development by reverse-current etching, the cracks are filled with chromium or chromic oxide. Figure 2 shows an etched cross section of a microcracked chromium deposit. The formation of microcracks and how they are affected by the plating conditions are discussed in this paper, which also examines the correlation of the number of microcracks with the brightness and hardness of the deposits.

Microcrack Formation

The formation of microcracks was observed and recorded by videotaping during electrodeposition at 48 A/dm² in a conventional chromium plating solution at 55° C containing 250 g/L of chromic acid and 2.5 g/L of sulfuric acid. Observations commenced 30 min after plating was started. The sample was a l-cm rod located approximately 1 mm from the side of a 1-L beaker. The plated area was 0.4 cm wide and 1.0 cm high. A magnetic stirrer was turned off during recording to eliminate vibrations. A projection microscope! with a magnification of 100 was focused on an area at the bottom of the sample to reduce interference from hydrogen bubbles. An image of the plated surface on the projection microscope screen was videotaped and the tape was then observed on a 62-cm (25-in.) television screen, which provided a total magnification of 650. The area under observation was 1.2 percent of the total plated area.

The plated surface was clearly visible, but there were some out-of-focus gas bubbles in the foreground. Although gassing appeared to be uniform to the unaided eye, microscopic observations at 100X showed that gassing occurred almost exclusively at surface discontinuities such as pits, microcracks and edges adjacent to (or under) the masking material. Very few bubbles occurred at smooth

'Monoscopic Dynascope, Vision Engineering Inc., New Milford, CT.



PLATING AND SURFACE FINISHING

surfaces. Copious amounts of hydrogen gas evolved from microcracks. Although the microcracks were barely visible, the gassing made them appear dark. Microcracks formed rapidly and appeared to grow in length. As microcracks were plated over, gassing became restricted to line segments and then to single points.

The frequency and duration of microcracking episodes are reported in Table 1. Nine episodes of microcracking were observed during a 44-min plating period. Episode cycles ranged from about 2.5 to 11 min and time intervals between gassing up to about 10 min. However, the duration of gassing periods was more consistent and much shorter, lasting about 0.6 to 1.2 min. Periodic microcracking has recently been detected by acoustic monitoring of chromium plating.³Microcrack patterns traced onto transparent films are shown in Figs. 3, 4 and 5. Each figure shows three patterns, as designated in Table 1. Figure 6 is a composite of all nine episodes. Although appearing to be continuous on a macro scale, microcracking is discontinuous on a microscopic scale.

The depth of microcracks can be estimated from the gassing duration data in Table 1 and the etched cross section in Fig. 1. Table 1 data indicating that gassing persists for about 1 min while a microcrack is plated over would correspond to a chromium thickness of about 0.33 μ m (0.01 mil) at the deposition rate forth is sample. Figure 2 shows that microcracks range in depth from 5 to 10 μm (0.2 to 0.4 mil), however. The plating rate in a microcrack is greater than on the surface, therefore the microcracks are deeper than 0.33 µm. A shorter reverse etch will produce a microcrack that is shallower than 5 to 10 µm.

The Fig. 6 composite obtained during a 44-min plating period shows a density of 200 microcracks/cm by comparison with a pattern of 170 microcracks/cm for this plated sample. These densities are considered to be statistically equivalent. Thus the reverse-current etch used evidently developed all of the microcracks formed during 44 min of plating. About 15 µm (0.6 mil) of chromium was deposited in 44 min of plating and about 10 µm (0.4 mil) was dissolved during the development of the microcracks. Microcrack patterns are imprinted downward as chromium is etched. Microcrack episode No. 7 covered the field of view in less than 33 msec. Thus the microcrack pattern was fully developed in this single video tape frame.

time,	previous start,	of gassing,	de braise
o. min.	min.	min.	Figure
0.00		0.70	3()
2.37	2,37	1.15	• 3 ()
4.87	2.50	1.17	3 ()
14.64	9.75	1.02	4()
17,89	3.27	0.86	4 ()
25.90	8.01	0.57	4()
36.90	11.00	1.17	5()
40.09	3.19	1.18	5 ()
43.87	3.78	1.17	5 ()



Fig. 3-Microcracks transferred from video tape; see Table 1, episodes 1 to 3.







Fig. 5-Microcracks transferred from video tape; see Table 1, episodes 7 to 9.

In any single video tape frame, the microcracks that formed most recently were the most evident, but microcracks from previous episodes were visible as lighter lines. When the plating current was momentarily turned off during episode No. 4, gassing stopped and the microcracks disappeared. When the current was turned on, the same microcracks started gassing. Brittain and Smith' observed this same behavior when they interrupted the current for several hours.

Bath Composition, Current Density And Temperature Effects

Microcracking in three proprietary baths was compared with data obtained by plating in the conventional, nonetching bath prepared with a single (sulfuric acid) catalyst. The three proprietary solutions included a mixed-catalyst (etching) bath' an etch-free solution with an efficiency of 25 percent' and an etch-free bath with an efficiency of 40 percent." The mixed catalyst bath contained a fluoride-

^bHCR 840 chromium plating process, M&T Chemicals, Inc., Rahway, NJ. ^cHEEF 25 chromium plating process. M&T Chemicals, Inc., Rahway, NJ. ^cHEEF 400 chromium plating process, M&T Chemicals, Inc., Rahway, NJ.

containing catalyst in addition to sulfate ions. Seven samples were plated in each of the four solutions, using the sulfate concentrations, temperatures and current densities indicated in Table 2.

The substrate was a 1.0-cm rod of AISI 1085 steel with a surface finish of 0.4 μ m, rms, and a sample area of 5.1 cm². Before plating, samples were cleaned, rinsed in cold water and reverse-current etched in chromic acid solution. Weight gain by plating Was used to calculate deposition efficiency. Microcracks were developed by boiling the samples for 30 min in water followed by anodic etching at 46 A/dm²for 2 min in a 100 g/L sodium hydroxide solution at room temperature.

Microcracks were counted at six different locations on the surface of each sample; 10 measurements with a 100-g load were made with a Knoop indenter to determine microhardness. Appearance was classified as bright, semi bright or frosty. A scale from 1 (dull) to 10 (bright) also was adopted.

Table 2 shows that microcrack density ranged from less than 4 to about 3200 cracks/cm. Although the density cannot be determined with a high degree of precision, the

Table 2 Chromium Deposition Conditions Appearance, Microcrack Density and Microhardness											
			Current	Chromium		Microcrack		Microhardness			
Sample number*	Sulfate conc., g/L	Temp., °C	density, A/dm ²	deposition efficiency, %	Appearance rating**	density cracks/cm	sigma (n-1)	KHN ₁₀₀	sigma (n-1)		
A1	2.5	55	8	8	3	≪4	1 <u>7</u> 25	870	50		
A2	2.5	55	16	12	10	300	40	990	40		
A3	2.5	55	46	14	7	300	70	860	40		
A4	2.5	50	16	14	10	400	170	1000	40		
A5	2.5 .	60	16	10	2	250	70	810	50		
A6	1.5	55	16	10	5	50	10	870	20		
AŻ	3.5	55	16	12	10	650	180	870	60		
B1	1.7	55	16	27	10	700	140	1110	60		
B2	1.7	55	46	28	10	700	90	1140	60		
B 3	1.7	55	62	26	10	950	110	1200	50		
B 4	1.7	50	46	27	10	1250	70	1100	40		
B5	1.7	60	46	26	10	1000	160	1150	60		
B6	1	.55	46	27	10	550	90	1130	60		
87	2.5	55	46	26	10	1650	360	1150	70		
C1 ,	2.5	55	46	26	10	1950	260	1220	70		
-C2	2.5	55	62	26	10	2150	240	1160	70		
C3	2.5	55	78	26	10	1950	230	1270	60		
C4	2.5	50	46	26	10	2250	270	1210	60		
C5	2.5	60	46	26	10	2250	400	1200	30		
C6	1.5	55	46	25	10	2300	270	1170	80		
C7	4.0	- 55	46	24	10	3200	290	1120	40		
D1	2,5	55	46	42	10	800	70	1030	40		
D2	2.5	. 55	78	46	4	900	200	1050	50		
D3	2.5	55	108 ×	48		600	140	1040	40		
D4	2.5	50	78	48	1 ALA *** 1997	450	70	1110	40		
D5	2.5	60	78	46	7	1150	70	1070	40		
D6	1.5	- 55	78	46	6	550	80	1010	20		
D7	4.0	55	78	45		850	160	1020	60		

*All A samples obtained from a conventional chromic-sulfuric acid plating bath; B chromium was deposited in a mixed sulfate-fluosificate bath; C chromium was deposited in a HEEF 25 proprietary bath; and D chromium in a HEEF 400 proprietary bath. **Deposite with a rating of 7 or 10 were bright; those with a rating of 2 through 6 were semibright. **Frosty appearance.

PLATING AND SURFACE FINISHING



Fig. 6-Composite of microcracks from Figs. 3105.

data indicate that deposits from the conventional bath have the lowest number of cracks, whereas chromium deposited in the solution giving an efficiency of 25 percent[®] had the highest crack count—about twice as many as the deposits from any other bath. Figure 7 shows that increasing the sulfate concentration resulted in an increase in microcrack density, especially for the mixed catalyst and 25-percent baths.

Figure 8 shows the effects of changing the temperature on the density of microcracks; Fig. 9 reports the results of increasing the current density. The microcrack density in deposits from the conventional bath increased from less than 4 to 300 microcracks/cm as the current density increased from 8 to 16 A/dm².



Fig. 7—Microcrack density as a function of sulfate concentration; al deposits are identified in Table 2.



Fig. 8—Microcrack density as a function of bath temperature; deposits are identified in Table 2.



Fig. 9—Microcrack density as a function of current density; deposits are dentified in Table 2.

APRIL 1989



Fig. 10— Microhardness as a function of microcrack density; deposits from conventional bath shown by solid circles; squares show deposits from the mixed catalyst bath; triangles designate deposits from the 25 percent bath and hexagonals show deposits from the 40 percent bath.

Microcrack Density, Microhardness and Appearance

The data in Fig. 10 shows a general trend of increasing microhardness with an increasing microcrack density. However, the increases in both microhardness and microcrack density relate to the chemistry of the solutions. Chromium deposited in the conventional bath was relatively low in both microcrack count and microhardness, whereas deposits from the 25-percent bath were high in both cases.

The scatter of points in Fig. 11 indicates that there was no correlation between microcrack density and brightness. Deposits from the mixed catalyst bath appeared consistently bright, whereas chromium deposited in the conventional and 40-percent baths had varied in appearance depending upon plating conditions.

Corrosion and Post Finishing

Microcracks are filled in and are not voids. The corrosion protection provided by deposits with a thickness of more than about 25 μ m (1.0 mil) does not change when microcrack density ranges from 100 to 800/cm (250 to 2000/in.). However, if microcrack density is too low, macrocracks may expose the basis metal.

Finishing processes such as machining and lapping increase the microcrack density by a factor of two to three. The number of cracks/cm before and after finishing typical deposits increased as follows: 390 to 910; 630 to 1700; 710 to 1700; 750 to 1500; 790 to 1300 and 870 to 2100. Finishing or baking electrodeposited chromium either increases the number of microcracks or makes them more detectable.

Conclusions

From microcracks that form rapidly during plating, hydrogen gas is evolved until the cracks are sealed with more chromium. Microcrack density varies from less than 4 to 3,200/cm depending on the composition of the bath. An increase in the sulfate concentration increased microcrack density in each of four baths studied. Temperature and current density changes in some baths had some influence on the microcrack density. Microhardness of the deposits increased as the microcrack density increased.

References

- J.E. Stareck, E.J. Seyb and A.C. Tulumello, *P/sting*, 41, 1171 (1954).
- 2 A. Brenner, P. Burkhead and C. Jennings, J. Res. Nat. Bur. Standards, 40,31 (1948).
- 3 M.T. Todaro, G.P. Caosimales and E.S. Chen, Report Number AR CC B-T R-87007, U.S. Army Armament Research, Development & Engineering Center, Benet Weapons Laboratory, Watervliet, NY (Mar. 1987).
- 4 C.P. Brittain and G.C. Smith, Trans. Inst. Metal Finishing, 33, 289 (1 956).



Fig. 11 —Data points for brightness and microcrack density; symbols are described in the Fig. 10 caption.



About the Author

Dr. Allen R. Jones, CEF, is a senior research chemist and group leader in the plating division of M&T Chemicals, P.O. Box 1104, Rahway, NJ 07065. His research interests are high efficiency and improved performance of hard chromium electrodeposits, as well as tribology and corrosion of advanced coatings. Dr. Jones earned his PhD degree in physical chemistry at Rensselaer Polytechnic Institute and his BA in chemistry at Linfield College. He is a member of the AESF Garden State Branch, the Electrochemical Society, and the American Chemical Society.