The Effects of Pulse Plating On Low-Contraction Chromium Electrodeposits

By Mark Miller and S.K. Pan

Pulse plating of low-contraction (LC) chromium using low pulse frequencies (less than 50 Hz) and high pulse frequencies (greater than 90 Hz) was evaluated and compared to direct-current-plated LC chromium, with respect to microstructure and mechanical properties. Low-frequency pulse plating significantly increases the hardness and cathode current efficiency (CCE) over de-plated LC electrodeposits, but results in lower tensile strengths. High-frequency pulse plating produces poor quality deposits with lower hardness, CCE, and ultimate tensile strengths (UTS) than those obtained by d-c plating.

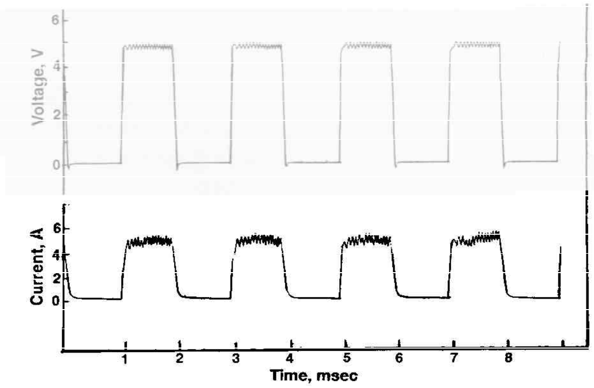


Fig. 1—Voltage and current profile of high-frequency pulse plating at 1.0 msec on-time/1.0 msec off-time.

Electroplating of LC chromium resulted in deposits which were crack-free and of relatively high tensile strength.[1] Further improvements by Pan, Miller and Nelson[2] on the LC chromium plating procedure have resulted in optimal de-plated deposits with a UTS of 87,000 psi, hardness of 760 KHN (50-g load), and a CCE of 11.9 percent. In an effort to improve the quality of the deposits, the application of pulse plating to LC chromium was evaluated.

Pulse plating is a method of depositing metal on a substrate, using interrupted direct current. The pulses, often employed at a rate of 10 to 10,000 per second, have benefits which include increased plating speeds, improved distribution and lower deposit stress, refined grain structure, increased ductility, increased CCE, and reduced hydrogen embrittlement.[3] When the current is turned on in conventional d-c plating, the metal ions near the cathode deposit immediately. The rate at which they deposit is greater than the diffusion rate of the ions, resulting in a concentration gradient in the immediate area of the cathode.[4] In addition, an electric field in the electrolyte aligns itself to a direction causing polarization near the edges of the cathode, resulting in a thicker deposit near the end of the cathode.[5] When pulsed current is used instead of conventional direct current, a short pulse is sufficient to deposit all the metal ions in the immediate vicinity of the cathode. During the off-time of the pulse cycle, solution equilibrium is re-established, eliminating any concentration gradient that may exist. Also, the polarization level on the cathode surface is no longer concentrated near the end of the cathode, but is evenly distributed across the layer of diffusion.[5]

Pulse plating affects only a small number of solutions because the diffusion rate of metal ions not only varies from metal to metal, but depends upon

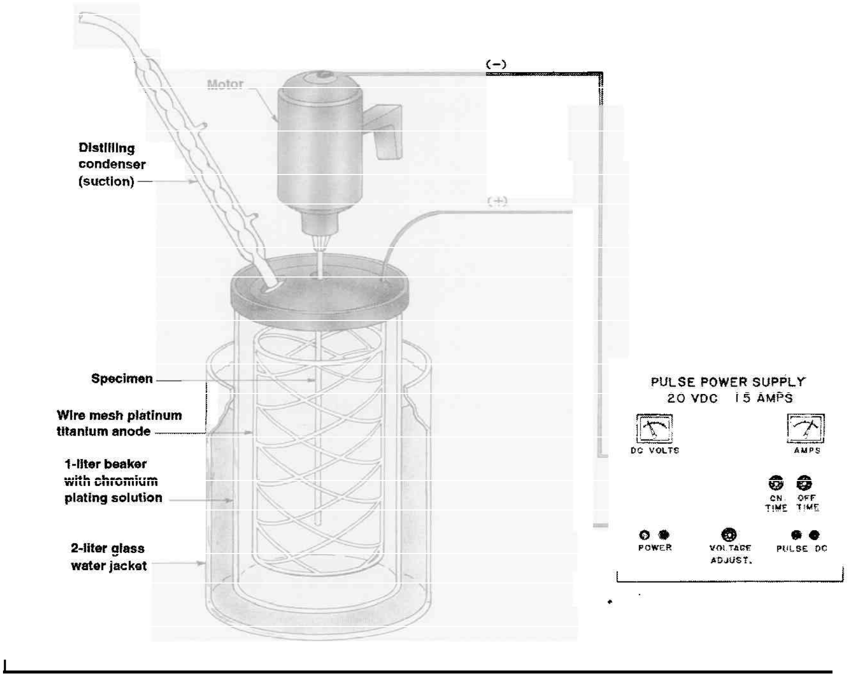


Fig. 2—Schematic diagram of a pulse plating cell for electrodeposition of LC chromium.

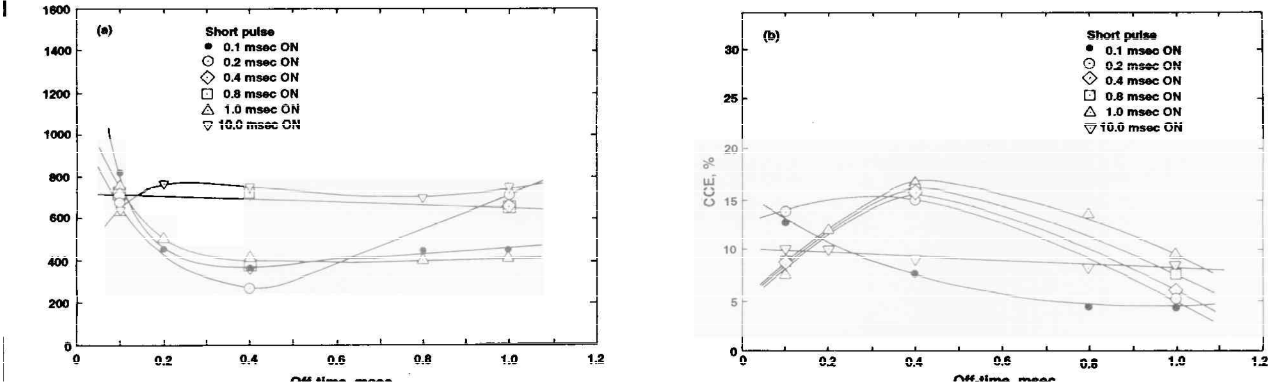


Fig. 3—Effects of high-frequency pulse plating on the hardness and CCE of LC chromium.

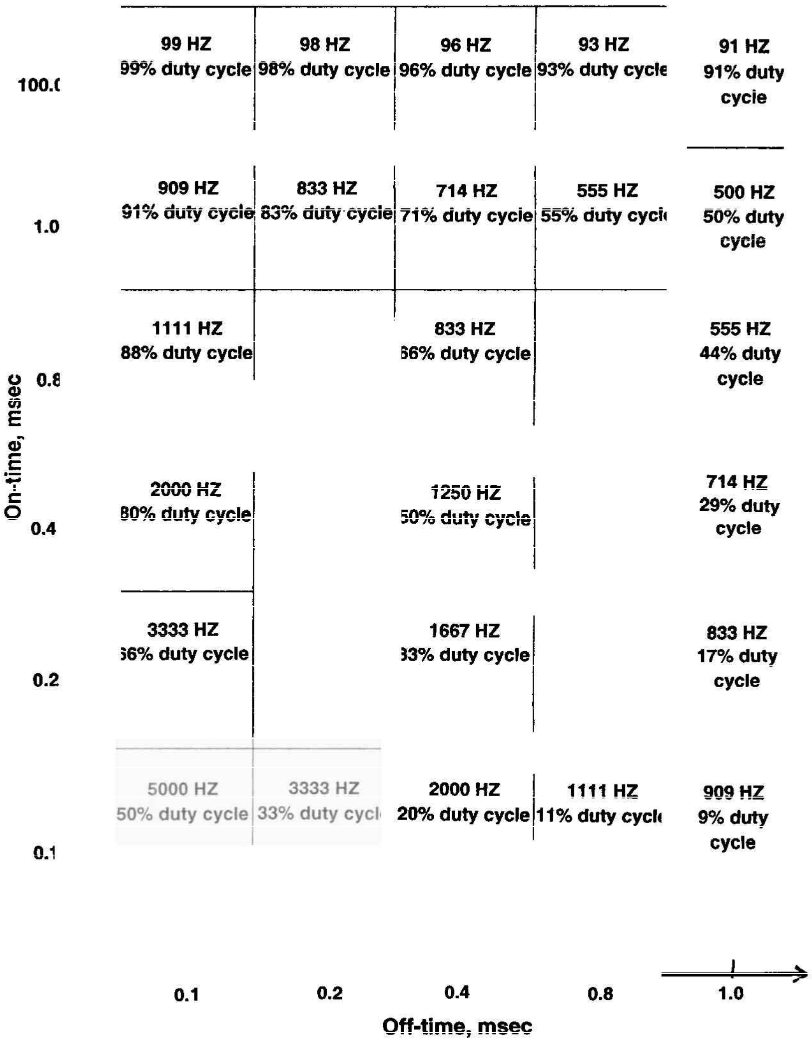
the solution composition, temperature, pH, and the presence additives as well. Reports on the effects of pulse plating on chromium electrodeposition have been contradictory. Chin and Zhang reported that while pulsed current increased coulombic efficiencies at some duty cycles, it tended to increase the internal stress of the chromium deposits, resulting in an increase in cracks.' On the other hand, Pearson and Dennis reported that pulsed current reduced internal stress and reduced or eliminated cracking chromium deposits.[8]

This study was a systematic investigation of on/off pulsed current (called ideal orunipolar, as shown in Fig. 1) deposition of LC chromium to determine which pulse conditions, if any, improve on the mechanical and microstructural properties of de-plated deposits.

Experimental Procedure

The experimental procedure was carried out exactly as described in a previous report,[2] except for the electrodeposition process. A standard plating arrangement, having a peak current density of 100 A/dm^2, a chromic acid/sulfuric acid ratio of 100:1, and a trivalent chromium concentration of 4.0 g/L- was used. A schematic diagram showing the pulse plating cell is shown in Fig. 2.

In order to use the plated specimens in tensile tests, they were electroformed in the shape of cylinders. A copper tube with a 0.40-cm outer diameter was used as the mandrel (cathode) and was masked to a plating area of five cm^2. The cathode was placed vertically in the center of the test vessel and rotated at 150 rpm during plating. A cylindrical mesh platinum-coated titanium anode, 10.8 cm in diameter and 12.7 cm in length, was placed at a distance of 5.2 cm from the cathode. For X-ray diffraction (XRD) analysis, specimens were prepared by depositing pulse-plated LC chromium on a 2.8 x 2.8-cm copper cathode, masked on one side, and positioned and rotated in the same manner as the cylindrical cathode.



On-time, msec	0.1	0.2	0.4	0.8	1.0
100.0	99 HZ 99% duty cycle	98 HZ 98% duty cycle	96 HZ 96% duty cycle	93 HZ 93% duty cycle	91 HZ 91% duty cycle
1.0	909 HZ 91% duty cycle	833 HZ 83% duty cycle	714 HZ 71% duty cycle	555 HZ 55% duty cycle	500 HZ 50% duty cycle
0.8	1111 HZ 88% duty cycle		833 HZ 66% duty cycle		555 HZ 44% duty cycle
0.4	2000 HZ 80% duty cycle		1250 HZ 50% duty cycle		714 HZ 29% duty cycle
0.2	3333 HZ 66% duty cycle		1667 HZ 33% duty cycle		833 HZ 17% duty cycle
0.1	5000 HZ 50% duty cycle	3333 HZ 33% duty cycle	2000 HZ 20% duty cycle	1111 HZ 11% duty cycle	909 HZ 9% duty cycle

Fig. 4—Frequency and duty cycle for each on/off-time condition evaluated during high-frequency pulse plating (also "map" of Figs. 5 and 6).

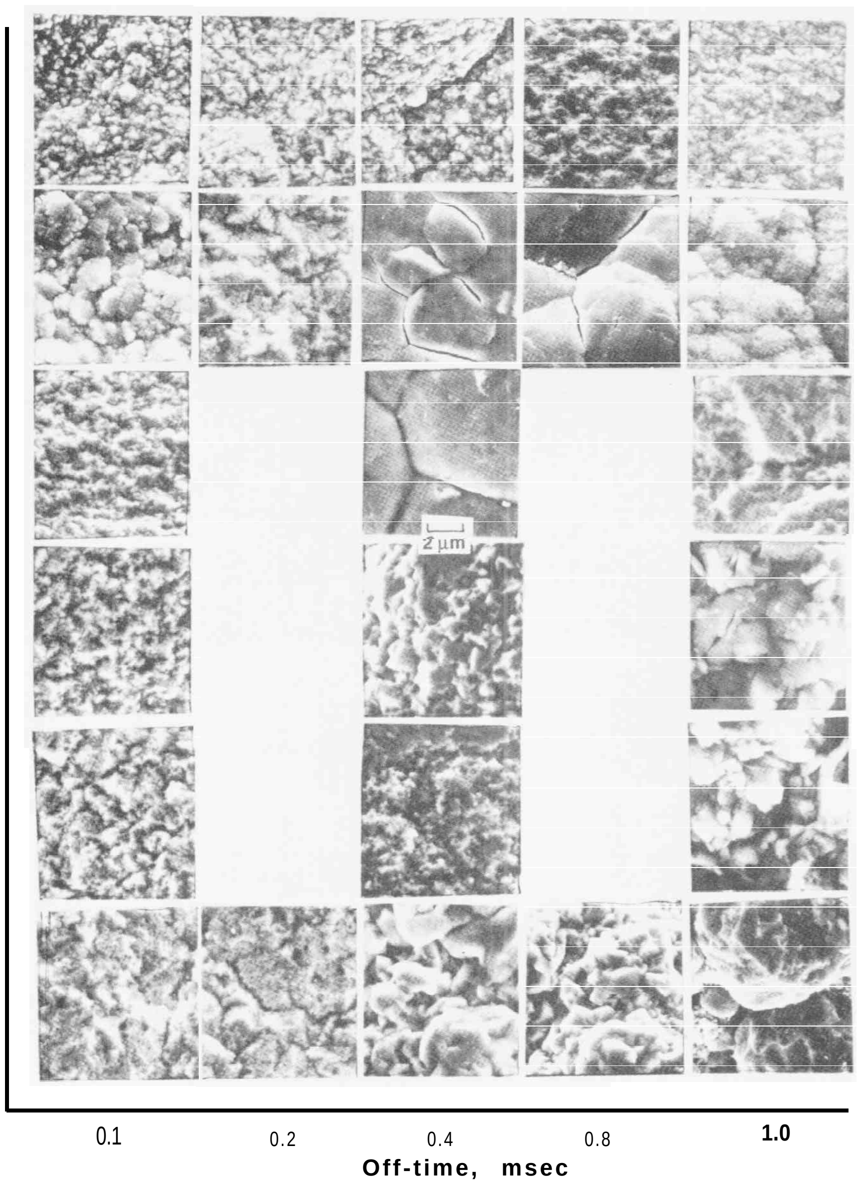


Fig. 5—Topographical photomicrographs of LC chromium deposited by high-frequency pulse plating.

A rectangular pulsating current, fluctuating between zero and the constant peak cathodic current value, was used to deposit the chromium. Plating time was adjusted so that the total charge transfer was kept constant at 240 A-hr/dm^2.

The on/off pulsing was done in two parts-high frequency (short pulse cycle) and low frequency (long pulse cycle). For high-frequency pulse plating, on-times of 0.1,0.2,0.4,0.8,1.0, and 10.0 msec were used, and off-times of 0.1,0.2,0.4,0.8, and 1.0 msec were evaluated. The frequency range of the pulsing cycle varied from 91 to 5000 Hz; the duty cycle varied from 9 to 99 percent. For low-frequency pulse plating, on-times of 10,20, 40,80, and 100 msec were used, and off-times of 10,20,40,80, and 100 msec were evaluated for each on-time. The frequency range of the pulsing cycle varied from 5 to 50 Hz; the duty cycle varied from 9.1 to 91 percent.

Results and Discussion

Four specimens were prepared for each of the plating conditions investigated. The CCE, microhardness, and UTS results are the average of measurements for the four specimens.

Effects of Hiqh-Frequency Pulse Plating

The quality, mechanical properties, and microstructure of the LC chromium deposits were greatly affected by the duty cycle and pulsing frequency. Pulsing in the short pulse routine (less than 10 msec) produced deposits of poor quality. Most deposits, particularly those plated at on- and off-times less than 1.0 msec (pulse frequencies greater than 900 Hz), contained large needlelike grains, poor adhesion (the deposit often flaking off the substrate), and increased stress.

The reason for such poor quality deposits at short pulse times was explained by Saiddington.[9] After the first interruption, numerous growth centers corresponding to established nucleation sites develop. As the deposit grows thicker, growth centers coalesce and develop into larger, individual domelike nodules. Saiddington clearly shows that as the number of interruptions increases, a growth of well-defined nodules develops. As the number of interruptions is increased beyond a critical point (a plating frequency greater than **900** Hz in our case), however, the surface topography becomes an incoherent conglomerate of high peaks and deep cavities. A high frequency of interruptions prevents the establishment of an oriented growth of the deposit and inhibits the development of well-defined growth centers that would eventually lead to the formation of nodules. When interruptions are spaced too closely, one nucleation is followed by another, leading to a completely disoriented surface characterized by a dark gray appearance.

The effects of high-frequency pulse plating on the hardness and CCE of LC chromium electrodeposits are shown in Figs. 3a and 3b, and the corresponding frequency and duty cycle for each pulse cycle tested are shown in Fig. 4. Figure 3a shows that while an individual on-time was held constant and the off-time systematically varied from 0.1 to 1.0 msec, nearly every high-frequency cycle evaluated resulted in hardness values lower than the value of 760 KHN (50-g load) obtained under optimal de-plating conditions.[2] At most off-times, hardness values tended to increase as the on-time increased, suggesting that lower frequencies and higher duty cycles result in increased hardness.

Because there were a few exceptions to this trend, specific correlations were difficult to make. For example, at an off-time of 0.8 msec, an on-time of 0.1 msec (111 1 Hz) resulted in greater hardness than an off-time of 1.0 msec (714 Hz). These few exceptions agree with the results of Pearson and Dennis, who showed that an increase in plating frequency resulted in an increase in hardness.[8] Also of interest is the fact that hardness values at an on-time of 10.0 msec remain basically unchanged as the off-time is increased from 0.1 to 1.0 msec. This is strong evidence that the hardness is frequency- and duty cycle-sensitive, inasmuch as Fig. 4 shows that the frequency and duty cycle change very little at an on-time of 10.0 msec.

The effects of high-frequency pulse plating on the CCE are shown in Fig. 3b. The highest CCE obtained, 16.5 percent, was only a slight improvement over the CCE obtained through d-c plating of LC chromium. Many of the cycles tested, particularly those with pulse frequency greater than 1000 Hz, resulted in lower CCE than that obtained with d-c plating. This finding agrees with Han and Kwon, who also reported the same observation,[10] The highest CCE, 16.5 percent, occurring at 1.0 msec on-time and 0.4 msec off-time, corresponded to a 714-Hz pulse frequency and a 71.4-percent duty cycle. Figure 3b suggests that for on-times less than 10 msec, the CCE can be increased by lowering the pulse frequency, but the maximum CCE that can be expected is 16.5 percent.

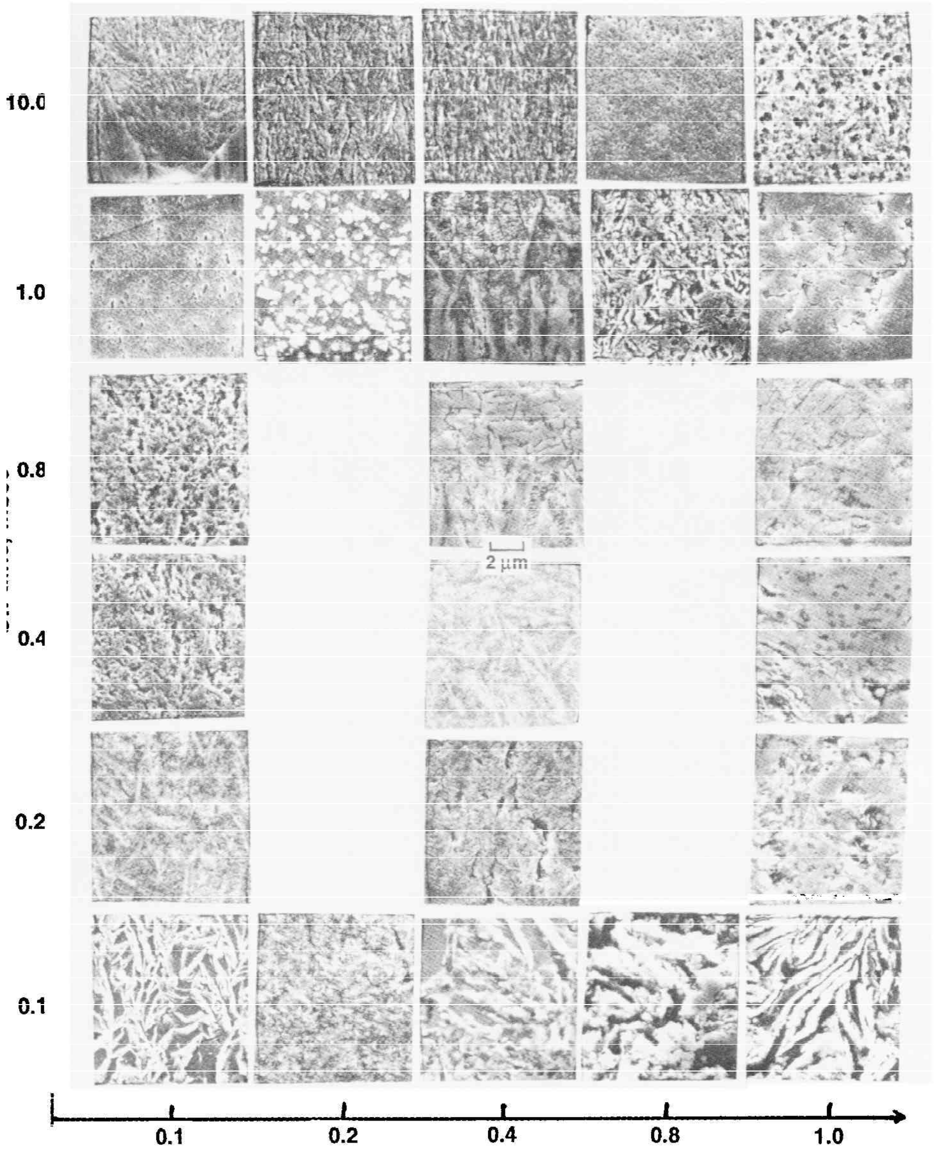


Fig. 6—SEM photomicrographs of the cross-sectional microstructure of LC chromium deposited by high-frequency pulse plating.

Electrodeposits made by pulsing with high frequency (greater than 90 Hz) were of such poor quality, poor adhesion, and high stress, that UTS measurements were not possible.

The topographical photomicrographs of LC chromium pulse-plated with high pulse frequencies are shown in Fig. 5. The morphology of LC chromium deposits plated with pulsed current differed significantly from that obtained with direct current. Grain growth in the high-frequency routine resembled isolated needlelike structures that became finer and darker in appearance as the pulse frequency increased.

Adhesion was very poor at frequencies greater than 2000 Hz (regardless of duty cycle) and at frequencies around 100 Hz when the duty cycle was greater than 98 percent. Cracks were present in most of the coatings prepared under these test conditions.

Scanning electron microscope (SEM) photomicrographs showing the cross-sectional microstructure of pulse-plated LC chromium are shown in Fig. 6. Only at pulsing frequencies near 100 Hz (on-times near 10 msec) did the microstructure represent a typical fibrous grain associated with LC chromium.

Effects of Low-Frequency Pulse Plating

The effects of low-frequency pulse plating on UTS, hardness and CCE of LC chromium electrodeposits are shown in Figs. 7a through 7c, respectively, and the corresponding frequency and duty cycle for each pulse routine are shown in Fig. 8. The data from the study of low-frequency pulse plating on the UTS of the deposits show (Fig. 7a) that the deposits were more stressed than those obtained by d-c plating. This finding agrees with Chin and Zhang, who reported that pulse current with on- and off-times less than one sec increased the internal stress of the chromium deposits.’ Several of the deposits, including all of those plated at 10 and 20 msec on-

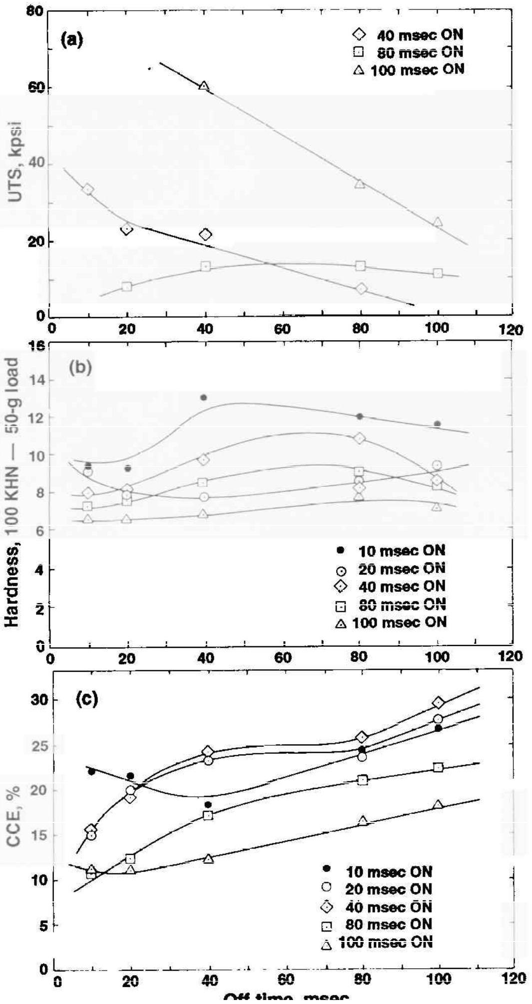
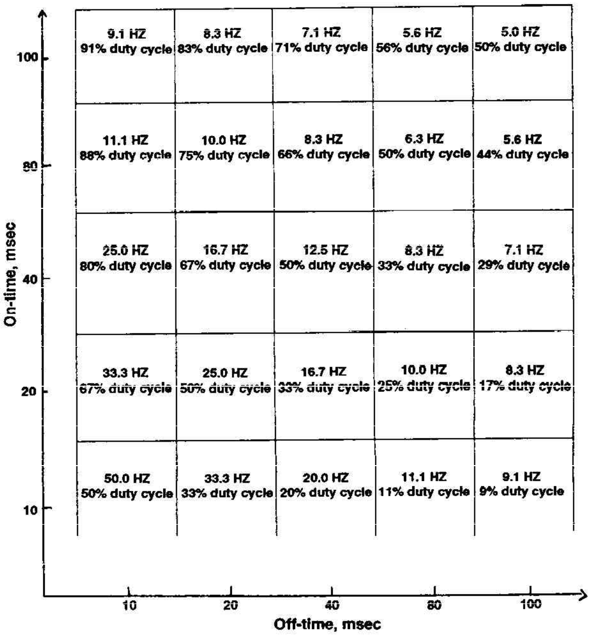


Fig. 7—Effects of low-frequency pulse plating on the UTS, hardness at CCE of LC chromium.

time, were of such high stress that UTS test measurements were not possible.

None of the conditions yielded a UTS as high as 87,000 psi—the optimal tensile strength of de-plated LC chromium. A maximum UTS of 60,000 psi (a 31 percent decrease over the UTS obtained with d-c plating) was produced at 100 msec on-time/40 msec off-time. This was the only condition to yield a UTS greater than 40,000 psi. A frequency of 7.1 Hz and a duty cycle of 71 percent corresponded to this plating condition.

Figure 7b shows that a large fraction of the low-frequency tests resulted in hardness values greater than those obtained at the optimal de-plating conditions (760 KHN). For on-times 40 msec or more, an off-time of 10 msec consistently yielded the highest hardness values. For all conditions evaluated, an on-time of 10 msec consistently yielded the hardest deposits. Maximum hardness values greater than 1175 KHN represent a 54-percent increase over the hardness values obtained with d-c plating. These maximum hardness values occur when the on-time is 10 msec and the off-time is 40 msec or more. In general, this suggests that hardness values in excess of 1175 KHN can be obtained by using pulse frequencies of 25 Hz or less and duty cycles 20 percent or less (on-times not to exceed one-quarter of the off-time). A few exceptions to this conclusion did exist. For example, an on/off ratio of 20/100 msec (8.3 Hz, 17-percent duty cycle) resulted in a hardness of only 880 KHN.

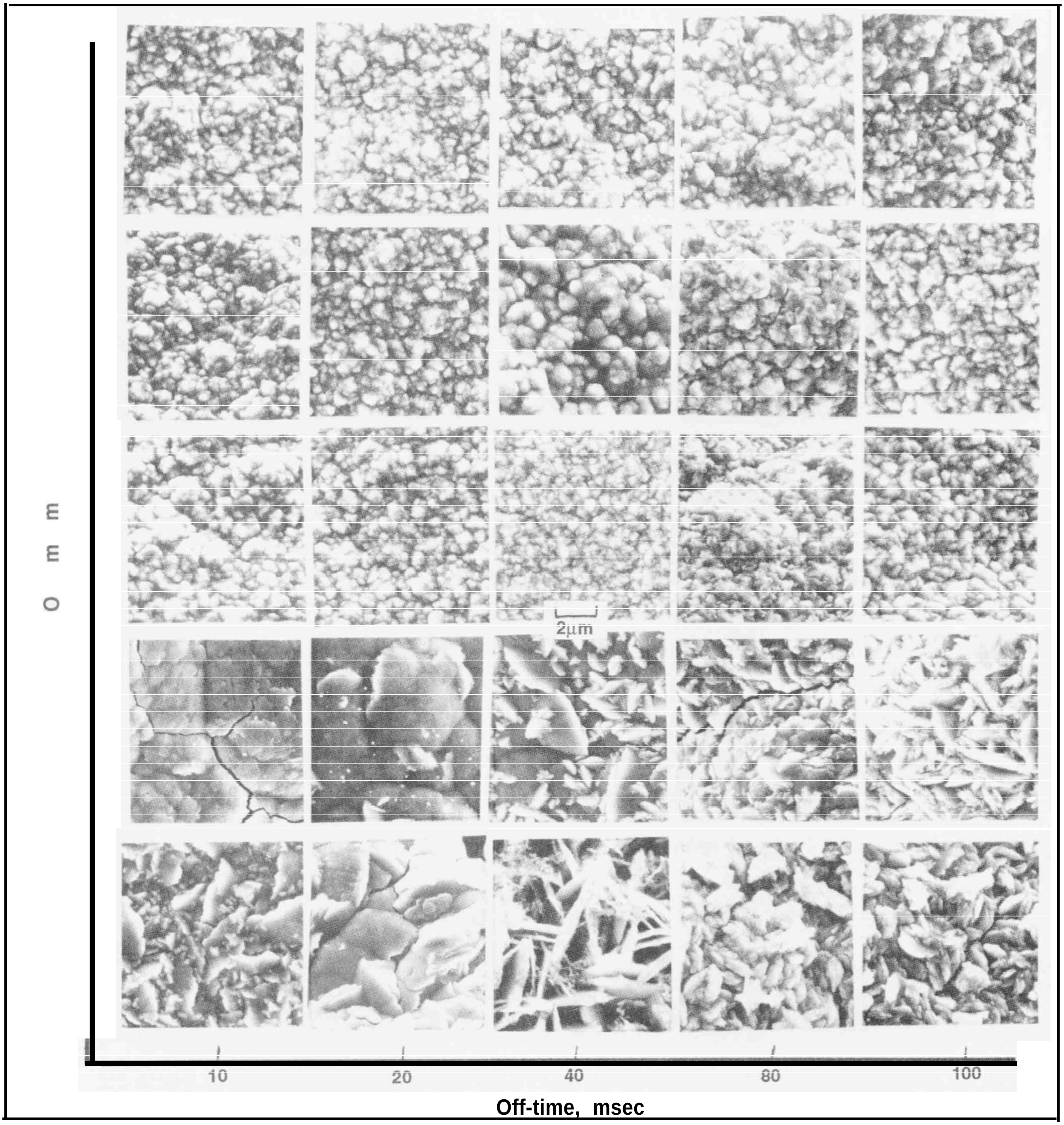


On-time, msec \ Off-time, msec	10	20	40	80	100
100	9.1 HZ 91% duty cycle	8.3 HZ 83% duty cycle	7.1 HZ 71% duty cycle	5.6 HZ 56% duty cycle	5.0 HZ 50% duty cycle
80	11.1 HZ 88% duty cycle	10.0 HZ 75% duty cycle	8.3 HZ 66% duty cycle	6.3 HZ 50% duty cycle	5.6 HZ 44% duty cycle
40	25.0 HZ 80% duty cycle	16.7 HZ 67% duty cycle	12.5 HZ 50% duty cycle	8.3 HZ 33% duty cycle	7.1 HZ 29% duty cycle
20	33.3 HZ 67% duty cycle	25.0 HZ 50% duty cycle	16.7 HZ 33% duty cycle	10.0 HZ 25% duty cycle	8.3 HZ 17% duty cycle
10	50.0 HZ 50% duty cycle	33.3 HZ 33% duty cycle	20.0 HZ 20% duty cycle	11.1 HZ 11% duty cycle	9.1 HZ 9% duty cycle

Fig. 8—Frequency and duty cycle for each on/off-time condition evaluated during low-frequency pulse plating (also "map" of Figs. 9 and 10).

The effects of low-frequency pulse plating on the CCE of LC chromium electrodeposits are shown in Fig. 7c. It is quite apparent that low-frequency pulse plating significantly improves the CCE over that obtained with d-c plating. All conditions tested resulted in a CCE greater than 11.9 percent, which is the optimal CCE obtained by d-c plating of LC chromium. The increase in CCE is a result of the decrease in concentration polarization and elimination of the concentration gradient that occurs during d-c plating. As can be seen in Fig. 7c, for each on-time tested, the CCE increased as the off-time increased, with each on-time reaching its largest CCE at an off-time of 100 ms. This suggests that lower frequencies and lower duty cycles result in CCE increases. A maximum CCE of 28 percent occurred at 40 msec on-time/l 00 msec off-time, and several values in excess of 25 percent were obtained. This value of CCE is a 135-percent improvement over the CCE obtained by d-c plating. It can be concluded from Fig. 7c that CCE in excess of 22 percent can be obtained when the pulse frequency is less than 12 Hz and the duty cycle is less than 33 percent. This increase in CCE, as the pulse frequency decreased, is in agreement with Han and Kwon who reported that, pulse plating with frequencies less than 100 Hz resulted in a CCE 40 percent greater than that obtained from d-c plating.'"

The topographical photomicrographs of LC chromium pulse-plated at low pulse frequencies are shown in Fig. 9. For 10 and 20 msec on-times (pulse frequencies between 50 and 33 Hz), the topography resembled a pattern of interwoven platelets, some with visible cracks, such as those shown for the 20 msec on-time/l O msec off-time sample. This structure would explain why UTS test measurements at 10 and 20 msec on-time were not possible. When the on-time was 40 msec, or more, and the off-time 10 msec or more, the topography resembled the hemispherical nodular appearance typical of de-plated LC chromium.



g. 9—Topographical photomicrographs of LC chromium deposited by low-frequency pulse plating.

SEM photomicrographs showing the cross-sectional microstructure of low- frequency pulse-plated LC chromium are shown in Fig. 10. As with the topography, the microstructure at on-times of 20 and 10 msec was of poor quality, with a porous grain structure and cracks prevalent throughout. Only when the on-time was increased beyond 20 msec (pulse frequencies less than 30 Hz and duty cycles greater than 70 percent) did the microstructure represent a typical fibrous grain associated with LC chromium.

X-ray diffraction patterns of low-frequency pulse-plated LC chromium reveal two general trends. First, as the off-time decreases (frequency increases), the crystal orientation becomes less random, as evidenced by the intensity of the <110> peak decreasing. Second, as the on-time increases (frequency decreases), the relative intensity of the <211> peak increases, suggesting a <211> preferred orientation at high on-times.

Conclusions

Based on the results of our experimental studies, the following conclusions were reached:

1. Low-contraction pulse-plated chromium, using pulse frequencies less than 50 Hz results in significant improvements in the CCE and increases in the hardness of the electrodeposits, as compared with values obtained through d-c plating.
2. Hardness values in excess of 1175 KHN can be obtained by pulse plating with frequencies of 25 Hz or less and duty

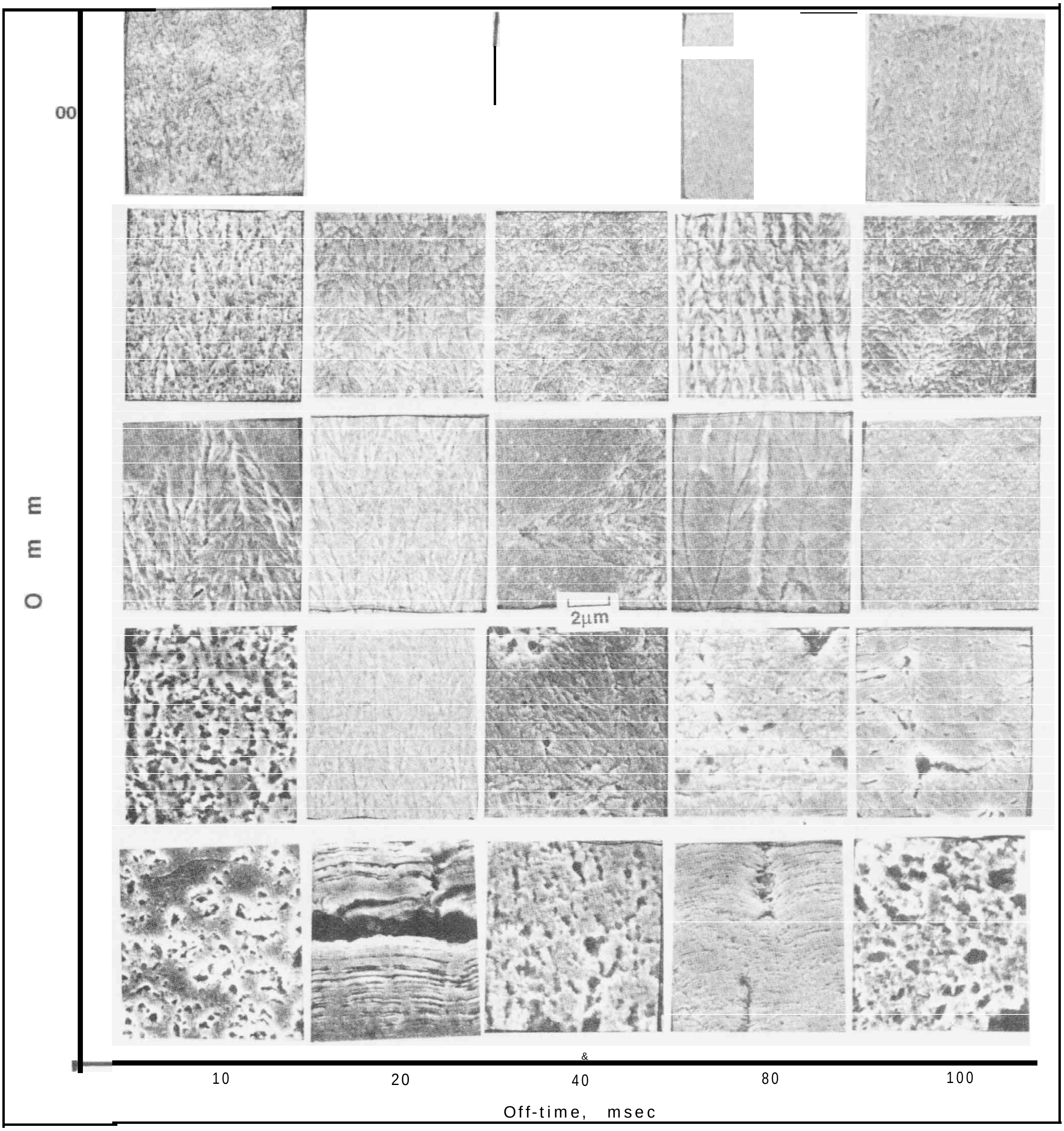


Fig. 10—SEM photomicrographs of the cross-sectional microstrucrure of LC chromium deposited by low-frequency pulse plating.

cycles 20 percent or less. This represents a 54-percent increase in the optimal hardness obtained with dc- plating.

3. Cathode current efficiency in excess of 22 percent can be obtained when pulse frequencies less than 12 Hz and duty cycles less than 33 percent are used. This is double the optimal CCE obtained with d-c plating.

4. Pulse plating, using low pulse frequencies (less than 50 Hz), does not reduce the stress of the electrodeposits. Maximum tensile strength was actually 31 percent lower than that obtained with d-c plating.

5. Pulse plating using high pulse frequencies (between 91 and 5000 Hz) results in poor quality deposits with poor adhesion, reduced hardness, CCE, UTS, and a needlelike grain structure.

References

1. E.S. Chen, “Improved Electrodeposited Low Contraction Chromium;” ARLCB-TR-82009, Benet Weapons Laboratory, Watervliet, NY (April, 1982).
2. S.K. Pan, M.D. Miller, and F.J. Nelson, “Optimization of Plating Parameters For Low Contraction Chromium Electrodeposits,” ARCCBTR-89024, Benet Laboratories, Watervliet, NY (October, 1989).
3. Vanguard Research Associates, Inc., “Improvement in Selective Stripe Plating Through Periodic Reverse Plating,” Vanguard West Inc., Phoenix, AZ (April, 1983).
4. A.J. Avila and M.J. Brown, *Proc. 57th Annual Technical Conference,* American Electroplates Society, Montreal, Quebec, Canada, June 1970.

5. Gemdata Group and Techno Instruments Ltd., *Finish. Ind.,* **19 (March, 1982).**
6. *Finishing, 7,41* (March, 1983).
7. D.-T. Chin and H. Zhang, *Electrochim. Acts, 31, 299 (1986).*
8. T. Pearson and K. Dennis, *P/at. and Surf. Fin., 76, 64* **(Nov., 1989).**
9. J.C. Saiddington, *P/at. and Surf. Fin., 65,45* (Jan., 1978).
10. S.H. Han and S.C. Kwon, *J. Met. Finish. Sot. Korea, 19,* 59 (June, 1986).


iiiler


Pan

About the Authors

Mark D. Miller is a chemical enqineer in the Research Division, Benet Laboratories, U.S. Army Armament Research, Development and Engineering Center, Watervliet Arsenal, Watervliet, NY 12189-4050. He has six years' research experience in electrodeposition of chromium, including LC chromium, laminated chromium, pulse plating, chromium alloy plating, and statistical process control. He received a BS in chemical engineering from Rensselaer Polytechnic Institute.

Dr. S.K. Pan is a metallurgist at the Research Division, Benet Laboratories, Watervliet, NY. He received a BS in chemical engineering from the National Cheng-Kung University, Taiwan, and a PhD in metallurgy from Stevens Institute of Technology. His research interests include electrodeposition, refractory metals and X-ray metallography.