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*On the electroplating of laminated chromium**

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A microprocessor-controlled flow plating process was developed to deposit laminated chromium consisting of alternating layers of low contraction (LC) and high contraction (HC) chromium. The automated plating system contains a large number of variable parameters designed to allow the use of multiple plating modes. The available modes include a combination of direct current, interrupted, periodic reverse, pulse and laminated chromium plating.

The laminated plating experiments were conducted at LC/HC solution temperatures of 85 and 55° C, current densities of 120 and $45\,\mathrm{A\,dm^{-2}}$, and at LC/HC duty cycles to produce spacings between 0.01 and 2.7 μm. Under these plating conditions, deposits with hardness values between 655 and 1089 KHN (Knoop hardness number, $\mathrm{kg\,mm^{-2}}$) and tensile strengths between 6.8 and 57.2 were obtained.

1. Introduction

Electrodeposited chromium plays a key role in supplying the decorative and engineering needs of numerous manufactured products. The deposits in use are of two general classes: (i) HC and (ii) LC chromium. The term 'HC' stands for high contraction and refers to the tendency for as-plated hard chromium to shrink on heating. Because of the high hardness, HC chromium is commonly used as a protective coating to reduce galling and wear. Where corrosion is of concern, low contraction or 'LC' chromium is used to take advantage of its crack-free and high-strength characteristics. Conventional HC deposits are weakened by the presence of cracks and are extremely brittle, while LC deposits are much softer and are therefore susceptible to swaging under intense loading. It would be advantageous to produce deposits which combine the favourable characteristics of HC and LC chromium. One approach is through laminated plating.

The properties of laminated chromium deposits have been observed in a number of studies [1–3] and have been reported with reference to adhesion [4] and crack formation [5]. In all cases, the natural cyclic nature of the plating process, current interruptions or variations in plating temperature are responsible for the formation of the laminated structure. The present investigation differs from previous studies in that the laminations consist of alternating-layers of two distinct types of chromium deposits rather than discontinuities brought about by a periodic current interruption or current reversal. Through the use of a microprocessor-controlled plating system, the preparation of laminated deposits through programmed current modulation and precise switching of plating solutions is made possible. In principle, such laminated structures should exhibit greatly altered mechanical properties and provide a means of tailoring the strength and hardness of the deposit by varying the thickness of HC/LC layers.

2. Experimental procedures

Chromium plating solutions were prepared by dissolving technical grade chromic acid ($250\,\mathrm{g\,l^{-1}}$) and sulphuric acid ($2.5\,\mathrm{g\,l^{-1}}$) in distilled water. The solutions were pre-electrolysed for

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$250\,\mathrm{A\,h\,l^{-1}}$ (aged) and stored in two 10-gallon polyethylene tanks maintained at 55 and 85 ± 1°C. Laminated deposits were prepared by pumping plating solution through a flow cell and synchronizing the switching of current with the arrival of the respective HC or LC solution. The electrolytic flow cell consists of an outer hollow cylindrical lead anode and inner tubular brass cathode having a masked area of $10\,\mathrm{cm^2}$.

Two series of laminated deposits were prepared for characterization. The first was prepared at HC/LC current densities of $45/120\,\mathrm{A\,dm^{-2}}$ and at duty cycle times to produce layer thicknesses between 0.01 and 2.7 μm. The second series was plated at HC/LC current densities of $300/120\,\mathrm{A\,dm^{-2}}$ with layer thicknesses between 0.36 and 0.77 μm. Electroformed chromium samples were obtained by dissolving the brass substrate in dilute nitric acid. Tensile strengths were measured with a table model Instron tensile machine using a crosshead speed of $0.05\,\mathrm{cm\,min^{-1}}$. The procedures for mounting and testing the specimens have been reported elsewhere [6].

A Knoop diamond indentor was used to measure hardness at a load of 50 g.

3. Results and discussion

Fig. 1 shows a schematic diagram of the automated plating system used in the preparation of laminated chromium. An Allen Bradley microprocessor controlling 128 I/O ports is central to the system and is used to provide manual and automatic sequencing of valves, pump states, temperatures, flow rates and current modulation. While the construction of this system is similar to a prototype developed at Benet Weapons Laboratory [7], it was designed specifically to provide hardware–software implementation of the laminated plating mode. Other modes can be activated by selecting appropriate switches to enable conventional HC or LC plating, HC or LC with current interrupt, HC or LC with cur-

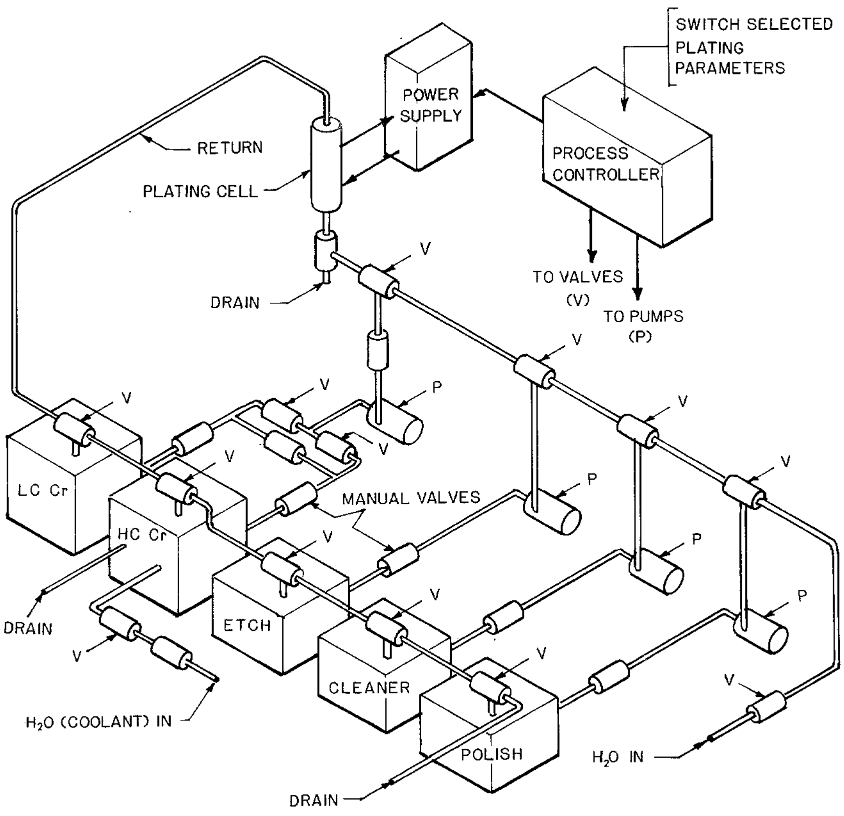

Fig. 1. Schematic diagram of the automated plating system.

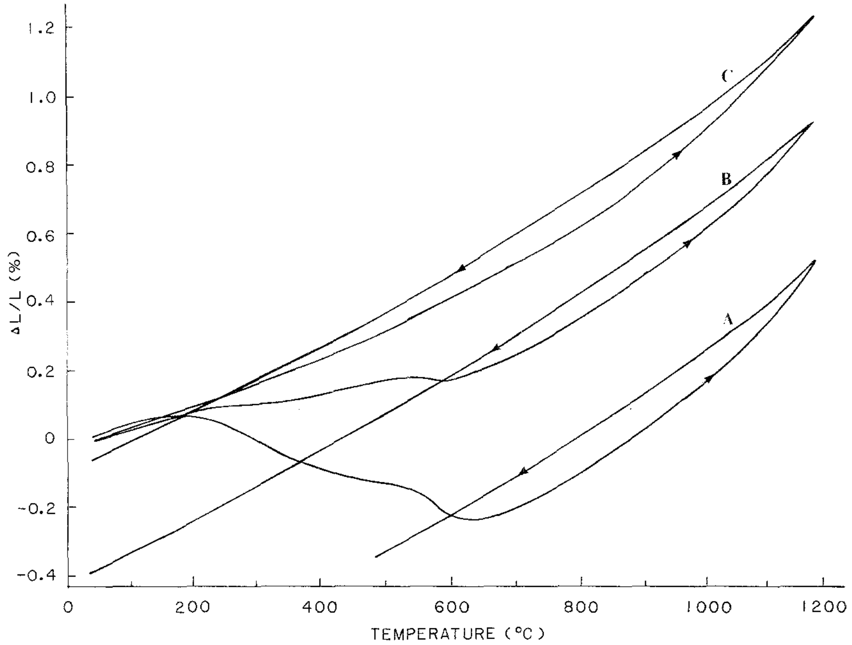

Fig. 2. Thermal expansion of electrodeposited chromium with temperature for the range between 25° and 1200° C. (A) HC chromium plated at 55° C and $45\,\mathrm{A\,dm^{-2}}$; (B) laminated chromium plated at HC/LC cycles of 3/30 s, $300/120\,\mathrm{A\,dm^{-2}}$ and 55/85° C; (C) LC chromium plated at 85° C and $120\,\mathrm{A\,dm^{-2}}$.

rent reversal, and laminated plating with current interrupt or current reversal. Each of these modes can be integrated with a clean, polish and etch cycle to provide for a reproducible and complete plating cycle.

Fig. 2 shows a comparison of the thermal expansion or dilation behaviour of as-plated chromium for the temperature range between 25 and 1200° C. The measurements were made on electroformed chromium samples perpendicular to the growth direction. For HC chromium (curve A) an abnormality in thermal expansion occurred as a series of contractions between 20 and 600° C. The contractions are commonly observed in HC chromium [8] and are reportedly associated with the evolution of hydrogen from the deposits. Since these contractions are irreversible, an 0.8% decrease in length was observed. The LC chromium (curve C) did not show contractions, although a 0.1% decrease in length was obtained. Curve B shows the thermal expansion behaviour of a laminated deposit containing HC/LC layer thicknesses of 0.36 and 0.77 μm. As was expected, the characteristics of laminated deposits vary between that of HC and LC chromium.

Table 1 lists the strength and hardness of as-plated chromium in relation to the deposition conditions. The hardness was measured on surfaces perpendicular to the growth direction on coatings, 5 ml thick. The results clearly show that hardness can be systematically varied between HC and LC chromium, i.e. 1089 and 655 KHN, by varying the lamination thickness. The harder deposits (run numbers 1 through 4) show a microcracked structure, the severity of which appears to decrease with increasing LC layer thickness. Cracking in the deposits is also reflected in unpredictable strength values. The medium-hardness deposits (run numbers 5 through 7) are crack-free. However, these deposits are severely stressed and longitudinal cracking occurs on removal of the substrate. Run numbers 8 through 11 resulted in crack-free deposits. A softer and stronger deposit was produced progressively by decreasing the thickness of the HC layer. Run numbers 12 and 13 show deposits with comparable hardness to HC chromium. These deposits, while crack-free, are also highly stressed.

It should be emphasized that an unlimited combination of current–time cycles may be

Table 1. Layer thickness, tensile strength and hardness of laminated chromium electrodeposits

Run no.	*Layer thickness HC/LC (μm)**	*Duty cycle HC/LC (s)*†	*UTS (KSI)*	*Hardness (KHN)*	*Deposit structure*
1	All HC	–	6.8	1089	Microcracked
2	0.30/0.77	30/30	15.9	1034	Microcracked
3	0.30/0.90	30/40	26.9	961	Microcracked
4	0.30/1.35	30/60	8.1	938	Microcracked
5	0.10/1.35	10/60	–	849	Crack-free, stressed
6	0.16/2.7	16/120	–	826	Crack-free, stressed
7	0.08/2.7	8/120	–	777	Crack-free, stressed
8	0.04/2.7	4/120	16.5	754	Crack-free
9	0.02/2.7	2/120	29.4	726	Crack-free
10	0.01/2.7	1/120	46.1	703	Crack-free
11	All LC	–	57.2	655	Crack-free
12	0.6/0.77	5/30	–	1084	Crack-free, stressed
13	0.36/0.77	3/30	–	1052	Crack-free, stressed

* Layer thicknesses were calculated from plating rates established for 55° C and 45 A dm^{-2}; 55° C and 300 A dm^{-2}; 85° C and 120 A dm^{-2}.

† The HC/LC duty cycle was 45/120 A dm^{-2} for run numbers 1 to 11 and 300/120 A dm^{-2} for numbers 12 and 13.

employed to plate a given layer thickness. In the present study these cycles are selected on the basis of two general guidelines. First, current–time cycles are used to limit the buildup of HC chromium layers to 0.5 μm. Applying controlled interruptions below a critical thickness of 0.5 μm has been reported to produce crack-free chromium deposits [9]. Secondly, high current densities between 200 and 300 A dm^{-2} are used during the HC cycle to encourage the formation of random orientation. X-ray diffraction spectra from HC chromium in Fig. 3 clearly demonstrate that the HC laminations are random at these high current densities. Comprehensive studies have been documented on this aspect of chromium electrodeposition [10–12]. Since the coalescence of crystallites is a primary cause of plating stresses [13, 14], the promotion of random orientation will favour a reduction in stress.

Figs 4–6 are typical photomicrographs of laminated chromium deposits after etching in a Murakami solution. The HC layers appear as prominent dark striations in these micrographs and LC layers as light striations. The crack structure seen in Fig. 4 is representative of the deposits associated with run numbers 2, 3 and 4. It is evident that interrupting with LC layers is ineffective in preventing crack formation when the HC layer thickness is above 0.3 μm. Nevertheless, it is interesting to note in these structures that all the cracks originate and terminate within the HC layers. When interruptions are imposed to limit the HC layer thicknesses between 0.3 and 0.08 μm, the laminated deposits are crack-free. Fig. 5 shows such a microstructure which is typical of deposits in run numbers 5, 6 and 7. Apart from the regular striations which are observed as a series of lines parallel to the plane of deposit growth, Fig. 5 also reveals a fibrous structure which intersects the laminations to produce discontinuities on the dark striations. The fibrous structure is also present in the photomicrograph of Fig. 4, although the finer and more numerous fibre growth makes it more difficult to distinguish. Fig. 6 shows the microstructure typical of deposits produced in run numbers 12 and 13. It is particularly encouraging to note the decrease in the presence of fibrous structure. These deposits were intentionally plated with randomly oriented HC layers in order to promote the epitaxial growth of LC layers. One can reasonably conclude from the relative absence of fibrous structures that the deposits from run numbers 12 and 13 are more randomly oriented.

Continuing investigations are planned to characterize the deposits by X-ray diffraction, particularly with respect to the effects of random orientation and very thin laminates.

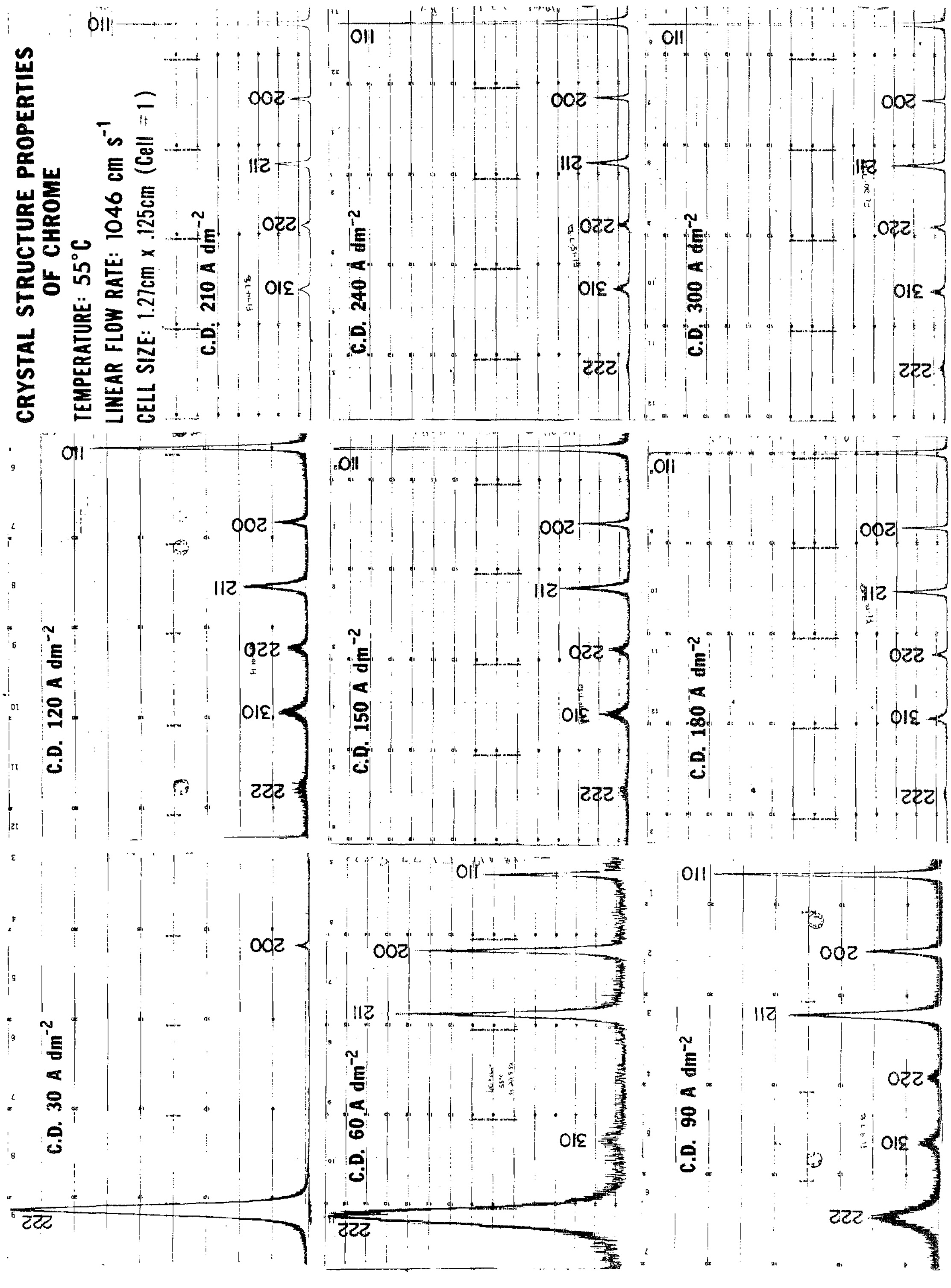

Fig. 3. Comparison of crystal structure of chromium deposits at 55°C.

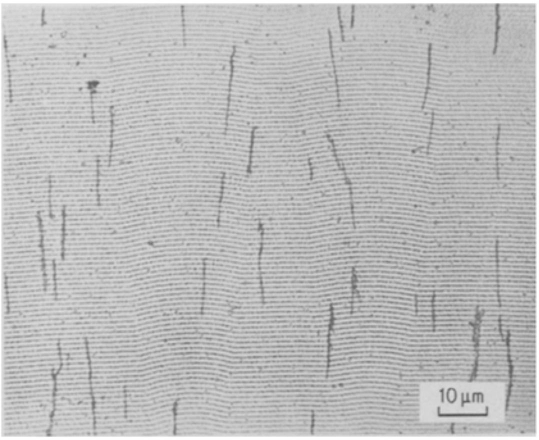

Fig. 4. Microstructure of laminated chromium plated at HC/LC cycles of 30/30 s, 45/120 A dm^{-2} and 55/85° C.

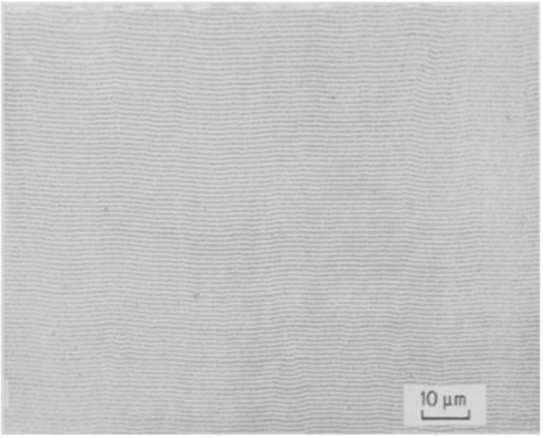

Fig. 6. Microstructure of laminated chromium plated at HC/LC cycles of 3/30 s, 300/120 A dm^{-2} and 55/85° C.

4. Conclusion

It has been shown that the structural and mechanical properties of electrodeposited chromium can be modified by plating laminated deposits consisting of alternating layers of HC and LC chromium. The features of the laminated process include: (i) the capacity of plating deposits with a hardness between 655 and 1089 KHN by varying the thickness of the HC/LC layers; and (ii) the plating of laminated deposits with random orientation and the prospect of reduced plating stress.

Conventionally, the properties of electrodeposited chromium can be varied by controlling the current density and plating temperature. However, this approach is incapable of the flexibilities available with the laminated process. For example, if high hardness is specified then one must contend with a deposit containing a crack structure. For the present case, the fact that crack-free laminated deposits can be produced with a hardness comparable to HC chromium affords both promising and challenging opportunities for future chromium deposition studies.

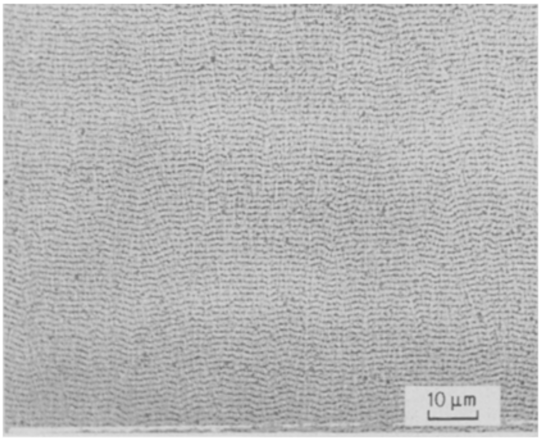

Fig. 5. Microstructure of laminated chromium plated at HC/LC cycles of 10/60 s, 45/120 A dm^{-2} and 55/85° C.

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