ELECTRODEPOSITION OF CHROMIUM AT INCREASED CURRENT DENSITIES AND ITS PROPERTIES

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An examination is made of the feasibility and desirability of chromium electrodeposition at substantially increased current densities. It is shown that an intensification of the process may have an adverse effect on the quality of chromium electrodeposits.

Increasing the current density as a means of intensifying the chromium plating process produces a marked change in the rates of the reactions taking place on the electrode and an even greater change in the physicomechanical properties of the resultant deposits. With the usual (standard and tetrachromate) types of chromium plating solution, high current densities are employed when electrolysis is performed in an ultrasonic field [1-8] or in a circulating electrolyte [9-11]. Electroplating under such conditions actually improves the physicomechanical properties of deposits: it increases their microhardness and reduces internal stresses and hydrogen pickup [6-8, 11].

With the new chromium plating electrolytes [12] containing various proportions of the anions SO_4^{2-} and SiF_6^{2-}, the current density in the absence of forced agitation may attain 600 A/dm^2 in the deposition of chromium in the form of decorative coatings (5 μ thick). The deposition rate in such a case rises to 10 μ/min from the usual 0.5 μ/min, and the deposits obtained are harder, smoother, brighter and nonporous.

In the present work, a study was made of chromium electrodeposition from such solutions at current densities of up to 500 A/dm^2 and of some of the most important physicomechanical properties of the resultant chromium coatings. Electrodeposition was performed using a stationary electrode and chromic acid solutions (250 g/liter) with additions of the anions SO_4^{2-} and SiF_6^{2-} and also, for purposes of comparison,

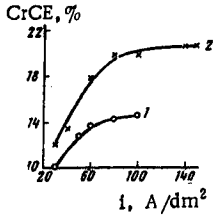

Fig. 1

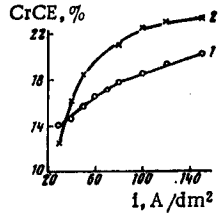

Fig. 2

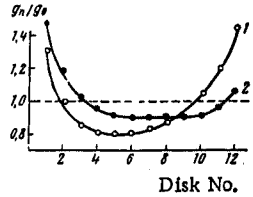

Fig. 3

Fig. 1. Effect of current density on current efficiency in satin chromium deposition from standard (1) and high-speed (2) electrolytes at 70°C.

Fig. 2. Effect of current density on current efficiency in bright chromium deposition from standard (1, at 50°C) and high-speed (2, at 70°C) electrolytes.

Fig. 3. Uniformity of satin chromium distribution along height of cylindrical cathode in standard (1, i = 40 A/dm^2) and high-speed (2, i = 100 A/dm^2) electrolytes at T = 70°C.

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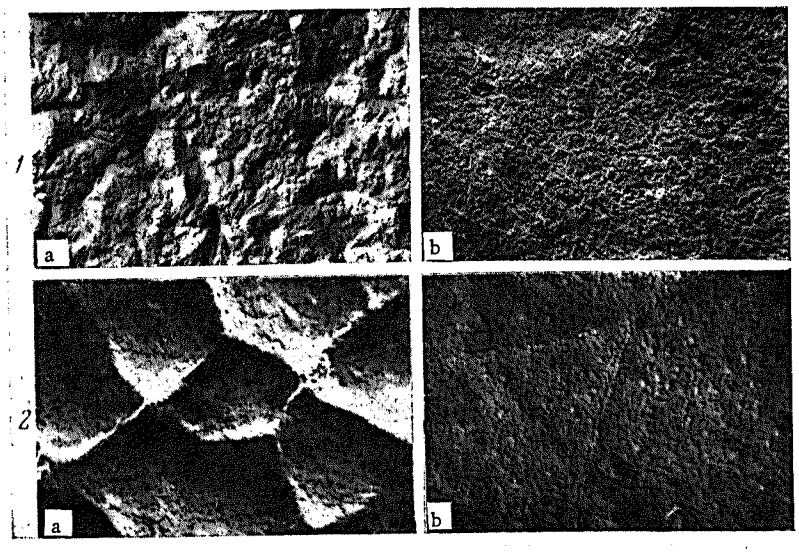

Fig. 4. Electron micrographs of surfaces of satin (a) and bright (b) chromium deposited from standard (1) and high-speed (2) electrolytes, ×6300. Electrolysis conditions: 1a) T = 70°C, i = 40 A/dm^2; 1b) T = 50°C, i = 50 A/dm^2; 2a) T = 70°C, i = 100 A/dm^2; 2b) T = 70°C, i = 100 A/dm^2.

the standard electrolyte. Internal stresses in chromium electrodeposits were measured by the flexible cathode method during the electrolysis process. Their hydrogen content was determined by the method of vacuum extraction at 400°C. Microhardness measurements were made on a PMT-3 tester under a load of 100 g. Chromium was deposited onto one side of disk-shaped copper specimens mounted in Teflon holders. Current efficiency in metal deposition was computed by determining specimen weight gains in a chromium bath and in a coulometer.

Irrespective of the temperature (in the range 18-70°C) and sulfate ion (or SO_4^{2-} and SiF_6^{2-} mixture) concentration (in the range 2.5-10 g/liter) employed, chromium current efficiency rises with increase in current density, but only up to 200 A/dm^2. Increasing the current density above this value has no effect on the current efficiency of the deposition, but the structure of the cathodic deposit becomes coarse and an increased tendency for dendrite formation is observed, particularly in thick coatings and at higher temperatures. In view of this, most of the experiments were carried out at current densities of 30-150 A/dm^2.

In a chromic acid solution, current efficiency in the deposition of satin-finish chromium at 70°C (Fig. 1) is higher with two acid additions – 1.25 g/liter H_2SO_4 and 1.8 g/liter H_2SiF_6 (high-speed electrolyte, curve 2) – than with a 2.5 g/liter H_2SO_4 addition (standard electrolyte, curve 1). As a function of current density, metal current efficiency rises more rapidly in the range 30-80 A/dm^2 than at higher values. It is known that, in the standard electrolyte, satin chromium is deposited in the current density range 30-40 A/dm^2, i.e., where chromium current efficiency is a minimum (19-12%). In the high-speed electrolyte, however, satin chromium is obtained in the current density range 80-150 A/dm^2, i.e., in the region of maximum efficiencies (20-25%). Thus, lowering the amount of sulfate ions and adding SiF_6^{2-} anions to chromic acid can increase the rate of satin chromium deposition six to eight times by doubling metal current efficiency and enabling current density to be raised three- to fourfold.

To obtain bright chromium deposits, in electrodeposition from the standard solution the temperature is lowered (from 70 to 50°C) and the current density is increased, while in deposition from the high-speed solution the silicon fluoride concentration is raised, but the temperature and current density remain the same. Effective bright chromium deposition takes place at current densities of 50-60 A/dm^2 and a current efficiency of about 16% in the standard electrolyte, and at current densities of 80-120 A/dm^2 and a current efficiency of 21-23% in the high-speed solution (Fig. 2). As a result, the rate of bright chromium deposition in the high-speed electrolyte is almost three times that in the standard electrolyte. Thus, the high-speed solution enables higher process rates to be achieved in the deposition of both satin and bright chromium.

TABLE 1

Property of Cr deposit	Satin Cr		Bright Cr	
	standard	high-speed	standard	high-speed
Internal stress (1 μ), kg/cm^2	6550	9170	10 000	17 400
Microhardness (50 μ), kg/mm^2	600	800	900—1000	1100—1000
Hydrogen content (25 μ), cm^3/g	1,67	3,87	5,6	6,48

Increasing the current density in chromium deposition not only intensifies the process, but also reduces the nonuniformity of distribution of deposited chromium on the surface of a cathode of complex configuration by decreasing the dependence of metal current efficiency on current density at high values of the current density. A study was made, using the method of weighing the disks of a composite cylindrical cathode, of current distribution on the cathode surface in the deposition of satin chromium from the standard and high-speed solutions. The curves in Fig. 3 have been constructed with the ratio between the chromium deposit thickness on each disk and the mean thickness as ordinate and the disk number as abscissa. In chromium deposition from the high-speed electrolyte at a current density of 100 A/dm^2 (curve 2), more disks have the same deposit thickness, which is also closer to the mean thickness, compared with deposits produced from the standard solution at a current density of 40 A/dm^2 (curve 1). This means that the distribution of chromium along the height of a cylindrical cathode is more uniform in the high-speed than in the standard electrolyte.

Some properties of satin and bright chromium deposits obtained from the standard and high-speed electrolytes are listed in Table 1. Internal stresses in satin and bright chromium deposits from the high-speed electrolyte are about 40 and 75%, respectively, higher than those in similar deposits from the standard electrolyte. Deposition from the high-speed solution increases the hardness of satin and bright chromium coatings by 20-30%. The greatly increased hydrogen content of satin chromium deposited from the high-speed electrolyte compared with that produced from the standard solution (about 2.5 times) is apparently mainly attributable to the high current density at which deposition is performed. As regards bright chromium deposits, here the effect of increased current density is counterbalanced by the opposing effect of higher temperature, in consequence of which the hydrogen content of chromium deposited from the high-speed electrolyte increases only negligibly.

X-ray diffraction investigations have established that chromium electrodeposited from both the standard and high-speed solutions has a bcc lattice, which is unoriented in the case of satin chromium and structured about the (111) axis in the case of bright chromium. In contrast to the usual satin chromium deposits, which have an ordered lattice, satin chromium deposited from the high-speed electrolyte is characterized by crystal lattice distortions which are as severe as those in bright deposits. Judging from the character of the distortions, an appreciable amount of hydrogen is occluded in the crystal lattice. It would appear that, in the case of satin chromium deposited from the standard electrolyte, the small amounts of hydrogen (Table 1) become incorporated directly into the lattice, which is responsible for the formation of an ordered structure.

Electron micrographs (Fig. 4) of the surfaces of satin (a) and bright (b) chromium deposited from the standard (1) and high-speed (2) electrolytes show that satin chromium from the high-speed electrolyte has a coarser grain than satin chromium from the standard solution. Bright chromium has a much finer grain, and its surface structure does not vary greatly as a function of method of deposition.

Thus, increasing the current density to 180-200 A/dm^2 in the deposition of chromium from electrolytes with SO_4^{2-} and SiF_6^{2-} additions markedly alters the structure and physicomechanical properties of the resultant metal deposits: their hydrogen content rises, their crystal lattice exhibits greater distortions, and the stresses set up in them grow. In view of this, greater caution must be exercised in chromium electrodeposition processes intensified by the use of such electrolytes. As raising the current density with the aim of intensifying the electrolysis process adversely affects some physicomechanical properties of chromium deposits, it should be employed only in those cases where relatively high internal stresses in deposited metal may be tolerated.

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