The Mechanism of Electrodeposition of Chromium Coatings with Different Phase Structure

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Study of chromium phase structure and the surface composition of chromium deposited by pulsed current has shown that when the hcp structure forms, the thickness of oxy-hydroxide Cr(III) compounds film increases on the deposit surface. Increase of this film thickness over some value (about 100 Å) results in maintenance of the hydride CrH as the first stage of chromium crystallization. Study of the phase structure of chromium from solutions with formic acid has shown that formation of the hcp structure is promoted by oxidation of the organic additive by chromic acid (*i.e.*, by increasing the Cr(III) concentration in the solution and by decreasing its acidity). This intensifies the formation of oxy-hydroxide Cr(III) compounds on the chromium surface during electrolysis.

Many different theories have been published on the mechanism of chromium electrodeposition from solutions of chromic acid. The role of catalytic anions (SO_4^{-2}, Cl, F) in the process of reduction of Cr(VI) anions to the metal is one of the basic arguable questions in all the existing theories. A considerable number of researchers1-15 have explained the positive influence of catalytic anions by the formation and destruction

of colloidal film on the cathode. This film is formed as a result of the interaction of products of the incomplete reduction of Cr(VI) anions with solution components (H₂O, chromate anions and catalysts). There is opinion¹⁶ also about complex formation between chromate anions and catalysts (species of heteropoly acids) (*i.e.*, on increasing the ability of these complexes to complete reduction).

In recent years, the concepts of the influence of catalysts on reduction of Cr(VI) ions has received more thorough development in the investigations of J.P. Hoare.¹⁷⁻¹⁹ He offered a model of the intermediate complex formation between incompletely reduced chromium ions and catalytic anions. For example, in solutions with sulfate additions, a chromousoxybisulfate complex can be formed. This complex is then reduced to chromium metal.

Without entering into discussion of the existing theories of the mechanism of chromic acid reduction to metallic chromium (because it is not the purpose of this paper), it is necessary to note that the mechanism of chromium electrocrystallization with different crystal structure has been barely addressed by researchers. Only in the work of C.A. Snavely²⁰ was it assumed that the pH near the cathode

Cr°

575

Cr(OH), Cr.O.

Cr,O,

2

з

580



Fig. 1—XPS spectra of the Cr 2p 3/2 line from chromium deposited by (a) direct, and (b) pulse current $t_{off} = 10$ msec): Curve 1 - without etching; Curves 2 and 3 - after ionic etching for 20 sec (2) and 120 sec (3). Etch rate $\frac{1}{3}$ $\frac{3}{4}$ /µA min.

influenced the formation of the chromium crystal structure.

It is known that a chromium coating deposited from chromic acid solution can have two different crystal structures: A body-centered cubic (bcc) lattice, designated α -Cr, and a hexagonal, close-packed (hcp) lattice, designated β -Cr.^{20,21} It is known also that the amount of hydrogen in β -Cr is considerably more than in α -Cr and that electrolytic β -Cr is practically chromium hydride, CrH.²² The transformation of hexagonal chromium into cubic is accompanied by evolution of a large amount of hydrogen.

The phase structure of a chromium deposit is governed by electrolysis conditions, mainly by the temperature.²¹ Bodycentered chromium is deposited at 45-55 °C and is used as functional, protective and decorative coatings. Hcp chromium deposition requires special conditions, such as low temperature (below 10 °C) and very high chromic acid concentration (more than 500 g/L),²⁰ as well as bichromate^{23,24} and organic substance additions.²⁵ Electrodeposition with pulsed current instead of direct current enhances formation of β -Cr.²² In this case, hcp Cr can be deposited from a solution having lower chromic acid concentration (350-400 g/L) and a higher temperature (up to 30 °C).

It is considered^{20,21} that in chromic acid electrolytes, electrocrystallization of bright chromium with bcc structure proceeds in two stages. Hexagonal chromium forms at the initial stage of the crystallization. As the deposit grows, it becomes unstable and breaks down, forming bcc chromium. There are several opinions concerning the process of twostage bright chromium crystallization which will be summarized below.



Fig. 2—XPS spectra of the Cr 2p 3/2 line from electrolytic chromium hydride before etching (1) and after ionic etching for 20 sec (2) and 120 sec (3). Etch rate was 0.3 Å/ μ A·min.

Conditions of hexagonal and cubic chromium formation have been discussed, based on the molecular and statistical theory of a new phase formation.²¹ It was established that for the small-sized crystallites, the free energy of the hexagonal chromium is lower then that of the cubic chromium. Accordingly, under conditions providing bright chromium deposition, accompanied by formation of fine crystalline deposits, crystallization proceeds with formation of a hexagonal lattice. While crystals are growing, the free energy of the cubic lattice decreases and, at a certain crystal radius, it becomes lower than the free energy of hexagonal lattice. As a result, the hexagonal structure becomes less stable than the cubic structure, resulting in the transformation of hcp chromium into bcc chromium.

Formation of the hexagonal phase at the initial stage of crystallization is also enhanced by adsorption of atomic hydrogen. Hydrogen adsorption decreases the surface energy of the newly formed structure while increasing stability of the very small-sized crystalline centers. It should be noted that hexagonal chromium shows an interstitial hydrogen phase (or chromium hydride) and that it has an elementary cell volume eight percent higher than that of cubic chromium. The interstitial hydrogen atoms located in the chromium lattice also decrease the energy required for crystalline lattice formation.²¹ As the deposit grows, however, and the deposited layer moves away from the surface, where hydrogen evolves, the phase formed at the beginning of electrocrystallization becomes unstable and hcp chromium is transformed into bcc chromium.

It is also considered²⁰ that the formation of hexagonal chromium or chromium hydride during crystallization is associated with the reduction mechanism of Cr(VI) ions and specifically with the reduction of chromium ions of an intermediate valency into chromium hydride by atomic hydrogen. As the chromium hydride is covered by the newly deposited layers, it loses contact with the atomic hydrogen and breaks down, forming bcc-chromium.

Experimental confirmation of the fact that unstable hcpchromium, formed at the beginning of electrodeposition, is transformed into bcc-chromium by the electrolysis, would be a considerable contribution to the development of chromium electrocrystallization theory.



Fig. 3—Diffractograms showing kinetics of disintegration at 110 °C. Time of warming (min): 1 - 0.2, 2 - 42, 3 - 132, 4 - 210.

Table 1				
Phase Composition, Structure & Hydrogen Content of Chromium				
Coatings at Different Polarizing Currents				

	Polarizing current	Hydrogen content	Structure of Deposit Surf by method		ace Comp.
		of Cr, %	X-ray	Electrography	XPS
1	Direct	3.2	bcc Cr texture {111}	bcc Cr texture	Cr ⁰
2	f = 100 Hz sinusoidal	2.3	bcc Cr texture {111}	bcc Cr texture	Cr ⁰ texture
3	$f = 50 \text{ Hz}$ $t_{on} = t_{off} = 10 \text{ mse}$	31.2 c	bcc Cr CrH, hcp	$Cr(OH)_3$ Cr_2O_3 , Cr^0	$Cr(OH)_3$ Cr_2O_3 , Cr^0
4	f = 1000 Hz $t_{on} = t_{off} = 0.5 \text{ msc}$	38.6 ec	bcc Cr CrH, hcp	$\begin{array}{c} \operatorname{Cr(OH)}_{3} \\ \operatorname{Cr}_{2}\operatorname{O}_{3}, \operatorname{Cr}^{0} \end{array}$	$Cr(OH)_3$ Cr_2O_3 , Cr^0
5	f = 95.23 Hz $t_{on} = 10 msec$ $t_{off} = 0.5 msec$	3.2	bcc Cr	bcc Cr	Cr ⁰

Temp 55 °C , Current density 50 A/dm²

Influence of Current

On Structure & Surface Composition

Crystal Structure of Electrodeposited Chromium The influence of non-stationary currents on the phase structure of electrolytic chromium were investigated²⁶ by the Institute of Physical Chemistry of the Russian Academy of Science. Chromium was deposited from the standard Sargenttype electrolyte (250 g/L CrO₂ and 2.5 g/L H₂SO₄) at 55 °C and 50 A/dm². Sinusoidal current obtained by full-wave rectification of alternating current at 50 Hz (Table 1, Row 2), was used for electrolysis, as well as rectangular pulsed current at different frequencies (Table 1, Rows 3-5). The structure of electrolytic chromium, composition of the deposit surface and hydrogen content of the chromium were examined. The structure of the chromium deposits was studied by X-ray and electronographic methods, and the composition of the chromium surface by XPS. The amount of hydrogen was determined by the method of vacuum-extraction at 500 °C and residual pressure of 10⁻⁶ mm Hg.

It was previously determined²⁶ that bcc chromium (Table 1, Row 2) can be obtained using pulsed current with sinusoidal waveshape when the duration of the current pulse is 10 ms and without off time. In this case, the hydrogen content of the deposit is 2.3 at pct, which is 40 percent less than that of the deposits plated by direct current (Table 1, Row 1).

If chromium is deposited with pulsed current when the ontimes (t_{off}) and off-times (t_{off}) are equal (10 msec, frequency 50 p/sec), the hydrogen content of the deposit increases to 31.2 at. pct (Table 1, Row 3) and hcp structure appears in the deposit simultaneously with the bcc lattice. If the pulse current frequency increases to 1000 p/sec, while the t_{off} and t_{off} duration decrease to 0.5 msec, the hydrogen content increases to 38.6 at. pct (Table 1, Row 4) and the hcp fraction of the chromium deposit increases. If the pulse duration increases to 10 msec, while the off-time remains at 0.5 msec, the hydrogen content of the deposit decreases to 3.2 at. pct and the hcp structure disappears again (Table 1, Row 5).

During chromium electrodeposition at low-frequency pulsed current (0.1 Hz) with $t_{on} = t_{off} = 10$ sec, the hydrogen content of the chromium does not change significantly compared with directcurrent plating.²⁷ The same phase structure (bcc-chromium) is obtained, therefore, in both cases.

Experiments show that the presence of a short pause (t_{off}) and specific ratio of t_{on}/t_{off} (the duty cycle) are required to obtain the hcp-structure in the standard chromic acid electrolyte at high temperature.

Composition of the

Chromium Surface Change of the chromium phase structure by the specified pulse current regime is accompanied by a change of state of the metal sur-

face. It can be determined by an electrochemical method, by recording an oscillogram of the potential transition curve after the polarizing current is switched off. If, at the deposition of bcc chromium, the current is switched off, the potential (NHE) of the cathode would correspond to that of the active chromium (-0.5 V) in 5 x 10^{-4} sec. In the case of hcp chromium deposition, the electrode potential that would be reached in the same time span (5×10^{-4} sec) after switching off the current would correspond to the potential of the passive chromium (-0.2 V).

The X-ray and electronographic analyses of the electrolytic chromium surface allowed determination of the change of composition of the surface layer of the deposited hcp structure. The data presented in Table 1 show that only metallic chromium is found on the surface of the deposits having bcc structure (Table 1, Rows 1 and 2). Oxy-hydroxide compounds of Cr(III), Cr(OH)₃ and Cr₂O₃ are revealed on the deposit surface when both hcp and bcc structures are present in the deposit.

The Cr 2p 3/2 XPS spectra of chromium having different phase structures are shown in Fig. 1. The peak of oxyhydroxide Cr(III) compounds and the vague peak of metallic chromium reveal the surface of bcc chromium deposited by direct current (Fig. 1a, curve 1). Ionic etching of the surface layer (thickness of the removed layer is 18-20 Å, Fig. 1a, curve 2), causes the disappearance of the initial peak of the oxy-hydroxide Cr(III) compounds and the appearance of a clear peak of metallic chromium.

Another picture is observed in the case of chromium deposits obtained by pulsed current and having both hcp and bcc structures (Table 1, Row 3). Metallic chromium as well

as oxy-hydroxide Cr(III) compounds are revealed on the deposit surface before argon etching. After etching off the surface layer of the deposit (thickness of the removed layer is 18-20 Å, Fig. 1a, curve 2), the metallic chromium peak becomes clearer, but the peaks of Cr_2O_3 and $Cr(OH)_3$ remain clear as well. These compounds are still present in the deposit after removal of a surface layer of 100 Å (Fig. 1b, curve 3), although the peaks are not as clear as before. These results demonstrate that a considerably thicker layer of oxy-hydroxide Cr(III) compounds is present on the surface of chromium with hcp structure, compared with bcc chromium. It can be supposed, therefore, that a certain connection exists between the hcp-chromium stability and thickness of the oxy-hydroxide Cr(III) compounds on the chromium surface.

Stability of Electrolytically Deposited Chromium Hydride & Composition of Its Surface

The results obtained have served for an assumption that a substantially thicker film of oxy-hydroxide Cr(III) compounds exists on the surface of chromium having single-phase hcp structure (*i.e.*, in the case of pure chromium hydride). To check this assumption, single-phase chromium hydride was obtained according to the reported technique of Proskurnikov and Krilov,²⁸ that is, from concentrated electro-

 Cr_2O_2

Cr(OH)₃

 $Cr_2O_7^{-2}$ $Cr_2O_4^{-2}$

Cr°

lyte (500 g/L of CrO_3 and 5 g/L of H_2SO_4), at low temperature (5-8 °C), by pulsed current electrolysis ($t_{on} = 1$ msec and $t_{off} = 2$ msec) and at current density of 40 A/dm². The X-ray study of the deposit has actually shown²⁹ that, under these conditions, chromium with single-phase hcp structure has been deposited (*i.e.*, pure chromium hydride). The electron diffractometry has revealed the presence of Cr₂O₂ and Cr(OH)₃ compounds. As for the Cr and CrH, it is impossible to state with confidence that they are present on the surface of the deposit having single-phase structure. The Xray method did not permit discovery of Cr or CrH on the surface of single-phase hcp-chromium as well. The Cr 2p 3/ 2 spectra of chromium before (curve 1) and after the ionic etching for 20 sec (curve 2) and 120 sec (curve 3) are shown in Fig. 2, which shows that only oxide Cr(III) compounds Cr_2O_3 and $Cr(OH)_3$ are present on the deposit surface both before and after etching. The peak of metallic chromium or CrH, however, does not appear even after five min of etching, when the thickness of the removed layer reached 125 Å.

Neither hydride nor metallic chromium, therefore, which could appear as a result of the hydride breakdown in the process of investigation, are not found on the surface of the electrolytic chromium hydride. There are two possible explanations of these results: (1) The presence of oxv-hydroxide



Fig. 4—XPS spectra of the Cr 2p 3/2 line of chromium from vacuum melting before (a) and after (b) cathodic polarization at potential of -0.3 V (NHE) in chromic acid electrolyte at 55 °C: 1 - without ionic etching, 2 & 3 - after ionic etching for 20 sec (2) and 80 sec (3).

Potential, eV



Fig. 5—XPS spectra of the Cr 2p 3/2 line from chromium deposited from a solution of 250 g/L CrO_3 with 1-pct $H_2SO_4(1)$, 0.2-pct $H_2SO_4(2)$ and without $H_2SO_4(3)$. Dashed lines - without ionic etching.

films with thickness up to several hundreds of Ångstroms and which masks the hydride on the deposit surface; (2) The absence of CrH compounds in the deposit having an hcp lattice. In the latter case, it could be supposed that hcp chromium is the hydroxide $Cr(OH)_3$ modification that saturates with hydrogen because of large adsorption capacity of the hydroxide. In this case, the deposit oxygen content must correspond to $Cr(OH)_3$. Two different methods: Neutron-activation and preparatory gas chromatography under the melting have demonstrated that the oxygen content of the deposit is about one wt pct (0.8 at pct). This is 50 times less than the quantity of oxygen corresponding to $Cr(OH)_3$.

These data show clearly that the deposits studied are not chromium hydroxide. The results of the investigation of thermal stability of hcp chromium deposits confirm this conclusion. The continuous X-ray study at 110 °C has shown that hcp chromium is transformed completely into bcc chromium in 2.5 hr (Fig. 3), not into chromium hydroxide with various structural modifications.^{30,31} It confirms that the investigated deposits are the chromium hydride, covered with a layer of oxy-hydroxide compounds.

Presence of the oxy-hydroxide Cr(III) layer thicker than 100 Å, which was found on the surface of the electrolytic hcp chromium, leads to the following possible conclusions. First, these results explain the stability of the electrolytic chromium hydride CrH, compared with that of the hydride obtained by direct synthesis-the latter is unstable under normal pressure and temperature.32 Apparently, oxy-hydroxide film of rather large thickness encapsulates the hydride, preventing its breakdown. Second, these results can serve as an experimental proof of the fact that CrH formation is the first stage of chromium electrocrystallization. As the outer layer of the growing deposit (where the hydrogen evolves) moves away from the inner deposit layers, hcp chromium decomposes. This means that bcc chromium obtained under usual electrolysis conditions is the product of hcp chromium decomposition proceeding during electrolysis, because, under these conditions, the thick film of oxy-hydroxide Cr(III) compounds does not form.

Forming & Thickening Conditions of Oxy-hydroxide Cr(III) Compounds

on the Chromium Surface

The oxy-hydroxide Cr(III) compound films on the cathode surface can be of a different thickness, depending on their formation conditions. Films formed as a result of redox interaction of a cathode metal with chromic acid (i.e., without current applied) are very thin.33 They do not mask metallic chromium, contrary to the films formed under cathodic polarization. This can be confirmed by examining the change of surface composition of high-purity chromium in chromic acid solution. Figure 4a demonstrates the Cr 2p 3/2 spectra for the vacuum-melted chromium, which is of higher purity than electrolytic chromium. In this case, the peak of chromium Cr⁰ is revealed clearly, even without ionic etching (curve 1) despite presence of the oxide (Cr_2O_2) . After shortterm (20 sec) ionic etching (curve 2), the oxide peak (Cr_2O_2) disappears and the chromium peak becomes clearer. Shortterm cathodic polarization of vacuum-melted chromium, however, in chromic acid electrolyte at potential -0.3 V (NHE) and 55 °C results in disappearance of the pronounced peak and appearance of a $(Cr_2O_3 + Cr(OH)_3)$ -phase (Fig. 4b, curve 1). The 20-sec etching of a deposit surface (Fig.4b, curve 2) is insufficient for the complete removal of the oxyhydroxide layer. A clear Cr⁰ peak appears only after 80-sec etching (Fig. 4b, curve 3).

The above data prove that oxy-hydroxide layers masking the chromium peak are the products of incomplete cathodic reduction of Cr(VI) ions to Cr(III).^{34,35} This reduction precedes and accompanies the chromium deposition. Products of this reaction form the cathode film, which creates conditions for metal deposition.^{9,10} This film consists of a compact part (insoluble in the electrolyte) and a liquid part (soluble in the electrolyte when the current is switched off). This film performs a dual role. On the one hand, it inhibits the easy reactions: Cr(VI) —> Cr(III) and H⁺ —> H; on the other hand, it promotes the reduction of chromium ions into metal, which proceeds with participation of the cathode film products—obviously, products present in the compact part.



Fig. 6—Dependence of oxidation of formic acid on concentration (a) in the chromic acid electrolyte and on the time (b). Temp 30 °C, conc. HCOOH, M: \bigcirc 0.05, \square - 0.1, Δ - 0.2, x - 0.4.

The surface investigation of the chromium deposits obtained in chromic acid electrolyte with different concentrations of H₂SO₄³⁶ provides additional proof of the masking action of oxy-hydroxide Cr(III) compounds. Figure 5 shows corresponding Cr 2p 3/2 spectra. It can be seen that, for chromium deposited from the solution of CrO_3 + one-percent H_2SO_4 , removal (by ionic etching) of a surface layer only 20 Å thick leads to disappearance of Cr_2O_2 and $Cr(OH)_2$ peaks and to appearance of a clear Cr peak (curve 1). For chromium deposits obtained from the CrO₂ solution with lower concentration of $H_2SO_1(0.2\%)$, removing even as much as 500 Å of the surface layer (curve 2) does not lead to appearance of a clear Cr peak, but reveals only a small plateau. In the case of electrodeposition from chromic acid solution without H₂SO₄ (curve 3), when only "black" chromium is deposited, ionic etching of the deposit surface does not reveal the presence of Cr⁰ even after removal of 500 Å of the surface layer. These results confirm the influence of sulfate ions on the thickness

of film containing oxy-hydroxide Cr(III) compounds on the cathode surface. Obviously, it is connected with formation of soluble complexes between Cr(III) and sulfate ions.

Accordingly, formation and changing of the thickness of oxy-hydroxide Cr(III) film on the cathode surface during electrolysis of chromic acid is related to the process of incomplete reduction of Cr(VI) ions and with its rate, which depends on electrolysis conditions, including solution composition.

Mechanism of Chromium Hydride Formation A natural question arises: Why does a compact film of oxyhydroxide Cr(III) compounds on a chromium surface develop a thickness sufficient for encapsulation of chromium hydride forming only under specific electrolysis conditions? It can be supposed that formation of thick cathode films able to encapsulate CrH results from the change of equilibrium between the rate of Cr(III)-ion formation and the rate of their further reduction or transport into solution. From this point of view, the influence of pulse current can be interpreted as follows. During a current pulse, some part of the Cr(III)hydroxide particles, having a certain orientation, and being part of a compact cathodic film, undergoes reduction into metal. During t_{off}, a process of hydroxide Cr(III)-particles reorientation can proceed because of potential change. This leads to a decrease of the rate of their further reduction at the next current pulse and, consequently, to an accumulation of Cr(III) hydroxide, and to a thickening of the compact part of the cathode film, promoting in this way, conservation of the

initially formed chromium hydride. The occurrence of current interruptions (t_{off}) are, therefore, a necessary condition for chromium hydride formation. The equilibrium can be re-established, however, and the film thickness will not increase if the pulse duration is longer than that of the pause. Not only pause occurrence, but a specific pulse duty cycle is necessary for obtaining hcp chromium. The analysis of the influence of pulse current parameters on the hcp structure formation proves that at $t_{on} = t_{off} = 10$ msec, the deposit reveals hcp structure (Table 1, Rows 3 and 4). If t_{off} duration is decreased to 0.5 msec, with t_{on} of 10 msec, hcp structure disappears (Table 1, Row 5).

The assumption of the upset of the equilibrium between the rate of Cr(III) formation and the rate of its removal (by further



Fig. 7—Influence of formic acid on hydrogen content in chromium deposits. Temp 30 °C, current density 40 A/dm², $t_{add} = 0.5$ hr.



Fig. 8—Dependence of hydrogen content in chromium deposits on conc. of formic acid and on time after addition of HCOOH to electrolyte. Conc. HCOOH (M): 1 - 0.02, 2 - 0.03, 3 - 0.06, 4 - 0.1, 5 - 0.2.

reduction or by transport into solution) also permits understanding of the influence of other factors promoting electrolytic chromium hydride (CrH) formation, in particular, the influence of organic additives.

Influence of Formic Acid on Structure Dependence on Additive Concentration

Formic acid (HCOOH) can serve as an example of an organic substance that promotes production of the electrolytic chromium hydride. As was shown earlier,²⁵ formic acid allows formation of hcp chromium structure by d-c electrodeposition at elevated temperature (30 °C) in solutions containing low CrO_3 concentration (100 g/L). It is interesting to note that single-phase hcp chromium structure (*i.e.*, 100 percent CrH) can be obtained at a certain concentration of formic acid. As the concentration of formic acid decreases or increases, the chromium hydride fraction of the deposit diminishes, then disappears completely.

To understand the reasons for such specific influence, particular features of chromium electrodeposition from chromic acid solutions with formic acid additives were studied in the Institute of Physical Chemistry of the Russian Academy of Science.³⁷ The studies were carried out in a solution of 100



Fig. 9—Stroke diagrams obtained for chromium deposited without addition of HCOOH (a) and with addition of 0.03 M HCOOH for $t_{add} = 0.5$ hr (b), 1.5 hr (c), 2.0 h (d), and with addition of 0.1 M HCOOH for $t_{add} = 0.5$ hr (e) and 1.5 hr (f); thin line - bcc Cr, thick line - hcp Cr.

Influence of F	Table 2 Influence of Formic Acid on Current Peak I _m				
HCOOH Conc. M	Current Peak Value, Stationary electrode	I _m , mA/cm ² Rotating electrode rpm			
0.0	180	1060			
0.05	310	970			
0.44	285	1100			

g/L CrO₃ + 5 g/L H₂SO₄ at 30 °C and at 40 A/dm². Chromium was deposited on steel cylinders. As the formic acid was oxidized by chromic acid (2H₂Cr₃O₁₀ + 9HCOOH + 18H⁺ -> 6Cr + 9CO₂ + 20H₂O), the elapsed time from the moment of the formic acid addition into the electrolyte (t_{add}) was taken into account during experiments. Preliminary work has shown that regardless of the initial concentration of formic acid, the amount of oxidized additive is about 50 to 60 percent in four hr, although the oxidation rate increases linearly with the increase of formic acid concentration (Fig. 6).

Figure 7 shows the dependence of the hydrogen content of the chromium on the formic acid concentration. These results were obtained for $t_{add} = 0.5$ hr (*i.e.*, chromium was deposited for 0.5 hr immediately after addition of formic acid). It can be

seen that for 0.04 M HCOOH, 1 g of Cr contains 200 cm³ of H_2 , or 0.93 gram-atoms of H_2 / gram-atom of Cr. This ratio corresponds to the formation of the hydride, $CrH_{0.93}$. The hydrogen content of chromium decreases at higher and lower concentrations of formic acid and bcc chromium appears in the deposit together with hcp chromium.

Figure 8 illustrates the variation of hydrogen content of the chromium, depending on time t_{add} for different formic acid concentrations in the electrolyte. Chromium was deposited for 30 min during 2-3 hr intervals, changing samples every 0.5 hr. When plating with low additive concentration, samples were changed every 10-20 min, because at longer deposition time, coating quality was poor. Figure 8 shows that the "hydrogen content-t_{add}" relationship has a clearly defined maximum at a formic acid concentration of 0.02-0.06 M (curves 1-3). The higher the concentration of formic acid, the longer the duration of increase of hydrogen in the chro-

mium. At HCOOH concentration equal to 0.02 M, therefore, maximum hydrogen content is reached at $t_{add} = 20$ min; for 0.03 M, the maximum is reached at $t_{add} = 30$ min, and at 0.06 M, the maximum is reached at $t_{add} = 60$ min. The maximum hydrogen content of the chromium increases also, from 164 to 238 cm³ per gram of chromium. For formic acid concentrations of 0.1 and 0.2, the hydrogen content of the chromium is substantially lower (100 and 40 cm³/g of Cr, accordingly), although these values are high enough, compared with the bcc-chromium. Also, the hydrogen content of the chromium increases with t_{add} , reaching approximately the same maximum in 2-3 hr (i.e., increasing to the level corresponding to the chromium hydride $CrH_{0.93}$.

X-ray studies have shown conformity between change of the hydrogen content of the chromium and the alteration of the chromium crystal structure with increase of t_{add} . Figure 9 shows the stroke diagrams obtained for chromium deposition from solution without (a) and with (b) addition of 0.03 M of formic acid for $t_{add} = 0.5$ hr, (c) 1.5 hr and (d) 2.0 hr. It can be seen that the same result is obtained regardless of the x-ray angles. Addition of formic acid at $t_{add} = 0.5$ hr leads to disappearance of bcc chromium reflex lines and to appearance of the reflex lines of hcp structure, or the chromium hydride. This corresponds to the maximum hydrogen content of chromium. After 1.5 and 2.0 hr of electrolysis, when the hydrogen content of chromium decreases substantially, the

bcc lines appear and gradually become clearer, whereas the lines of hcp chromium become weaker. The opposite picture is observed for chromium deposited from an electrolyte containing 0.1 M HCOOH: At $t_{add} = 0.5$ hr, the lines of hcp chromium are not clear, but at $t_{add} = 1.5$ hr they can be seen clearly (*i.e.*, in accordance with the increase of hydrogen content.

The given data show that hcp chromium formation depends not only on the concentration of formic acid, as previously established,²⁵ but the elapsed time from the moment of formic acid addition to the chromic acid electrolyte is a very important factor as well. The higher the concentration of the formic acid addition, the longer the time t_{add} required to obtain single-phase hcp chromium.

Mechanism of Formic Acid Influence

The reason for the specific influence of formic acid on chromium hydride formation during chromium electrodeposition can be easily explained on the basis of the above stated hypothesis on the encapsulation of chromium hydride formed during the initial stage of electrodeposition. Indeed, the formic acid can influence the thickness of a compact-phase part of a cathodic film because of the increase of the amount of oxy-hydroxide Cr(III) compounds. This looks quite possible for the following reasons. First, the Cr(III) concentration increases because of oxidation of the formic acid in solution. This in turn should delay the transfer of Cr(III) ions formed on the cathode, into solution, and should increase the Cr(III) concentration on the cathodic film. Second, the consumption of H⁺ ions during oxidation of the formic acid and chromic acid electroreduction leads to increase of the solution pH and particularly to the increase of pH near the cathode surface (pH_a). For example, within 30 min of electrolysis, the solution pH increases from 0.09 to 0.14. With 0.03 M HCOOH and after 2.5 hr of electrolysis, it reaches pH 0.27 and remains constant with further electrolysis. This process, together with increase of Cr(III) concentration, will promote the formation of Cr(III) oxy-hydroxide compounds. Naturally, the increase of Cr(III) oxy-hydroxide compounds near the cathode surface increases the thickness of the compact part of the cathode film because there is not enough time for reduction of Cr(III) compounds.

Based on the change of influence of formic acid with time and, in particular, the character of the relationship between hydrogen content of the chromium and t_{add} can be interpreted as follows. Apparently, the formation of a sufficiently thick film (for encapsulation of hydride) of Cr(III) oxy-hydroxide compound on the cathode surface requires a certain amount of time. During this time, appropriate changes of the Cr(III) concentration and pH should occur in the solution after addition of formic acid. As a result, the maximum hydrogen content of chromium is reached after t_{add} , but, as the oxyhydroxide Cr(III) film becomes thicker, it becomes more voluminous and its density is decreased. In turn, looser films probably have a weaker encapsulating action on the chromium hydride. A portion of the hydride, therefore, decomposes, the hydrogen content of chromium decreases and the hcp chromium fraction diminishes.

To understand the reason for the maximum hydrogen content of chromium shifting to longer t_{add} , it is necessary to consider the following. Formic acid is a complexing agent for Cr(III) and, as a weak acid, it displays buffering properties. If the solution contains high concentration of formic acid, a film of the necessary density and thickness to sustain the

chromium hydride can be formed on the cathode surface after a greater time lag.

Obviously, change of the thickness and density of a compact-phase cathode film dependent on the formic acid concentration and t_{add} , must influence the rate of chromium deposition also. The curves in Fig. 10 show that, depending on the t_{add} , the current efficiency actually changes, as well as the hydrogen content of the chromium, which goes through maximum, shifting toward longer t_{add} with increase of formic acid concentration. In other words, as the cathode film becomes thicker, current efficiency increases, and as the film becomes thinner or looser, current efficiency decreases. As was stated earlier, this is connected with the fact that the cathodic film, on the one hand, inhibits the accompanying side reactions, (*i.e.*, hydrogen evolution and incomplete reduction of Cr(III) ions) and, on the other hand, creates conditions for chromium deposition.

Change of the deposit quality with increase of t_{add} supports the above-mentioned view on the role of oxy-hydroxide Cr(III) compounds in the process of chromium electrodeposition. Indeed, at small concentrations of HCOOH, cracking and peeling of the chromium deposit begins a short time after the beginning of electrolysis. Presumably, this is connected with a large quantity of oxy-hydroxide Cr(III) compounds on the cathode surface, with loosening of the compact-phase portion of the cathode film and its inclusion in the deposited metal. This does not happen at high concentrations of formic acid, even with prolonged electrolysis, apparently because of the buffering and complexing properties of the formic acid.

The change of the current maximum of the potentiodynamic voltammetric curves confirms the buffering and complexing action of formic acid during chromium deposition. It is known that formation of the cathode film, because of variation of concentration near the cathode surface, results in current decrease as negative potential increases, which leads to the appearance of the current maximum on voltammetric curves.^{9,34,38} Table 2 shows that on the stationary electrode, the peak current value, I_M , increases about 1.6-1.7 times with the addition of formic acid. This means that the concentration changes in the solution near the cathode surface become smaller in the presence of formic acid. The values of the peak current obtained on a rotating electrode in solutions with and



Fig. 10—Dependence of current efficiency on time after addition of formic acid (t_{add}) of different conc. (M): 1 - 0.02, 2 - 0.03, 3 - 0.06, 4 - 0.1, 5 - 0.2.

without formic acid addition are almost the same, meaning that the influence of formic acid vanishes when there are no concentration changes in the solution near the cathode surface.

In this case, clearly, an accumulation of formic acid oxidation products does not occur because of the short times necessary to obtain potentiodynamic voltammograms. Under these conditions, the influence of HCOOH on the concentration changes prevails in the near-cathode liquid film. These changes occur even in the absence of formic acid, but not to such an extent as to cause formation of hcp chromium structure.

Study of the influence of formic acid on the process of chromium electrodeposition has shown that formation of the hcp structure is mainly a result of chemical oxidation of formic acid by the chromic acid. This process increases the Cr(III) concentration in the solution and decreases its acidity. These changes promote increase of Cr(III)- and OH-ion concentrations in the near-cathode-surface liquid film during electrolysis. As a result, the rate of formation of oxy-hydrox-ide Cr(III) compounds on the cathode surface increases. Because the rate of their further reduction to metallic chromium does not change, the compact-phase portion of the cathode film becomes thicker. This leads to accumulation of chromium hydride, or hcp structure, which is the first stage of chromium electrocrystallization.

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