

40-50%. In the same figure we show values for the magnetostriction in the plane of the film, which at iron contents of 35-50% was somewhat higher, and at higher contents lower than that of polycrystalline metallurgical alloy (Fig. 2c). The coatings had high internal tensile stresses and a large, positive value of magnetostriction in the plane of the film; for uniaxial extension one would have expected high rectangularity of the hysteresis loop in this case ( $\gamma > 0.5$ ) [3]. It must be taken into account, however, that in our case the internal stresses were distributed uniformly in all directions in the plane of the film. In addition the process of remagnetization undoubtedly was influenced by the anisotropy in the shape of the crystals which, according to metallographic studies of transverse thin sections of the deposits, were extended along the [111] axis perpendicular to the plane of the film (Fig. 3). It is likely that the low values of rectangularity of the hysteresis loop were caused by the combined effect of factors such as the crystal orientation with the long axis (which is at the same time the crystal axis of easy magnetization) perpendicular to the magnetizing field, and of the isotropic internal stresses in the plane of the film.

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#### SULFATE ION ADSORPTION DURING CHROMIC ACID ELECTROREDUCTION

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Opinion is divided [1] as to the mechanism by which the anions of strong acids ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SiF}_6^{2-}$ ) influence the reduction of chromate ions to the trivalent state. The most likely viewpoint is that of an activating effect of the additives upon the electrode surface, which is due to destruction of the metal's oxide film in the chromic acid solution by the anions which are added [2-5].

In the present work we have used a radiochemical technique involving the isotope  $^{35}\text{S}$  to study  $\text{SO}_4^{2-}$  adsorption on surfaces of chromium and nickel from chromic acid solutions as a function of potential, in order to gain a better understanding of the mechanism by which the added anions influence chromic acid reduction. The studies were done at room temperature with samples in the shape of discs with  $d = 18$  mm and a thickness of 3 mm which were made of nickel or of copper coated with a chromium layer ( $20 \mu\text{m}$ ) free of microcracks; the solutions were 0.5-2.5 M chromic acid containing  $\text{H}_2\text{SO}_4$  (1.25-5.0 g/liter). The specific radioactivity of the solutions was  $0.6-0.8 \cdot 10^5$  pulses per 100 sec and ml.

The initial state of the chromium surface was stabilized before the adsorption experiment by holding the electrode in the test solution at a potential  $\varphi = 0.24$  V (sce) which was applied for 10 min from a P-5827 potentiostat (the auxiliary electrode was platinum). Then the potential was switched to the value where  $\text{SO}_4^{2-}$  adsorption was allowed to occur. After 10 min of exposure to the test solution the samples were lifted out in order to measure their activity, first with a drop of solution the activity of which was then subtracted in order to determine the total adsorption  $\Gamma_{\text{tot}}$ , and then after rinsing the samples in water for 5 min in order to determine the strong adsorption  $\Gamma_{\text{g}}$ .

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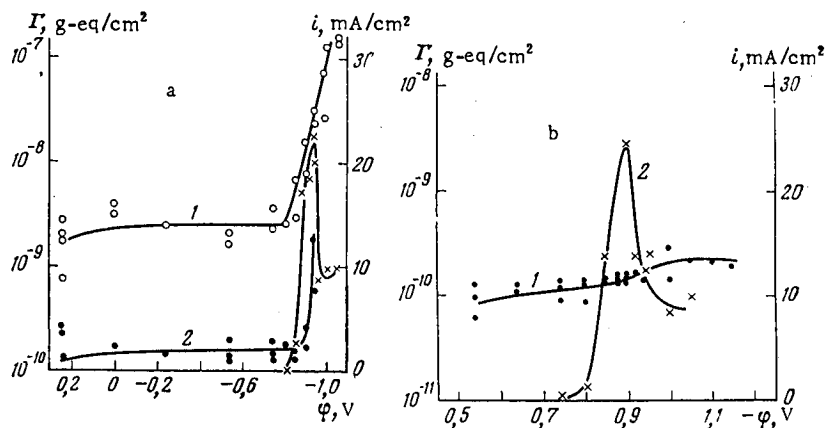


Fig. 1. a) The variation of  $\Gamma_{\text{tot}}$  (curve 1),  $\Gamma_s$  (curve 2), and the rate of reduction of Cr(VI) to Cr(III) (curve 3) with the potential (sce) of the chromium electrode;  $\Gamma_s$  was determined after  $\Gamma_{\text{tot}}$ . b)  $\Gamma_s$  was determined without  $\Gamma_{\text{tot}}$ : 1)  $\Gamma_s$ ; 2) the rate of reduction of Cr(VI) to Cr(III).

The variation of  $\Gamma_{\text{tot}}$  and  $\Gamma_s$  with the potential of chromium in 0.5 M chromic acid solution containing 2.5 g H<sub>2</sub>SO<sub>4</sub> per liter is shown in Fig. 1a. The same figure shows data on the variation of the rate of reduction of Cr(VI) to Cr(III) obtained simultaneously with the adsorption measurements (at the same electrode) and plotted from the average values of current after 10 min; the current changed substantially with time.\* It can be seen that  $\Gamma_{\text{tot}}$  and  $\Gamma_s$  are changing little over the potential range from 0.24 to -0.8 V, but chromate ions are not reduced as yet. If the roughness factor of the matte chromium is taken as 20, then  $\Gamma_{\text{tot}}$  corresponds approximately to a monolayer, while  $\Gamma_s$  corresponds to 2.5% of monolayer coverage. This shows that in chromic acid solutions, the SO<sub>4</sub><sup>2-</sup> ions are adsorbed on chromium in significant quantities, and the adsorption is predominantly weak.

The values of  $\Gamma_{\text{tot}}$  increase by an order of magnitude at potentials between -0.8 and -0.95 V when the reaction Cr(VI) → Cr(III) begins to occur at the cathode, and rapidly becomes faster. An equal increase in  $\Gamma_s$  occurs somewhat later (beyond -0.9 V). At potentials more negative than -0.95 V when a phase film of reduction products begins to form on the cathode [1], which causes a decrease in the rate of the cathodic process,  $\Gamma_{\text{tot}}$  continues to increase, attaining a level of fifty times that at the beginning of chromate ion reduction. Here it becomes difficult to measure  $\Gamma_s$ , since it is impossible to wash the cathodic-film particles from the cathode; this gives rise to drastically higher  $\Gamma_s$  measurements.

It can be seen from the above data that the start and rapid acceleration of the reaction Cr(VI) → Cr(III) coincide with the rapid increase in the amount of sulfate ions on the cathode surface. This correlation is upset when cathodic-film formation starts to occur, evidently because the SO<sub>4</sub><sup>2-</sup> ions are much more adsorbed by the material of the cathodic film than by the chromium surface.

To estimate the contribution to the measured values of strong SO<sub>4</sub><sup>2-</sup> adsorption which is due to cathodic-film formation, we determined  $\Gamma_s$  after a washing procedure which left the cathode surface free from visible film particles. This was accomplished by washing the sample in water (twice, for 5 sec each) right after it was pulled from the solution, i.e., the drying of the sample with drop, for the purposes of determining  $\Gamma_{\text{tot}}$ , was eliminated and the washing of the cathodic film improved in this manner. At potentials more negative than -0.95 V, the samples in addition were washed in 2.5 M CrO<sub>3</sub> solution (without SO<sub>4</sub><sup>2-</sup>) in order to remove the film; prior to film formation such washing had no effect on the  $\Gamma_s$  values.

It can be seen from Fig. 1b that after careful removal of the cathodic film,  $\Gamma_s$  is not increasing much over the potential range from -0.8 to -0.9 V, i.e., over the range where the rate of the reaction Cr(VI) → Cr(III) is rapidly increasing. This shows that strong SO<sub>4</sub><sup>2-</sup> adsorption, which is an order of magnitude lower than  $\Gamma_{\text{tot}}$ , correlates less than  $\Gamma_{\text{tot}}$  with the rate of chromate ion reduction. This is also confirmed by the results of adsorption kinetic studies:  $\Gamma_s$  does not change over times from 10 to 1000 sec, while  $\Gamma_{\text{tot}}$  is increasing by a factor of ten, and the cathodic process over the same period of time accelerates from 0.03 to 7.5 mA/cm<sup>2</sup>.

\* At  $\phi$  between -0.80 and -0.94 V the current increased owing to changing surface state as the incomplete reduction of chromate ions proceeded, but at potentials more negative than  $\phi = -0.96$  V it decreased because of formation of a phase film on the cathode surface.

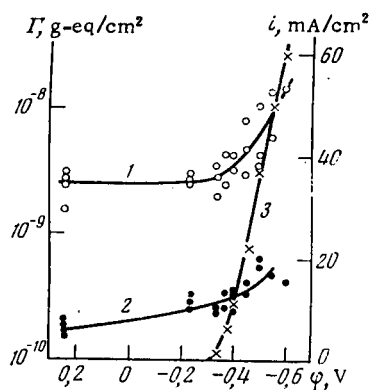


Fig. 2. The variation of  $\Gamma_{\text{tot}}$  (curve 1),  $\Gamma_s$  (curve 2), and the rate of reduction of Cr(VI) to Cr(III) (curve 3) with the potential ( $\phi$ ) of the nickel electrode.

That an increased activity of the samples is indeed characteristic for adsorption rather than exchange of  $\text{SO}_4^{2-}$  (as could have been suggested [6]) was confirmed by comparison of results obtained on electrolytic chromium and on diffused chromium,\* which is free from original anions on the surface.

Sulfate adsorption decreases by a factor of 2.5 to 3 when, at constant  $\text{H}_2\text{SO}_4$  concentration (2.5 g/liter), the chromic acid concentration is increased from 0.5 to 2.5 M; this appears to be due to stronger competitive chemisorption of chromate ions [7]. It is interesting to note that in sulfuric acid solutions (2.5 g/liter), the adsorption of  $\text{SO}_4^{2-}$  ions on chromium (in the absence of chromic acid) is very low ( $\Gamma_s \approx 5 \times 10^{-11}$  g-eq/cm²). When such a solution is neutralized to pH 5.8 in order to suppress chromium dissolution at negative potentials, then  $\text{SO}_4^{2-}$  ions can no longer be detected on the chromium surface. On the basis of these observations one can suggest that sulfate adsorption from chromic acid solutions at potentials between 0.2 and -0.8 V occurs on a surface of chromium oxides.

Chromium-containing oxides obviously are formed as well on other metals dipping into chromic acid, so that  $\text{SO}_4^{2-}$  ions are of course expected to be adsorbed on their surfaces in approximately the same way as on chromium. In fact, at potentials below the reduction of chromic acid,  $\text{SO}_4^{2-}$  adsorption on nickel (Fig. 2) is almost the same as that on chromium. With the start of chromate ion reduction ( $\phi = -0.35$  V) there is an increase in  $\Gamma_{\text{tot}}$  and  $\Gamma_s$ , but this is less pronounced than on chromium.

It can be seen from Fig. 2 that over the potential range from -0.35 to -0.6 V, the rate of incomplete chromate ion reduction (curve 3) is rapidly increasing, and attains values which are higher than those on chromium at  $\phi = -0.95$  V. The current does not drop off in this potential range, and products of chromate ion reduction which are hard to wash away are not seen to be formed on the cathode, i.e., no film is formed on nickel.

Thus, the results show that sulfate ions which are added for chromate reduction are adsorbed on the surfaces of chromium and nickel cathodes forming almost a monolayer over a wide range of potentials. At the potentials of incomplete chromium ion reduction there is a significant increase in the amount of sulfate on the surface, which becomes even larger when a cathodic film is formed.

From the present work one can make certain suggestions concerning the mechanism by which the sulfate ions influence the reduction of chromic acid. The observation that significant amounts of sulfate are present on the cathode surface before reduction is setting in gives rise to the suggestion that the increase in the surface concentration of  $\text{SO}_4^{2-}$  ions on the cathode during reduction may be the result rather than the cause of this reduction. It appears likely that the incorporation of  $\text{SO}_4^{2-}$  ions into the oxide film which is formed on the cathode surface in chromic acid leads to a change in its structure, and enables it to be reduced once a certain potential has been attained, the exact value of which will depend on the cathode metal, since the oxide is a mixed product. Destruction of the oxide film on the cathode creates conditions where the chromate ions can be reduced to Cr(III) which forms complexes with  $\text{SO}_4^{2-}$  [8, 9]. This possibly gives rise to the strong increase in  $\Gamma_{\text{tot}}$  when chromic acid begins to be reduced.

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## EFFECTS OF TEMPERATURE AND POTENTIAL ON PERPHOSPHATE SYNTHESIS

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Peroxyphosphoric acids and their salts were first obtained and their chemical behavior studied under various conditions in [1]. The conditions under which peroxyphosphates are obtained by anodic oxidation of the potassium and ammonium salts of phosphoric acid were studied by Fichter and coworkers [2], and later by the authors of [3, 4]. The kinetics of formation and the mechanism of decomposition of peroxyphosphates have been the subject of a number of studies [5-8], but the mechanism of the electrochemical formation of perphosphates has not been studied sufficiently. Perphosphates, as weak oxidizing agents, are of considerable interest in view of their practical use as detergents and bleaches of low toxicity. But at the present time they are not produced industrially, despite the existence of both Soviet [9, 10] and foreign [11] patents concerning electrochemical methods of production.

In the present work we used the techniques of potentiodynamic curves and of electrolysis under potentiostatic conditions followed by product analysis to investigate the electrooxidation of phosphates at platinum from 2 M  $K_2HPO_4$  + 4 M KF solution, which according to literature is the optimum electrolyte for producing peroxyphosphates [2].

The electrolytes were prepared with twice distilled water from "kh.ch." ["chemically pure"] grade recrystallized  $K_2HPO_4 \cdot 3H_2O$  and  $KF \cdot 2H_2O$ . The experiments were conducted in a three-electrode cell; the cathode and anode compartment were separated with a glass frit.

A Pt wire ( $S = 0.1 \text{ cm}^2$ ) served as the working electrode when recording the polarization curves; Pt electrodes with apparent surface areas from 2 to 20  $\text{cm}^2$  were used for electrolysis. Prior to experiment the electrodes were treated with dilute aqua regia (1:1), and then washed with twice distilled water. A saturated silver-silver chloride electrode served as the reference electrode. The electrolyte was agitated with a magnetic stirrer, and was thermostated or cryostated. Polarization was accomplished via a P-5827 potentiostat, the polarization curves were recorded as  $\varphi$  vs  $\log i$  by means of an L-1 logarithmic converter and an LKD-003 X-Y recorder. The pH of the working electrolyte was controlled with a pH meter; it was about 10. All values of potential are reported relative to the normal hydrogen electrode. The synthesis products, peroxymono- and peroxydiphosphate, were analyzed iodometrically using the techniques described in [8]. The amount of oxygen evolved was determined, either by volume or by chromatography, depending on the experimental conditions. The analytical accuracy was 0.5% for peroxydiphosphate, 5% for peroxymonophosphate, and 10% for oxygen.

Potentiodynamic polarization curves recorded in the "forward" and "reverse" scan on the platinum electrode at temperatures of 20, 0, and  $-20^\circ\text{C}$  with  $\partial\varphi/\partial\tau = 0.4 \text{ V/min}$  are reported in Fig. 1. The curves have a number of characteristic segments differing in the slopes and in the processes occurring there. The initial segment of the "forward" scan of the polarization curves (below 1.5 V) has a clear inflection which is linked to the first linear segment of the curve. It corresponds to oxidation of the platinum surface. Oxygen evolution on

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