CURRENT EFFICIENCIES IN CHROMIUM DEPOSITION FROM AQUEOUS SOLUTIONS OF CHROMIC ACID

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The cathodic polarization curve obtained in aqueous solutions of chromic acid with an addition of 1% H_2SO_4 is made up of three and sometimes four branches. In the course of the experiment one always observes a spontaneous jump of the potential φ from +0.3 to −0.1 V (E_0^H) and a sharp change (more frequently a drop) in current on transition to the last or fourth branch. Only the process Cr(VI)−Cr(III) occurs at the cathode up to the potential jump; after the jump discharge of H^+ ions occurs initially with Cr(III) formation but for further increase in the cathodic current density (D_c), chromium deposition begins i.e., three processes take place [1].

Determination of the percent yields of Cr(III), H_2, and Cr(0) in the region of unstable values of φ at constant current is difficult. We attempted to determine them with a pulsing current.

The dependence of the percent yields of Cr(III), H_2, and Cr(0) on D_c starting with small polarization up to 200 mA/cm^2 in a solution containing 268 g/liter CrO_3 and 4 g/liter H_2SO_4 at 50° was studied. The volume of the bath was 200 ml; a precisely constant current was obtained from batteries, and a pulsing current from a selenium rectifier. The percent fluctation was regulated using a condensor connected to the output and was determined oscillographically. The chromium yield was found by weighing the cathode, the H_2 yield, volumetrically, and the Cr^{3+} yield by difference: $100\% - (\eta_{Cr(0)} + \eta_{H_2})$. Polished nickel discs with a surface area of 2.25 cm^2, which had been chrome plated first in several runs, served as cathodes. In other experiments the nickel electrodes were pickled in a 1:1 HCl solution for a period of 5-7 sec. The electrolytic cell containing a saturated calomel reference electrode was thermostated. The electrolysis time was chosen such that sufficient chromium and H_2 were obtained at low D_c. In the unstable potential region the H_2 yield was determined as follows: the current density was set at 50-60 mA/2.25 cm^2, and at the moment when hydrogen started to evolve the current was lowered in 1-2 sec to the required value (15-20 mA). In this way hydrogen was still evolved for a period of 30-35 sec after which φ suddenly reached a more positive value and hydrogen evolution was terminated. The sum of the volumes of hydrogen evolved after 10 iterations of the operation allowed one to calculate the yield with respect to current in H_2, Cr(0), and Cr(III).

Although the reason is not completely clear to us, the principles of chromium deposition with purely constant, or pulsing current, or for very weak pulsations appear to be somewhat different. Thus, a larger current density is found at the beginning of chromium deposition with a pulsing current (Fig. 1, point C) than with constant current (point B_1). (The reason for the break in curves obtained at constant current (Fig. 1b) is not clear.)

As follows from Fig. 1c, the bend in the φ curve occurs after the start of chromium deposition. This bend is related to a gradual covering of the electrode surface with chromium since it is also observed for deposition of chromium on other metals.

The sharpest difference between purely constant and pulsing currents is found for chromium deposition on chrome-plated nickel, i.e., in fact, on chromium (Fig. 2). With a pulsing current for a lowering of D_c the Cr(III) yield increases monotonically, and the H_2 yield falls (to zero for $D_c = 10$ mA/cm^2). For a strictly constant current on lowering D_c to values less than 50 mA/cm^2, the rate of hydrogen evolution

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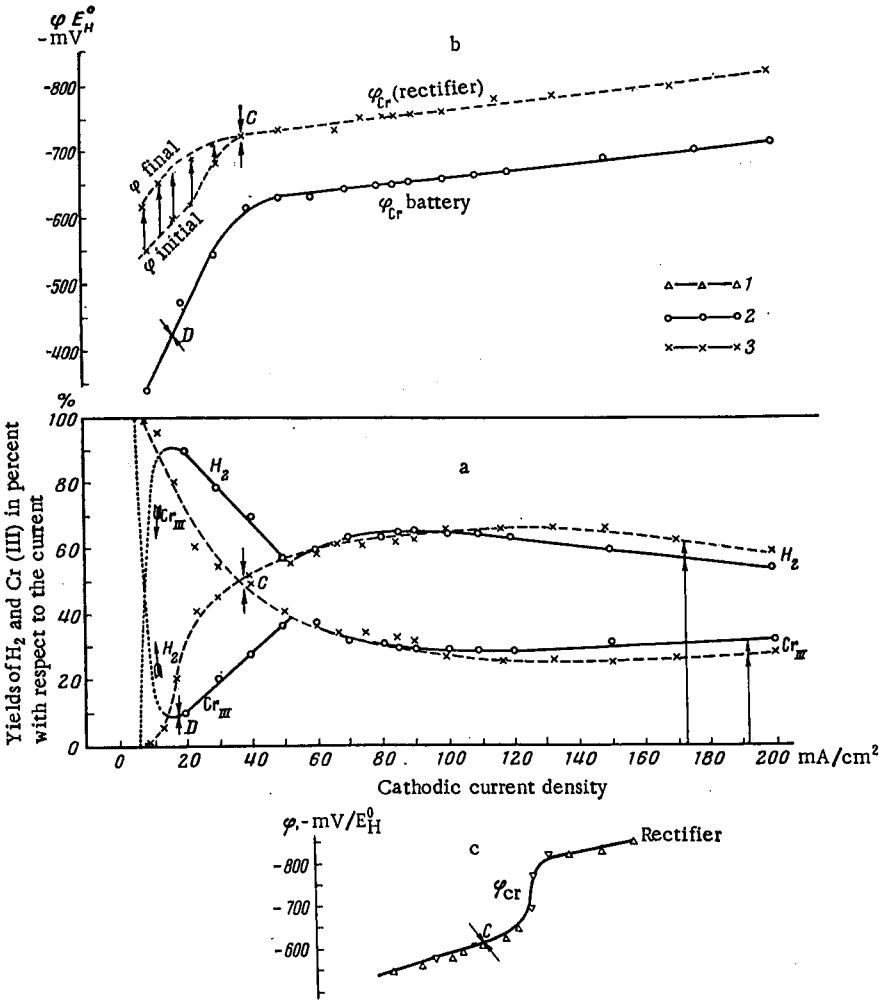


Fig. 1. Dependence of the cathodic potential and yields of H_2, Cr(III), and Cr(0) on current density D_c for chromium deposition on polished nickel. 1) Passivated nickel, current from a rectifier, 2.4% pulsation; 2) current from batteries during charging with rectifiers, active nickel without pulsation; 3) active nickel, current from batteries.

suddenly begins to increase and raches a maximum value for $D_c = 17$ mA/cm^2. Thus, the potential of spontaneous falls moves from the negative region (−0.5 to −0.6 V) to the positive (0.5 to 0.7 V); discharge of H^+ and evolution of H_2 immediately ceases and only the Cr(VI) → Cr(III) process takes place at the electrode. Of course, the Cr(III) yield curve is changed in the opposite direction. Such a change in the rates of the two processes is not observed, but is often found on chromium, and more rarely on nickel especially when it is passivated. In this regard a comparison of the break in the curves for nickel (Fig. 1a) with the break for chromium (Fig. 2a) is very characteristic. The similarity of these breaks points out the fact that both on nickel and on chromium for any value of D_c, a tendency to strengthen hydrogen ion discharge arises with lowering of D_c; however, on chromium the tendency, to some extent or other, becomes dependent on the structure of the metal surface and the degree of pulsation in the current.

From Fig. 2 it is obvious that the total cathodic process for chrome plating takes place with less overpotential for constant current than for pulsed current.

With the use of both pulsing and strictly constant current the critical current density for chromium deposition is higher on nickel than on chromium. It is also high for chrome plating on brass, platinum, iron, graphite, and copper.

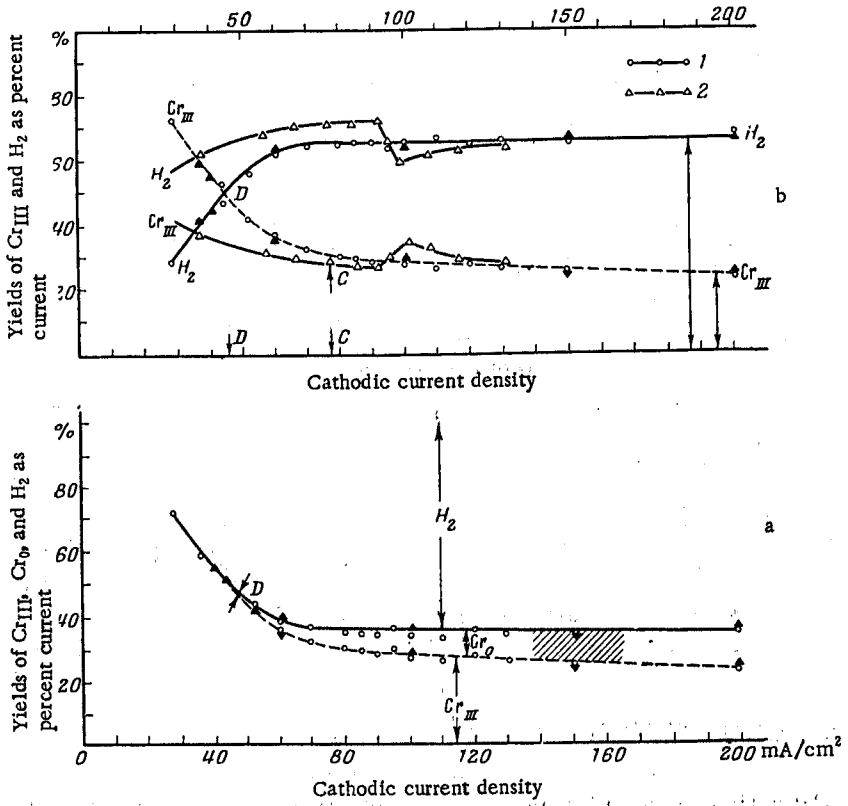


Fig. 2. Dependence of the cathodic potential and yields of H_2 and Cr(III) on current density D_c for deposition of chromium on chrome-plated nickel. 1) With batteries; 2) with a rectifier (pulsation 2.4%).

Analysis of the numerous curves for chromium yield as a function of D_c showed that the chromium yield is linearly related to the logarithm of the current density only in several cases as was first noted in [2]. This dependence is observed even when the weight ratio CrO_3:H_2SO_4 in the solution is higher than 100.

Accurate determinations of the chromium yields in the interval 10-300 mA/cm² for D_c showed that, for example, in solutions containing 40 g/liter CrO_3 + 0.8 g/liter H_2SO_4 (t = 23°) and 250 g/liter CrO_3 + 5 g /liter H_2SO_4 (t = 30°), the plot of chromium yield versus current density goes through a maximum in the region 50-100 mA/cm², a result which is rather unusual.

LITERATURE CITED

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2. R. Schneidewind and St. Urban, Trans. Amer. Electrochem. Soc., 53, 457 (1928); R. Schneidewind, St. Urban, and Adams, Trans. Amer. Electrochem. Soc., 53, 499 (1928).