COMPARISON BETWEEN THE ELECTROCHEMICAL PROPERTIES OF BULK CHROMIUM AND THIN-FILM CHROMIUM ELECTRODES

G. N. Mansurov, I. V. Boguslavskaya, O. A. Petrii, and B. I. Kozyrkin

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In present-day technology increasing use is being made of metallic films and coatings deposited in vacuum or obtained by pyrolysis of organometallic compounds in the gas phase. When films of chromium are used as anticorrosion coatings or in microelectronics (shadow masks, printing plates, resistors, etc.), it is necessary to have a knowledge of their electrochemical properties. However, most authors [1, 2] have discussed the preparation technology, structure, and mechanical properties of the coatings. Development of the electrochemistry of thin films began comparatively recently. The physical, electrochemical, and mechanical properties of chromium films have been investigated [1-5], and it has been established that chromium films possess good adhesion to the substrate, good mechanical strength, and chemical inertness. Such films are resistant to the action of concentrated acids and mixtures of acids; in the opinion of Gorgoraki et al. [5], this is due to the presence of carbides in the films, formed by pyrolysis of molecules of organometallic compounds.

Since the electrochemical properties of a massive chromium electrode depend on the manner of its preparation (thermal or electrolytic chromium) [6, 7], it seemed of interest to study the electrochemical behavior of thin-film chromium electrodes and compare it with the electrochemical properties of bulk chromium. Thin-film electrodes were obtained by cathode sputtering in vacuum and pyrolysis of organometallic compounds, so that we could also compare the behavior of films prepared in different ways.

A massive chromium electrode was prepared from chromium of 99.98% purity obtained by electron melting in vacuum. Before making the measurements we polished the effective surface of the electrode to mirror smoothness (class 10-12), treated it with concentrated sulfuric acid, and washed it with double-distilled water. The results of our study of the electrochemical properties of this electrode were compared with the results in [7-9].

Films of chromium 600-700 Å thick were deposited on a pyroceramic substrate by thermal evaporation in vacuum in a UVN2M-1 apparatus. The pyrolytic films were deposited between 350 and 500°C in the apparatus described in [10]. Analysis of the pyrolytic films for carbon content, made by the method in [11], revealed (Fig. 1) that the films with lowest carbon content were deposited at 400°C. However, it is rather difficult to obtain pyrolytic films with reproducible compositions. Thus the carbon content of the films on different regions of the same substrate can differ by 10-12% [12]. X-ray diffraction investigations of the phase composition of films obtained by pyrolysis of OMC revealed that the films contain Cr_2O_3 and carbides of various compositions [13].

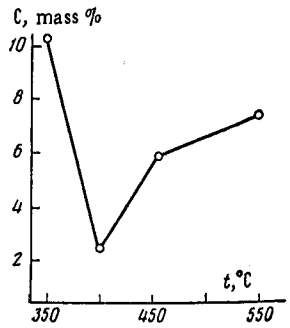

Fig. 1. Carbon content of pyrolytic chromium films vs deposition temperature.

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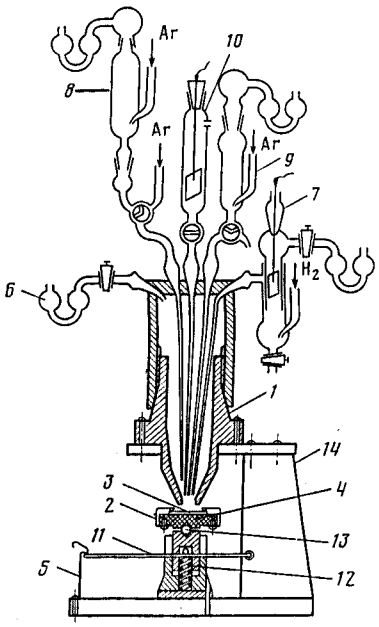

Fig. 2

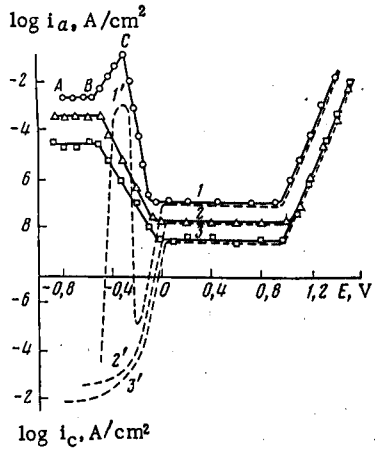

Fig. 3

Fig. 2. Electrochemical cell. 1) PTFE casing; 2) contact terminals; 3) sample; 4) stage; 5) catch; 6) water trap; 7) hydrogen reference electrode; 8, 9) vessels for base electrolyte solution and additives; 10) vessel for auxiliary electrode; 11) lever retaining stage; 12) spring; 13) ball bearing; 14) bracket supporting cell.

Fig. 3. Dependences of solution current (1-3) and potentiostatic external current (1'-3') in 0.1 N H_2SO_4 at t = 20°C on potential for compact (1, 1'), "vacuum" (2, 2'), and pyrolytic (3, 3') chromium. Here i_c is the cathodic hydrogen evolution current.

Polarization curves were recorded in 0.1 N H_2SO_4 solution by the potentiostatic method. The potentials E are given relative to a reversible hydrogen electrode in the same solution. Measurements were made in an atmosphere of argon at 20 ±1°C in a cell made of PTFE and quartz (Fig. 2); the carefully polished specimen is pressed from below against the end of the cell by a special device giving an adequate seal and preventing leakage of electrolyte solution. The design of the cell enables it to be used both to measure polarization curves and to measure the resistances of thin-film electrodes. An auxiliary platinized-platinum electrode was placed in a separate vessel; the spaces of the working and auxiliary electrodes had to be separated in order to avoid errors in determining the chromium ion concentration in the solution due to their adsorption by the developed surface of the Pt electrode. The solutions were made up with double-distilled sulfuric acid and double-distilled water. The rate of dissolution of chromium was determined by analyzing the solution for solution products of the metal. Samples of solution, taken during polarization of the electrode in the regions of the start of passivation and of the passive state, were analyzed by the kinetic method [14]. In the active and transpassive regions of solution we used the classical photocolorimetric method of determining chromium [15].

The polarization curve for bulk chromium was recorded by the method in [8], i.e., after preactivation of the electrode and attainment of the stationary potential of active chromium $E_{st} = -0.43$ V. In contrast with compact chromium, film electrodes could not be activated by cathodic polarization. This self-passivation phenomenon was described in [5, 16] for pyrolytic films of chromium and was theoretically explained [17] for chromium carbides. In this connection, polarization curves were recorded on unactivated electrodes, and measurements were begun after the electrode had reached a steady potential.

In recording the polarization curve, after establishing E_{st} we applied the given potential and polarized the electrode until a constant current was established. We then washed the cell free of chromium ions with 0.1 N H_2SO_4 solution and kept the electrode in a new portion of solution for 20-120 min.*

* The polarization time was determined by the need to accumulate chromium ions in a sufficient concentration for their determination by the diphenylcarbazide method.

We then took a sample for analysis of the solution for chromium ion content, and repeated the above operations at the next potential.

Figure 3 plots potential dependences of the rate of dissolution of chromium (curves 1-3) constructed on the assumption that in the active and passive regions chromium goes into solution in the form of Cr(II) and Cr(III) ions respectively, while in the transpassive region the proportions of the forms Cr(III) and Cr(IV) correspond to those found in [8] for compact chromium. To the negative side of −0.3 V on the polarization curve of compact chromium we can distinguish two sections [8]. In section AB (on the cathodic side of E = −0.55 V) the rate of dissolution of the metal is independent of the potential. In this region dissolution of chromium mainly occurs by a chemical mechanism [9]. In section BC the rate of dissolution increases when the potential shifts toward the anodic side, i.e., an electrochemical mechanism of dissolution predominates.

In the case of film electrodes, section BC is absent, and the rate of dissolution is independent of potential right up to the onset of passivation. The absence of a region of activation for chromium films can be explained by the presence of the impurities oxygen and chromium carbide throughout the volume of the film [18]. This also explains the shift of the onset of passivation of film electrodes 200 mV toward negative values in comparison with bulk chromium.

From Fig. 3 we see that for vacuum films the rate of dissolution by the chemical mechanism is one-third of that for compact chromium, and for pyrolytic films, about one-hundredth.

In the region of passivity the rate of dissolution of chromium films is 1-1.5 orders of magnitude less than for the bulk metal. In the transpassivity region, the slope of the polarization curves is the same for all the specimens and equal to about 100 mV, while the curves for "vacuum" and pyrolytic films coincide. In the transpassivity region the dissolution of bulk metal and films apparently follows the same mechanism, but the films dissolve more slowly.

It also seemed of interest to investigate the influence of carbon content of the pyrolytic films on the rate of dissolution of chromium. The marked scatter of the results in the recording of the polarization curves prevents us from drawing any definite conclusion concerning the influence of the amount of carbon on the rate of dissolution of the film; it is apparently due to inhomogeneity of the composition of its surface.

From the above results we can conclude that the change in the electrochemical properties of chromium as we go from bulk metal to thin films is due to the presence of foreign inclusions in the films. In pyrolytic films, carbides play the leading part, whereas in "vacuum" films, this is played by oxides and other products of reaction of chromium with residual gases.

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ACOUSTIC EMISSION DURING HYDROGEN ABSORPTION BY FERROSILICON

V. K. Pleshivtseva, A. K. Chirva, A. M. Berdnikov, and G. I. Khanukov

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Investigation of acoustic emission (AE), i.e., signals due to redistribution of internal stresses, has extended our information on processes occurring in metals interacting with hydrogen.

The process of hydrogen cracking develops at stress concentrators [1-5]; in the period between discontinuous elongations of a crack, the internal stresses in the metal near the tip of the concentrator increase to the value required for the next elongation [6].

The changes in the strength characteristics of structural alloys due to interaction with hydrogen present an urgent problem in the chemical resistance of materials [7-9]. To develop measures to prevent hydrogen embrittlement in metallic structures we need combined researches based on a close organic combination of electrochemical methods with methods of estimating changes in mechanical state (acoustic emission measurements and tensiometry).

In our present work this combination of methods was used to obtain combined information on the hydrogen absorption of ferrosilicon.

Our aim was to obtain more information on the causes of the increase in stress in the zone in question during hydrogen absorption by ferrosilicon and the consequent changes in the physicomechanical properties of the metal. We showed that it is possible to estimate the changes in the physicomechanical service characteristics of ferrosilicon by means of data on acoustic emission during cathodic hydrogen absorption.

The test specimens were rectangular plates measuring 1 × 10 × 50 mm with an acute-angled (60°) notch. In the zone of the tip of the stress concentrator we prepared a polished section in order to elucidate the density of surface dislocations by etching with Morris' electrolyte.

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