INFLUENCE OF CONTINUOUS RENEWAL OF THE SURFACE OF CERTAIN METALS ON THE CATHODIC PROCESS OF EVOLUTION OF HYDROGEN

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The investigation of the electrochemical and corrosion behavior of metals during continuous renewal of their surface under a solution is not only of scientific, but also of considerable practical interest, since cases of a simultaneous abrasive and corrosive influence of the medium on the metal are frequently encountered in industry. However, few studies devoted to this question have been published in the Soviet and foreign literature. They include investigations related chiefly to the study of anodic processes under conditions of continuous cleaning of the metal surface. The studies of Schwabe [1-3] were devoted to the anodic behavior and passivity under conditions of cleaning of the surface of Fe and Ni. In the studies of A. V. Turkovskaya and R. A. Machevskaya [4-6], the anodic and corrosion behavior of steels under conditions of friction were investigated. The influence of continuous cleaning of metals on cathodic processes has practically not been studied. Of course, in the cited works [4-6], the authors proposed that the influence of friction on cathodic processes reduces solely to a change in their intensity on account of the mixing that accompanies friction.

In this work we studied the influence of continuous renewal of the surface on the cathodic process of evolution of hydrogen on certain metals. This method is based upon continuous cleaning of the surface of the investigated metal under a solution with simultaneous cathodic polarization of the electrode from an external current source. The samples were cleaned with a corundum emery wheel on a ceramic base, possessing a grain size of 53-63 μ (granularity number 240). The rate of rotation of the emergy stone was kept constant during these experiments. However, it might vary from experiment to experiment, within the range from 250 to 4500 rpm, which corresponded to a linear displacement of the stone over the surface of the electrode (counted according to the center of the sample) at a rate of from 34.1 to 614 cm/sec, respectively. For standard conditions of cleaning, a translational motion to the surface of the sample to be cleaned, at a constant rate equal to 0.094 μ/sec, was simultaneously communicated to the emery stone, in addition to its rotational motion. A scheme of the apparatus is presented in Fig. 1.

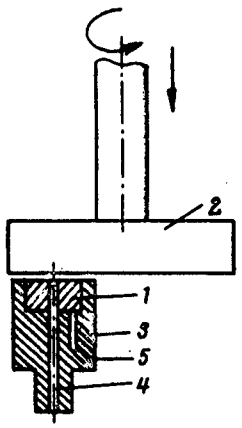

Fig. 1. Schematic depiction of the mutual arrangement of the test sample and emery stone during cleaning: 1) test sample; 2) emery stone; 3) Plexiglas mandrel for sample; 4) capillary for measuring potential of test electrode; 5) contact for external polarization. The arrows indicate the direction of rotation of the emery stone and its translation displacement during the process of continuous cleaning.

The samples, in the form of discs or cylinders 10 mm in diameter, were attached to a Plexiglas mandrel with epoxide resin in such a way that the working surface was only the cleaned end surface of the sample. To measure the potential of the metal under investigation, the capillary from the reference electrode was mounted on the axis of the test sample in such a way that its end emerged directly at the level of the surface to be cleaned. A more detailed discussion of the instrument for the investigation is given in [7].

The experiments were conducted in C. P. grade in H_2SO_4 at a content temperature of 20° in an atmosphere of argon. The maximum oxygen content in the argon was no more than 0.001%.

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TABLE 1

Item	Brand of metal	Chemical composition
Iron	Armco iron	0.03% C, 0.04% Mn, 0.016% Si, 0.029% S, 0.008 P
Nickel	N-1	No less than 99.9% Ni
Tin	Kal'baum brand tin	
Palladium		No less than 99.98% Pd
Lead	CO	No less than 99.99% Pb

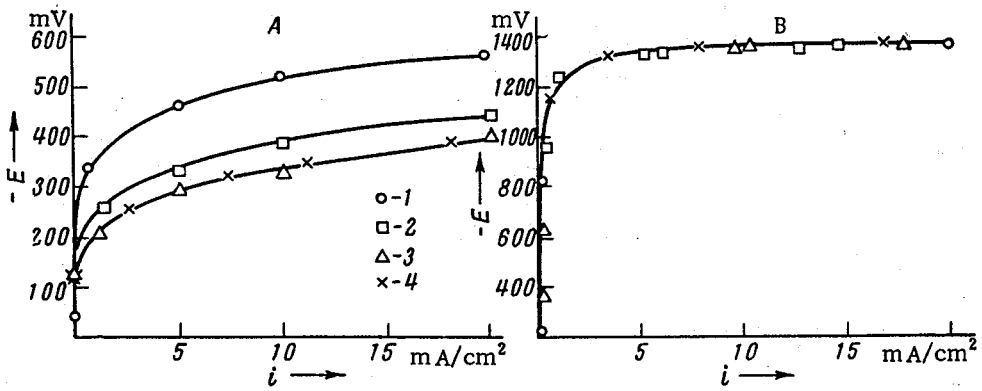

Fig. 2. Cathodic polarization curves obtained on Ni (A) and Pb (B) in 1 N H_2SO_4: 1) without cleaning of the surface. With cleaning of surface at rates of rotation of the emery stone: 500 (2), 1000 (3), 2000 rpm (4).

On all the figures cited, the values of the potentials are given with respect to the normal hydrogen electrode. Fe, Ni, Pb, Sn, and Pd were selected as the test metals. Their basic characteristics and chemical compositions are cited in Table 1.

Figure 2A presents cathodic polarization curves, taken on nickel without cleaning and with continuous cleaning of its surface at various rates of rotation of the emery stone. From this figure, it is evident that the overvoltage of the evolution of hydrogen is substantially lower on a continuously cleaned electrode than on an uncleaned electrode; moreover, with increasing rate of cleaning of the electrode surface, there is a shift of the electrode polarization curves in the positive direction.

It might be assumed that the decrease in the overvoltage during cleaning is due to intensive mixing of the electrolyte near the electrode surface. However, special experiments established that mixing of the electrode, even while rotating the emergy stone in direct proximity to the electrode surface (at a distance of 0.2 mm), has no significant effect upon the hydrogen overvoltage. Therefore, the decrease in the hydrogen overvoltage on the metal surface to be cleaned, noted in Fig. 2, cannot be attributed to the influence of mixing, which constantly accompanies the cleaning.

The cathodic polarization curves obtained under the same conditions on a lead electrode are presented in Fig. 2B. For lead, in contrast to nickel, no significant changes in the shape of the curves during cleaning and without cleaning of the surface are observed within the entire range of investigated current densities.

Comparing the data cited in Figs. 2A and B, we may conclude that continuous cleaning of the surface of Ni and Pb differently influences the value of the overvoltage of the evolution of hydrogen on these metals.

It may be assumed that such a sharp difference in the influence of cleaning is due to a different mechanism of the evolution of hydrogen on Ni and Pb. Nickel, as is well known, is one of the metals that adsorb hydrogen well. The overvoltage of the evolution of hydrogen on metals, in the case of substantial coverage of their surface with hydrogen, is determined to a commensurate degree both by the slow discharging of hydrogen ions, and by the slowness

TABLE 2. Overvoltage of Hydrogen (η) on Various Metals without Cleaning and with Cleaning of Their Surfaces and Quantitative Estimation of the Fraction of the Overvoltage Determined by Slow Discharging and by the Slowness of the Removal of Hydrogen. Data Calculated for a Current Density of 10 mA/cm^2

Metal	η_B without cleaning of surface	η_B with cleaning of surface	Fraction of inhibition of steps of removal of hydrogen, %	Fraction of inhibition of step of slow discharging, %
Pb	1.38	1.38	0	100
Sn	0.86	0.86	0	100
Fe	0.56	0.42	25	75
Ni	0.52	0.32	39	61
Pd	0.48	0.16	66	34

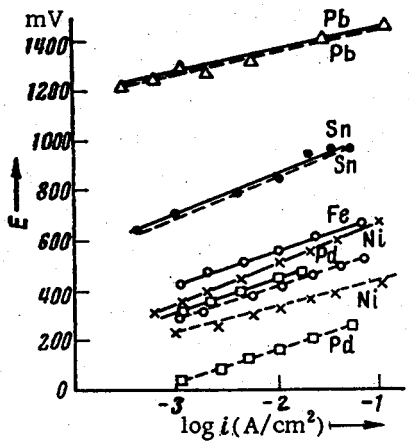

Fig. 3. Cathodic polarization curves obtained on Pb, Sn, Fe, Ni, and Pd in 1 N H_2SO_4 without cleaning of the surface (solid lines) and with cleaning of the surface, at a rate of rotation of the emery stone of 2000 rpm (dotted lines).

of the step of removal of adsorbed hydrogen atoms [8-10]. Unless the overvoltage is determined only by the step of discharging of hydrogen ions [8, 9]. In the case of continuous renewal of the electrode surface, the hydrogen discharge from the metal is immediately removed from its surface by mechanical means (cooling). As a result, the steps associated with the slowness of the removal of hydrogen from the metal surface are partially or entirely eliminated. This will lead to a decrease in the overvoltage of the evolution of hydrogen on metals that adsorb hydrogen well.

On nickel the process of discharging of hydrogen ions with the formation of adsorbed atoms, and their removal from the electrode surface, as is indicated above, proceed at comparable rates; therefore, in the case of continuous cleaning the effect of a decrease in the overvoltage of hydrogen on this metal is substantial.

Unless the overvoltage of hydrogen is determined only by the slowness of the step of discharging of hydrogen ions, continuous renewal of the surface has no significant effect upon the overvoltage of hydrogen on this metal.

To confirm this hypothesis on the influence of continuous cleaning upon the hydrogen overvoltage, we recorded the cathodic polarization curves on iron, palladium, and tin as well, both without cleaning and with cleaning of the electrode surface. From a consideration of the dependences obtained (Fig. 3), it follows that all the investigated metals may be divided into two groups according to their behavior during cleaning: 1) metals that readily adsorb hydrogen — Fe, Ni, Pd. When they are continuously cleaned, a substantial decrease in the overvoltage of hydrogen is observed in comparison with uncleaned electrodes; 2) metals that weakly adsorb hydrogen — Pb, Sn. On these metals, cleaning of their surface has no appreciable influence upon the overvoltage of hydrogen.

Such a distinct division of the investigated metals into two groups according to the change in the hydrogen overvoltage on them during continuous cleaning is a confirmation of our hypothesis that the decrease in the overvoltage during cleaning is associated with a partial or complete elimination of the part of the overvoltage of hydrogen that is determined by the slowness of the step of removal of hydrogen from the surface of the metal.

On the basis of the experimental data obtained we can give an approximate quantitative estimate of the fraction of the overvoltage determined by the step of slow discharging, as well as the fraction associated with the steps of removal of hydrogen.

For metals that adsorb hydrogen well, for example, nickel (Fig. 2A), it is evident that at a rate of rotation of the emery stone higher than 1000 rpm a rather complete removal of adsorbed hydrogen from the electrode surface is observed, since, when the rate of cleaning is further increased to 2000 rpm, there is no displacement of the cathodic polarization curves of the evolution of hydrogen in the positive direction. Consequently, we may arbitrarily assume that the overvoltage of the evolution of hydrogen on metals that adsorb hydrogen well (Fe, Ni, Pd), at a rate

of cleaning above 1000 rpm (curves 3 and 4 in Fig. 2A), is determined entirely by the step of slow discharging, since it can be assumed that mechanical renewal of the surface has no significant influence upon the step of discharging of the hydrated hydrogen ion. This follows from the absence of any appreciable influence of cleaning upon the overvoltage of hydrogen on lead (Fig. 2B and Fig. 3) and tin (Fig. 3). On this basis, the decrease in the overvoltage of hydrogen on nickel (difference between curves 1 and 3 in Fig. 2A), with some approximation, may be attributed to the elimination of the steps associated with the removal of hydrogen from the metal surface. Table 2 presents data calculated in the indicated way: the relative inhibition of the overvoltage of hydrogen by the step of slow discharging and by the step associated with the slowness of removal of hydrogen from the metal surface.

From the data of Table 2, it follows that for lead and tin the overvoltage of hydrogen is entirely determined by the step of slow discharging. For metals that adsorb hydrogen well, the hydrogen overvoltage is determined not only by the step of slow discharging, but also by the slowness of the steps of removal of hydrogen from the metal surface. Thus, for palladium, it has been established that at the indicated current density 10 mA/cm^2, two thirds of the total overvoltage (66%) is determined by the slowness of the steps of removal of hydrogen from its surface, and only $^1/_3$ by the step of slow discharging, which is in good agreement with the data obtained in the work of A. N. Frumkin and N. A. Aladzhalova on the investigation of the mechanism of the overvoltage of hydrogen on palladium in H_2SO_4 [10].

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of the first issue of this year.