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Abstract

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Electrode Potentials of Radioactive Samples of "Armco" Iron and Steel-2 in Distilled Water and Aqueous Solutions of Inhibitors

It was previously established that the corrosion of radioactive samples of "Armco" iron and steel-2 increases significantly in an atmosphere of moist air (⁀1). The study of corrosion in distilled water also showed a certain increase in the corrosion rate of radioactive samples of the same metals. In the present work we give the results of measuring the electrode potentials of radioactive "Armco" iron and steel-2 in distilled water and in aqueous solutions of sodium salts of nitrous and benzoic acids of various concentrations.

In discussing the corrosion behavior of one or another metal and in elucidating the mechanism of the corrosion process, electrode potentials are of great importance, although measurement of the latter is not regarded as a method for determining corrosion resistance (⁀2). The investigated samples of "Armco" iron and steel-2, which did not differ in their composition and dimensions from the samples used earlier (⁀1), were irradiated for 6 days with slow neutrons in a nuclear reactor at a flux of $0.87 \cdot 10^{13}$ neutrons/cm^2 · sec. The induced radioactivity at the time the experiments were carried out was 0.5 mCi/g, or about 5 mCi per sample, and depended on the formation of Fe^{59} ($T_{1/2} = 45.1$ days; β: $E_{\max} = 0.27,\ 0.46$, and 1.56 MeV; γ: $E_{\max} = 0.19,\ 1.10$, and 1.29 MeV). By the end of the investigation the specific radioactivity had decreased to 0.45 mCi/g.

The surface treatment of the samples was carried out according to the accepted procedure (⁀1). The electrode potentials were measured with natural aeration of the solutions in beakers of 125 ml capacity containing 100 ml of liquid. With the aid of a stop, the electrodes were always immersed in the corrosive medium to one and the same depth (3 cm), without protection with petroleum jelly. A calomel half-cell served as the reference electrode; the measurement was performed with an LP-58 potentiometer. The entry of chloride ions from the half-cell into the solution under study was prevented by using an electrolytic bridge separating the corrosive liquid from a saturated KCl solution, into which the half-cell was immersed. Measurements for obtaining the electrode-potential–time curve were carried out over four days at intervals of: 10, 30 sec.; 1 min., 5, 10, 30 min.; 1 hr, 2, 3, 6, 10, 18 hr; 1 day, 2, 3, and 4 days. The number of parallel measurements in inhibitor solutions was 3–5, and in distilled water,

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

because of poor agreement of the results, up to 8-10. The experiments were carried out at a temperature of 25°. All work was performed in a radiochemical hood with manipulators. In the operator' s room there was only the potentiometer, to which the leads from the electrodes were brought. Measurements of the potentials of nonradioactive samples were carried out in a room excluding the effect of radiation.

The results of measuring the electrode potentials of "Armco" iron and steel-2 in distilled water and in 0.1, 0.25, 1, and 10 mM $NaNO_2$ solutions are presented in Figs. 1 and 2 as curves of electrode potential—logarithm of time. Comparison of the E—$\lg t$ curves of radioactive and control samples in distilled water in the absence of a retarder shows that E of the radioactive samples is considerably more negative than the potentials of the control—

samples. In different portions of the curve E—$\lg t$, the difference in the potential values of the radioactive and control samples of "Armco" iron is 50-200 mV, and for steel-2 it is 40-175 mV. A substantial difference is observed in the initial values of E, which, however, become considerably closer with time.

In considering the results obtained, one should proceed from the fact that, given the clearly electrochemical character of corrosion in aqueous media, the acceleration of corrosion processes in radioactive samples of "Armco" iron

Fig. 1. Electrode potentials of "Armco" iron in distilled water and aqueous solutions of sodium nitrite: $1, 2, 3, 4, 5$—for radioactive samples; $1', 2', 3', 4', 5'$—the same, for inactive samples. The curves were obtained: $1, 1'$—in distilled water, $2, 2'$—in 0.1 mM, $3, 3'$—in 0.25 mM, $4, 4'$—in 1 mM, $5, 5'$—in 10 mM $NaNO_2$ solutions. t—in minutes

Fig. 2. Electrode potentials of steel-2 in distilled water and solutions of sodium nitrite: $1, 2, 3, 4, 5$—for radioactive samples; $1', 2', 3', 4', 5'$—the same, for inactive samples. The curves were obtained: $1, 1'$—in distilled water, $2, 2'$—in 0.1 mM, $3, 3'$—in 0.25 mM, $4, 4'$—in 1 mM, $5, 5'$—in 10 mM $NaNO_2$ solutions. t—in minutes

and steel-2 is associated chiefly with the intensifying action of radiation on the reactions of the anodic and cathodic processes. A shift of the E—$\lg t$ curves into the region of negative values usually arises in two cases: when the overvoltage of the anodic reaction decreases, or when the cathodic process is sharply retarded ([3]). In the first case this phenomenon should be accompanied by an increase in the corrosion rate, and in the second by its decrease. Since our investigations showed not a decrease but a noticeable increase in the corrosion rate, the shift of

Figure 3

Figure 3: Figure 3

Figure 4

Figure 4: Figure 4

the electrode potentials of the radioactive samples in the negative direction can readily be associated with a predominant decrease in the specific polarization of the anodic areas.

A substantial shift of the initial E values of radioactive samples in the negative direction also indicates the comparative "looseness"of the structure of the natural oxide film formed on the surface of the radioactive metal in the air atmosphere before the sample was immersed in water. One of the main causes of the change in the properties of the oxide film may be disruptions of the crystal lattice under the action of internal β- and γ-radiation ($^{4-6}$), as a result of which the ionic conductivity of the surface oxide film may increase (^{7}). On the other hand, the emission by the radioactive metal of β-particles and of electrons knocked by them out of atoms leads to the continuous formation, in the bulk of the sample and on its surface, of a multitude of electron holes. This circumstance, undoubtedly, should promote an intensification of ionization of the metal and the transfer of its ions from the surface into the solution. In addition, it is necessary to take into account the ener-

genetic effect of ionizing radiation on processes occurring at the metal-air or metal-liquid interface (8).

It should be noted that, under high diffusion cathodic control in unstirred water, an increase in the corrosion rate of radioactive specimens should occur with some facilitation of the cathodic process, which is probably brought about by the formation of products of radiation-chemical transformations of water, such as OH, HO_2, H_2O_2, which are active cathodic depolarizers. Formation of radiolysis products in a considerable concentration would lead to a sharp decrease in cathodic polarization and, consequently, to a shift of the overall potential in the positive direction. However, the substantial shift of E of radioactive specimens into the negative region of values, which persists over time, indicates a predominant facilitation of the anodic process.

Fig. 3. Electrode potentials of "Armco" iron in distilled water and sodium benzoate solutions. $1, 2, 3, 4$—for radioactive specimens, $1', 2', 3', 4'$—the same for inactive specimens. Curves obtained: $1, 1'$—in distilled water, $2, 2'$—in 1 mM, $3, 3'$—in 5 mM, $4, 4'$—in 10 mM sodium benzoate solutions. t—in minutes.

Fig. 4. Electrode potentials of steel-2 in distilled water and sodium benzoate solutions. $1, 2, 3, 4$—for radioactive specimens, $1', 2', 3', 4'$—the same for inactive specimens. Curves obtained: $1, 1'$—in distilled water, $2, 2'$—in 1 mM, $3, 3'$—in 5

mM, $4, 4'$—in 10 mM sodium benzoate solutions. t—in minutes.

It is of interest to study the electrochemical behavior of radioactive specimens in the presence of certain inhibitors. For this purpose, measurements of potentials were carried out in aqueous solutions of $NaNO_2$ and C_6H_5COONa. Their initial concentration corresponded to the minimum concentration which, according to literature data, provides a protective effect: 0.1 mM for nitrite and 1 mM for benzoate (9). The results of studying the influence of $NaNO_2$ additions on the electrode potential of "Armco" iron and steel-2 are represented by curves 3-10 (Figs. 1 and 2). If E of iron and steel in the absence of a retarder becomes strongly ennobled, then addition to the water of a typical anodic retarder, $NaNO_2$, leads to a sharp ennoblement of the potential. The entire increasing shift of E occurs both as a result of an increase in the inhibitor concentration and with the passage of time. However, it is easy to see that the shift of E of radioactive specimens of iron and steel in the positive direction occurs to a significantly lesser extent than for nonradioactive specimens. It is essential to note that the minimum protective concentration of nitrite for "Armco" iron and steel-2, approximately equal to 0.1 mM, is still insufficient for passivation of the surface of radioactive specimens and, consequently, for stopping the corrosion process. Therefore, at this concentra-

After a certain induction period, E of the radioactive specimens becomes sharply less noble and soon reaches the value of the corrosion potential of radioactive Armco iron and steel-2. A study of the corrosion of specimens with a specific activity of 0.5 mCi/g showed that visible corrosion of specimens completely immersed in distilled water begins already after 1-3 days, and for steel-2 after 3-6 days. Only a nitrite concentration of 0.25 mM is protective for the metals investigated. In this case the radioactive specimens did not undergo corrosion during 30 days of testing; nevertheless, by the end of the first day E of radioactive Armco iron shifts considerably in the negative direction, which indicates that the inhibitor concentration is insufficient for complete passivation of the specimen surface when it is not fully immersed in water. Consequently, a 0.25 mM nitrite solution is not a sufficiently reliable protective concentration for iron specimens with a specific activity of 0.5 mCi/g.

The effect of additions of sodium benzoate to water on the value of E of Armco iron and steel-2 is shown in Figs. 3 and 4. The addition of benzoate, analogously to nitrite, leads to a sharp ennoblement of E for both nonradioactive and radioactive specimens. However, E of the radioactive specimens is ennobled to a considerably smaller degree than that of the control specimens. It should be noted that a benzoate concentration of 1 mM is still insufficient to stop the corrosion process, and 5 mM is insufficient for complete and reliable passivation of the surface of radioactive specimens, although specimens with a specific activity of 0.5 mCi/g, when completely immersed in a 5 mM solution, showed no signs of corrosion for 30 days. It may be assumed that, under the action of continuous radiation, formation of a dense surface film is greatly hindered, while the protective film that does form has substantial microdefects and pores; as a result,

ennoblement of the potential of radioactive specimens occurs to a much smaller degree, and a higher concentration of inhibitors is required to heal weak spots and defects in the film. It should be noted that radioactive iron and steel require a greater increase in the concentration of an organic inhibitor for their passivation than of an inorganic one. At a specific radioactivity of 0.5 mCi/g, the minimum protective concentrations for Armco iron and steel-2 increase in the case of $NaNO_2$ by approximately 2.5–3 times, and in the case of C_6H_5COONa by up to 5–8 times. It is necessary to note that at low inhibitor concentrations a comparatively smaller ennoblement of E is observed for radioactive Armco iron specimens than for steel-2. The latter circumstance is indirect confirmation of previously obtained data on the considerably higher corrosion rate of radioactive Armco iron compared with steel-2 in a humid atmosphere (1).

The results described show beyond doubt the influence of radiation on the corrosion process of self-irradiating specimens in water and in aqueous electrolyte solutions.

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Note: Figure translations are in progress. See original paper for figures.