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STUDYING ANODIC BEHAVIOR AND CORROSION OF BINARY ALLOYS BY THE RADIOMETRIC METHOD

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A method is described to study the partial solution rates of binary alloy components, which is based on the simultaneous and continuous recording of copper and zinc in a corrosion medium by means of the γ isotopes ^{64}Cu and ^{65}Zn. An electrochemical cell and a block drawing of the two-channel selective γ radiometer are given. The use of the method is illustrated in the study of the anodic behavior of a Cu–Zn (6 at.%) alloy. The value of the given method was shown in choosing treatment conditions for the alloy surface before testing and in explaining the mechanism of the beginning stages in the solution of the alloy components during both anodic polarization and corrosion.

The determination of the total losses is inadequate for corrosion characterization of alloys [1]. Selective solution of an electrically negative component of an alloy, e.g., during the dezincing of brass, changes the composition of the alloy surface, and consequently, both its electrochemical and its corrosion properties. To determine the partial rates of solution of each of the alloy components, the highly sensitive radiometric method can be used with a continuous monitoring of the radioactive solution [2]. In contrast to the disk electrode method with a ring [3] and the polarography method [4], and also the chemical [5] and the atomic-absorption analysis [6] methods, which are related by the sampling of the corrosion medium, the radiometric method makes it possible to study starting partial solution rates of the components whose chief value lies in clarifying kinetics and mechanism of anodic solution of alloys. This method with the determination of the partial solution rate of one of the alloy components was used earlier to study the corrosion of the Ti–Pd alloy [7], and also the

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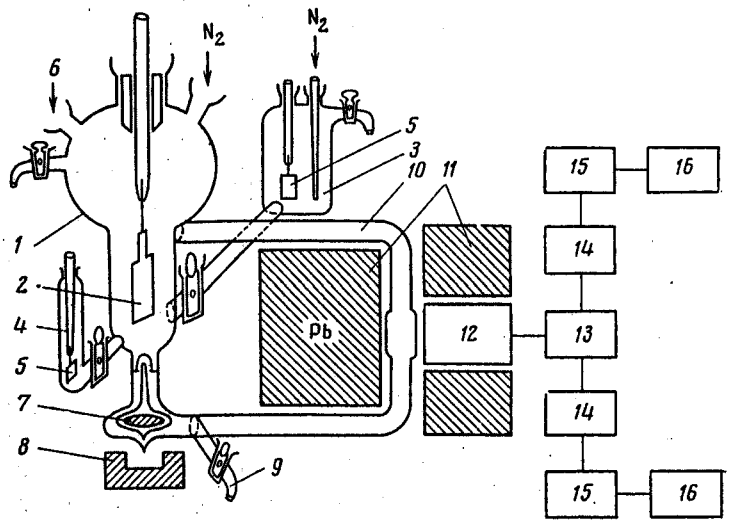

Fig. 1. The electrochemical cell and the block drawing of the apparatus: 1) basic cell; 2) electrode being studied; 3, 4) lateral cells; 5) auxiliary electrode; 6) electrolytic switch to the comparison electrode; 7) centrifugal pump; 8) magnetic stirrer; 9) stopcock for sampling; 10) circulation tube with cuvette; 11) lead shielding; 12) scintillation detector; 13) preamplifier; 14) amplifier; 15) one-channel differential discriminator; 16) counting-rate meter with automatic recorder or a radiation counter with digital printing apparatus.

dezincing of In–Zn [8] and Sn–Zn [9] alloys during polarization when the external current is a measure of the total solution rate of the alloy; and from the partial solution rate of the one of the components the partial solution rate of the other can be calculated. However, in the study of alloy corrosion when the total rate of solution and the time dependence are unknown, it is necessary to measure the partial solution rate of each component, i.e., in the case of a binary alloy the solution of two radioactive isotopes must be simultaneously and continuously monitored. Such a method was used in studying the discharge-ionization of tin on an amalgam electrode [10] and the corrosion of steels [11]. In the corrosion study of α-brass, monitoring of the ^{64}Cu and ^{65}Zn isotopes was done only on separately selected samples of the solution [12].

The method mentioned earlier [13] is described below for the study of partial solution rates of the components of binary alloys (brass in this case); it is based on the simultaneous and continuous monitoring of two γ isotopes (^{64}Cu ^{65}Zn) in the corrosion medium.

The electrochemical measurements were done (Fig. 1) in a basic cell 1 and the solution filling the cell by a pump 7 was continuously driven through the cuvette 10 for radioactivity measurement. For a more uniform polarization of the alloy, two auxiliary Pt electrodes 5 were used, which were separated from the main electrode 2 by stopcocks. A Cu–Zn (6 at.%) alloy, obtained by melting Cu (99.99%) and Zn (99.99%) at 1100° in a quartz ampul (10^{-3} mm Hg), was studied. The samples were rolled to a thickness of 0.5 mm and annealed in vacuum (10^{-4}–10^{-6} mm Hg). The temperature in the cell was 20°; the atmosphere, N_2; and the solution, 1 N NaCl + 0.01 N HCl.

To simultaneously register the two isotopes on apparatus in series, a two-channel selective γ radiometer was built which gives results in analogous and digital forms (Fig. 1). The spectrometric scintillation element BDBSZ with a NaI(Tl) crystal $\phi 40 \times 40$ mm in dimension was the radiation detector which was placed closely to cuvette 10. The lead shielding 11 lowers the background from the radioactive electrode. Each channel of the radiometer contains a one-channel amplitude discriminator PD-2 with an integrating block and a self-recording potentiometer (or a radiation counter PP-15A with a digital printing machine EUM-23). Power is obtained from a stabilized rectifier PV-2-2. For good recording statistics, the quick response of the apparatus can be brought up to 0.1 sec and is limited only by the selection of the recorder and the rate of the solution circulation.

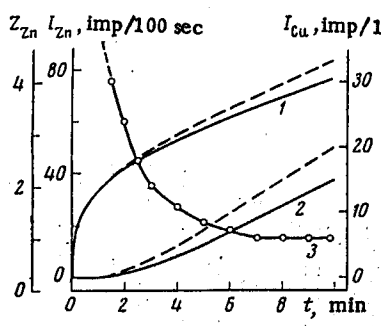

Fig. 2

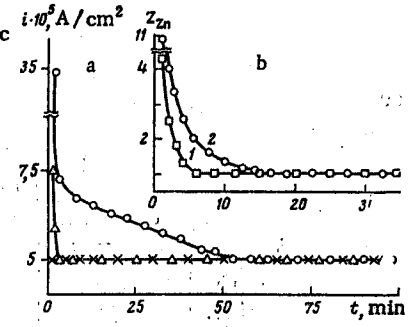

Fig. 3

Fig. 2. Change in radioactivity of the solution with respect to ^{65}Zn (1), with respect to ^{64}Cu (2), and the change in Z_{Zn} (3) as a function of time during anodic polarization ($i = 1 \cdot 10^{-5}$ A/cm^2) of the Cu–Zn (6 at.%) alloy. Broken lines are the original curves and solid lines are corrected curves.

Fig. 3. a) The dependence of the sum of the partial currents of solution of the components of the Cu–Zn (6 at.%) alloy on the time of anodic solution ($i = 5 \cdot 10^{-5}$ A/cm^2) for electrodes with different surface treatments: 1 (circles) and 2 (triangles) are without cleaning; 3 (×'s) is cleaned with emery paper. b) The dependence of the coefficient Z_{Zn} on the time during anodic solution ($i = 1 \cdot 10^{-5}$ A/cm^2) of the Cu–Zn (6 at.%) alloy for electrodes cleaned differently after anodic polarization: 1) cleaned with glass powder; 2) cleaned with emery paper.

The components of the alloy were tagged with the γ isotopes, ^{64}Cu [$E_\gamma = 1.34$ MeV (0.5%) and $E\gamma = 0.51$ MeV (38%) with $T_{1/2} = 12.8$ h] and ^{65}Zn [$E_\gamma = 1.11$ MeV (44%) and weak annihilation radiation ($E_\gamma = 0.51$ MeV) with $T_{1/2} = 245$ days] by radiation in a nuclear reactor in a flux of thermal neutrons of $2.4 \cdot 10^{13}$ neutrons/cm$^2 \cdot$ sec. The irradiation time (66-200 h) and the cooling time (5-7 days) were chosen so that an adequate specific activity for ^{65}Zn would be obtained and the ratio of the ^{64}Cu: ^{65}Zn radioactivities (10:1) would be suitable for monitoring.

As it follows from the stated properties of the ^{64}Cu and ^{65}Zn isotopes, their instrumental spectra mutually intersect:

$$N_1 = I_1 + K_2 I_2$$
$$N_2 = I_2 + K_1 I_1 \qquad (1)$$

where N_1 and N_2 are the impulse counts in the first and second channels; I_1 and I_2 are the impulse counts from the first isotope in the first channel and the second isotope in the second channel; and K_1 and K_2 are, respectively, the relative contribution of the first isotope to the impulse count by the second channel, and of the second isotope to the impulse count by the first channel. K_1 and K_2 are found by recording each isotope separately, and the channels were selected so that K_1 and K_2 would be minimum and less than unity at a maximum recording efficiency of the first isotope in the first channel and of the second isotope in the second channel. According to the given criteria, ^{64}Cu was calculated in the first channel according to the 0.51-MeV line at a 30% channel width (relative to the maximum of the photopeak); and ^{65}Zn, in the second channel according to the 1.11 MeV line at a 40% channel width. I_1 and I_2 are found according to the following equation obtained from (1):

$$I_1 = \frac{N_1 - K_2 N_2}{1 - K_1 K_2}; \quad I_2 = \frac{N_2 - K_1 N_1}{1 - K_1 K_2}. \qquad (2)$$

The curves (I, t) obtained during the simultaneous recording of the ^{64}Cu and ^{65}Zn isotopes during anodic solution of the Cu–Zn alloy are given in Fig. 2. In the beginning (1-2 min) the slope of the (I_{Zn}, t) curve, which is proportional to the partial solution rate of the zinc, is fairly high and the slope of the (I_{Cu}, t) curve is zero, which indicates no transfer of copper to the solution. Later on, the slope of the (I_{Zn}, t) curve decreases and the slope of the (I_{Cu}, t) increases until a constant slope is established for both curves. The partial solubility currents for the zinc (i_{Zn}) and copper (i_{Cu}) were calculated from these curves:

$$i_i = nF\partial C_i/\partial t = nFK_i\partial I_i/\partial t, \qquad (3)$$

where K_i is the coefficient of proportionality between the concentration (C_i) of the i-th component in solution and its radioactivity I_i, which was determined by measuring the radioactivity of known weights of pure components which had been irradiated under the same conditions as the alloy. The derivative $\partial I_i/\partial t$ in (3) on the portions of the (I_i, t) curves with the high slope was determined from the tangents to the given point and on portions with a low slope from the ratio $\Delta_i/\Delta t$:

$$i_i = nFK_i\Delta I_i/\Delta t. \tag{3'}$$

The following equation written in differential form was used to calculate the coefficient of selective solution of the zinc, Z_{Zn}:

$$Z_{Zn} = \frac{[(\partial C_{Zn}/\partial t):(\partial C_{Cu}/\partial t)]_{soln}}{(C_{Zn}':C_{Cu}')_{sp}}, \tag{4}$$

which with the calculation in (3) takes the following form:

$$Z_{Zn} = \frac{i_{Zn}n_{Cu}C_{Cu}'}{i_{Cu}n_{Zn}C_{Zn}'} = \frac{[(\partial I_{Zn}/\partial t):(\partial I_{Cu}/\partial t)]_{soln}}{(I_{Zn}':I_{Cu}')_{sp}}, \tag{5}$$

where $I_{Zn'}$ and $I_{Cu'}$ are the radioactivity (impulse/sec) of the ^{65}Zn and ^{64}Cu isotopes in a weighed portion of the original alloy, and $C_{Zn'}$ and $C_{Cu'}$ are the concentrations (at.%) of the Zn and Cu in the alloy. For a low slope of the (I_i, t) curves the calculation of Z_{Zn} was done according to the following expression:

$$Z_{Zn} = \frac{(\Delta I_{Zn}:\Delta I_{Cu})_{soln}}{(I_{Zn}':I_{Cu}')_{sp}}. \tag{5'}$$

From the data given in Fig. 2 it follows that during the first 7 min $Z_{Zn} > 1$, and subsequently $Z_{Zn} = 1$ (Fig. 2, curve 3), i.e., the dissolving becomes uniform. As is evident, the method of continuously monitoring simultaneously the two radioactive isotopes in solution permits the mechanism of the beginning stages of the solution of the alloy components to be studied. It must be emphasized that this method makes it possible to compute Z_{Zn} directly from the relationship of the growth of radioactivity in the solution and the radioactivity in the original solution [see Eqs. (5) and (5')].

Continuously monitoring simultaneously the two radioactive isotopes permits also the solution of the questions related to the preliminary surface treatment of the samples. As it was formerly noted [9] oxidation of the Zn occurs even during short holds of a Sn–Zn alloy in air, which results in zinc oxide at the surface and a zinc-depleted zone. Analogous effects can be observed also for other alloys, in particular, in brasses. The presence of a depleted zone, of course, has an effect on the nature of the subsequent solution of the alloy components [9]. Moreover, the presence of oxides on the alloy surface must result in the distortion of results of a selective corrosion study by an analysis of the corrosion medium because ultimately ions of the metal will be not only due to the electrochemical oxidation of the alloy components but also due to the chemical solution of the oxides. As a result, the partial currents i_i will be increased which can lead to erroneous conclusions concerning the kinetics of the beginning stages in the solution of the components, and consequently, concerning the mechanism of alloy solution as a whole. Therefore, in preparing the sample before testing it is necessary to completely remove from the surface both the oxides of the alloy components and also the surface layer which differs in composition from the original composition. With a suitable surface preparation the sum of the partial currents of solution of the components, e.g., for the Cu–Zn alloy, will equal the external current

$$i_{Cu} + i_{Zn} = i. \tag{6}$$

With the presence of oxides at the alloy surface, this sum will exceed the external current

$$i_{Cu} + i_{Zn} > i. \tag{7}$$

To illustrate the distortion effect of the oxides on the calculation of the beginning rates of solution of the alloy, let us consider the anodic behavior of brass with a varying oxide content on the surface obtained by annealing samples for 2 and 100 h in an evacuated ampul ($p = 10^{-3}$ mm Hg). From Fig. 3a it is evident that after a 100-h anneal of a sample (curve 1) the value for ($i_{Cu} + i_{Zn}$) is greater than the external current for 50 min. Consequently, in the surface layer to a depth of 200 monolayers there were oxides of the brass components which were chemically dissolved. With a 2-h anneal of the sample (curve 2) values of ($i_{Cu} + i_{Zn}$) above i were observed only for the first 3 min, i.e., both the oxide contents in the near-surface layers of the alloy and the depth of their penetration were much less. For the sample with the 2-h anneal and with a surface cleaned with emery paper (curve 3) Eq. (6) is maintained from the very beginning of the experiment.

Cleaning the alloy surface with emery paper does not always result in the complete removal of the oxides, especially in hard-to-reach places. Therefore, the following method was used to prepare the surfaces: the degreased sample was given an anodic etch at $i = 1 \cdot 10^{-3}$ A/cm^2 ($t = 5$ min); then the electrode was rinsed in doubly distilled water, was drained on filter paper, and cleaned with a fine glass powder to remove the zinc-depleted zone, which, as is noted in [9], could arise during anodic etching. With such a surface treatment Eq. (6) was fulfilled for $i = 5 \cdot 10^{-5}$ A/cm^2 for all values of t. A similar surface treatment can be used for corrosion studies. However, for this it is necessary to be preliminarily convinced of the absence of oxides on the alloy surface by verifying that Eq. (6) is maintained during anodic polarization by a comparatively low current.

The surface treatment effect on the behavior of the (Z_{Zn}, t) curves during anodic solution of the Cu–Zn (6 at.%) alloy is illustrated in Fig. 3b. Curve 1 refers to the sample which was prepared according to the method which included removal of the surface layer due to anodic polarization ($i = 1 \cdot 10^{-3}$ A/cm^2, $t = 5$ min) followed by the cleaning of the surface by glass powder. Curve 2 was obtained on a sample which was cleaned after the same anodic polarization not by powder, but with emery paper. Despite the fact that condition (6) was maintained for both samples, the time for establishing $Z_{Zn} = 1$ for curve 2 was ≈ 3 times greater than for curve 1. Evidently, this is related to the effect of different surface treatment on the diffusion coefficient of the Zn atoms in the thin surface layer of the alloy. Consequently, to obtain reproducible results it is necessary to maintain strictly identical conditions in the surface preparation of the alloy before testing.

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