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LAWS OF DEZINCING OF α-BRASSES DURING CORROSION IN CHLORIDE SOLUTIONS

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The mechanism of corrosion of α-brasses in chloride solutions is elucidated by the radiometric method with continuous registration of the radioactivity of the isotopes ^{65}Zn and ^{64}Cu. It is shown that at first there is selective solution of zinc accompanied by its nonstationary diffusion in the solid phase; uniform solution of the alloy then follows. When a certain copper concentration is reached in the solution, uniform solution changes to pseudoselective solution due to redeposition of copper from solution. The acceleration of corrosion of brass with time is due to the accumulation of Cu^+ ions in solution; they are oxidized by oxygen to Cu^{2+} ions, which are more effective depolarizers than oxygen.

Dezincing of α-brass during corrosion usually leads to primary uniform solution of copper and zinc followed by deposition of copper on the surface in the form of a finely crystalline layer [1,2]. This solution has been called pseudoselective [3]. However, it has been shown [4] that in the initial period of corrosion of α-brass there is preferential oxidation of zinc, and that solution then becomes uniform. As copper accumulates in the solution, conditions may be created for its reverse deposition as a separate phase. It is of interest to follow the changes in the character of solution of brasses during corrosion and to elucidate the conditions for transition from one dezincing mechanism to another.

The investigations were made by a radiometric method with continuous registration of the radioactivity of the gamma isotopes ^{65}Zn and ^{64}Cu [5] for brasses with the α structure containing 6 or 30 at. % Zn at 20°C in aerated solutions of 1 N NaCl + 0.01 N HCl. The electrode area was 5-6 cm^2; the volume of solution in the cell was 110 cm^3. The preparation of the alloys and their surface treatment by the method described in [5] avoided distortion of the test results on account of surface oxides.

Let us consider the corrosion behavior of brasses, taking as an example the alloy Cu — Zn (30 at. %). The radiometrically determined graphs of the partial solution currents i_{Cu} of copper and i_{Zn} of zinc, the total corrosion rate, and the coefficient of selective solution of zinc Z_{Zn} vs the corrosion time (Fig. 1) are very complicated. In the first period of corrosion (Fig. 1b), i_{Zn} decreases; after 4-5 min it passes through a minimum and then continuously rises. Copper begins to go into solution only 1-1.5 min after the start of corrosion; it continues to do so at a constantly increasing rate. Correspondingly, in the initial period Z_{Zn} is greater than unity, indicating selective solution (SS) of zinc. After about 5 min Z_{Zn} falls to unity and retains this value for 70-80 min, corresponding to uniform solution of both components of the alloy; then it again gradually rises (Fig. 1a). Over the first 2 min the total corrosion rate of the brass decreases appreciably; then it continues to rise throughout the experiment.

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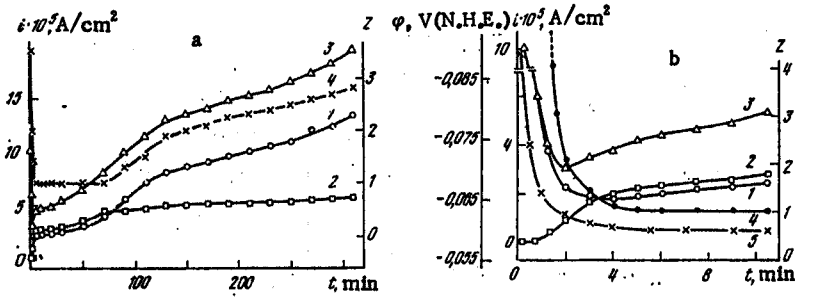

Fig. 1. Time dependence of partial solution currents of Zn (1) and Cu (2), their sum (3), the coefficient Z_{Zn} (4), and the potential φ (5) during corrosion of Cu — Zn alloy (30 at. %). a) Over 5 h; b) in initial period.

As we see from Fig. 1b, in the initial period the selective corrosion of brass is due to the fact that zinc dissolves faster than copper. As shown in [4], the solution of zinc is controlled by its nonstationary diffusion to the alloy — solution boundary, as shown by the linear dependence of the radioactivity I of the solution for zinc on $\sqrt{t}$ (where t is the time). As in the case of anodic polarization [4], at the moment of immersion of the specimen in the solution, its potential φ shifts towards the negative (not shown in Fig. 1). This type of potential change is due to the fact that in the initial period the rate of ionization of zinc is higher than the total rate of reduction of oxygen and hydrogen at the corrosion potential. As a result, some of the negative charges remaining on the electrode after ionization of zinc are expended on charging the double layer, and this is accompanied by a shift of potential toward the negative. With the passage of time, as i_{Zn} decreases these rates attain the reverse ratio and φ begins to shift toward the positive. This effect is a sign of selective solution of the negative component of the alloy. Note that if the preferential passage of zinc into solution were due to chemical solution of ZnO, this would not give the above potential changes.

Thus, the results in [4] and the present article for the initial period of corrosion — viz., the fact that $Z_{Zn} > 1$, the fall in i_{Zn} with time, the variation of φ with time, and the presence of a linear segment on the (I, $\sqrt{t}$) curve — indicate the SS of zinc from brass by a mechanism of nonstationary bulk diffusion. As also for anodic polarization of brass [4], the initial SS is replaced by uniform solution. However, later we again get SS, as shown by the gradual rise in Z_{Zn} beginning after about 1 h.

We can suppose that this rise in Z_{Zn} is due to reverse deposition of copper on the surface of the specimen, beginning after the attainment of some concentration of copper in the solution.

Calculations based on the radiometric data show that the rise in Z_{Zn} (Fig. 2, curve 1) is observed when the copper ion concentration in the solution is $1 \cdot 10^{-4}$ M. If during a long experiment we replace the solution by a new portion, not containing copper ions (arrow A on curve 3), every 45-50 min, so that the copper concentration never reaches this value, Z_{Zn} remains equal to unity throughout the experiment, i.e., there is no secondary SS. But if after establishment of uniform solution ($Z_{Zn} = 1$) we replace the solution by a new portion with a copper ion concentration above $1 \cdot 10^{-4}$ M (arrow B on curve 2), a sharp rise of Z_{Zn} begins at once. Consequently, secondary SS is undoubtedly associated with the attainment in solution of a certain concentration of copper ions, and is apparently due to reverse deposition of copper from solution onto the corroding specimen.

In general, copper can also get out of the solution onto the surface of the specimen as a result of deposition of CuCl. To test this hypothesis, after prolonged corrosion of brass, accompanied by a marked rise in Z_{Zn}, we determined the composition of the surface layer of the alloy by the method in [6] — by radiometric measurements with a high anode current density. For this purpose, after Z_{Zn} had increased, the aerated solution was replaced by deaerated solution not containing copper ions, and at time C (curve 3, Fig. 2) we imposed an anode current $i = 5 \cdot 10^{-4}$ A/cm² at which uniform solution of brass is usually observed [4]. The results of this experiment are plotted in Fig. 3. The sum of the partial rates of solution of the components of the alloy, calculated from the radiometric data, is constant and equal to the total current strength, i.e., $i_{Zn} + i_{Cu} = i$ (curve 3). If a CuCl deposit were present on the surface of the alloy it ought to dissolve after replacement of the solution without expenditure of electricity, creating excess copper in the solution, so that we would observe the condition $i_{Zn} + i_{Cu} > i$. We must also note that in our electrolyte the potential of formation of CuCl (0.14 V [7]) is not usually attained.

The conclusion that the rise in Z_{Zn} is due to reverse deposition of copper is also supported by analysis

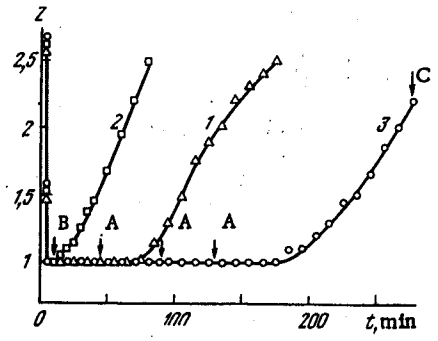

Fig. 2

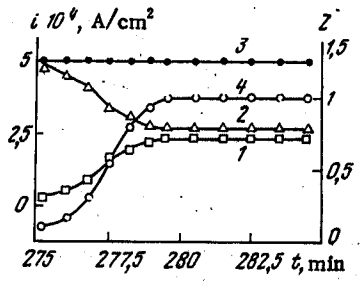

Fig. 3

Fig. 2. Time dependence of Z_{Zn} for corrosion of Cu — Zn (30 at. %) alloy. 1) Continuous accumulation of copper in solution; 2) replacement of solution at point B by solution containing $1.5 \cdot 10^{-4}$ M $CuCl_2$; 3) replacement of electrolyte by new portion at points A.

Fig. 3. Time dependence of partial currents of solution of Zn (1), Cu (2), their sum (3), and Z_{Zn} (4) after imposition at time C (see Fig. 2) of anodic polarization ($i = 5 \cdot 10^{-4}$ A/cm^2).

of the time dependencies of i_{Zn}, i_{Cu}, and Z_{Zn} during anodic polarization (Fig. 3). In fact, if $i_{Zn} + i_{Cu} = i$ (curve 3), the inequality $Z_{Zn} < 1$ shows that the surface of the alloy is enriched with copper. Several minutes after imposition of anodic polarization, the copper-rich layer is removed from the surface, Z_{Zn} rises to unity, and subsequently the brass dissolves uniformly. The excess of copper in this layer, calculated from the quantity of electricity passed until $Z_{Zn} = 1$, is about 300 monolayers. Such a thick copper-rich layer could not be formed as a result of SS of zinc in the initial stage of corrosion, occurring by a mechanism of bulk diffusion. In fact, if we carry out a similar experiment in which the solution is changed and anodic polarization imposed 30-40 min after the start of corrosion, i.e., in conditions with $Z_{Zn} = 1$ (Fig. 1a), no deviation of Z_{Zn} from unity is observed. The effective thickness of the zinc-depleted layer formed up to this moment, calculated by the method described previously [4], is only seven atomic layers.

Thus, the experimental data show that the corrosion of α-brass in the given conditions is accompanied by reverse deposition of copper as an independent phase. Similar results were obtained in the corrosion of brass containing 6 at. % Zn.

The start of the deposition of copper from solution onto the surface of the corroding brass depends on many factors which affect the overvoltage of formation of the first nuclei of the copper phase [3]. We note that in unstirred solutions of 0.1 N HCl the reduction of copper is observed on brasses containing over 25% Zn [2], whereas in 0.5 N NaCl it occurs on even zinc-richer brasses (40%) [3]. The use of radiometric methods showed that even α-brass with 6 at. % zinc after an initial period of SS of zinc followed by uniform corrosion undergoes pseudoselective corrosion. Consequently, the determination of so-called boundaries of onset of dezincing of brasses [2] is very arbitrary.

The distinctive feature of the corrosion behavior of brasses is an increase in corrosion rate with time. As we see from Fig. 1a (curve 3), the total corrosion rate increases by a factor of about six in 5 h. In the initial period of corrosion, the true rate of solution of the alloy found radiometrically agrees with the rate found by extrapolation of the Tafel part of the polarization curve of reduction of oxygen at zero-current potential. Later the true corrosion rate exceeds that found from electrochemical measurements. In similar conditions the rate of corrosion of pure copper increases more then tenfold in 4 h. Previous results [8, 9] also indicate an increase in the corrosion rate of pure copper in chloride solutions. This acceleration effect may be due to delayed reduction of oxygen on brasses, as on pure copper, and the formation in the corrosion process of Cu^+ ions which are capable of being rapidly oxidized to Cu^{2+} ions, which in turn act as a depolarizer [10-13].

Let us consider the influence of an increase in corrosion rate with time on the laws of SS up to the start of reverse deposition of copper. In particular, acceleration of the corrosion process, equivalent to a gradual increase in the anode current density, will influence the effective thickness of the zinc-depleted zone, δ_{eff}. As shown by a calculation based on the method in [4], this quantity increases for the first 5-6 min, then decreases in the next 60-70 min. The rise in δ_{eff} is a consequence of the fact that in the initial period of corrosion the solution of zinc from brass is represented by the laws of nonstationary diffusion, as also in anodic

polarization at low current densities [4]. However, when the velocity of the alloy — solution boundary is comparable with the rate of movement of the diffusion front into the alloy, which occurs when $Z_{Zn} = 1$, δ_{eff} should gradually decrease as the total corrosion rate increases. In the time interval from 4-5 to 60-70 min the corrosion rate increases by a factor of about 2.5 and δ_{eff} decreases from $5 \cdot 10^{-7}$ to $2 \cdot 10^{-7}$ cm. Such a decrease in δ_{eff} with increase in the corrosion rate of the alloy agrees with the laws of bulk diffusion [14,15], according to which with uniform solution of the alloy δ_{eff} should be inversely proportional to the rate of solution.

The kinetics of the initial stages of solution of copper and zinc with corrosion of a Cu — Zn (30%) alloy were also studied by Hari [16] by a radiometric method with simultaneous use of ^{64}Cu and ^{65}Zn markers. The experimental method consisted in immersing tagged brass for a certain time in a corrosive medium and then determining the quantity of these isotopes in the solution. It was found that the duration of SS is 5-10 sec, after which the alloy dissolves uniformly. The author suggested that SS is controlled by bulk diffusion, and that a zinc-depleted surface layer is formed as a result of SS. According to [16] (Figs. 1-3), δ_{eff} increases with the corrosion rate, in conflict with the theory [14,15]. Such a discrepancy may be due to defects of the method, in particular, to the fact that each point on the time dependence of the amount of zinc going into solution was in fact determined in a separate experiment. In addition, the distortion of the results [16] may be due to isotope exchange between surface radioactive particles of copper and stable copper ions in solution or to solution of surface oxides, the possible presence of which was not taken into account.

The results show the fruitfulness of the use of the radiometric method with simultaneous automatic registration in solution of both components of the binary alloy in order to study its corrosion. In fact, in the case of α-brass this method permits us, in one continuous experiment, to study the laws of SS over a wide range of times, starting with the earliest stages of solution, and to establish a very complex mechanism of corrosion, including a transition from SS controlled by the bulk diffusion of zinc in the alloy, to SS associated with reverse deposition of copper from solution. The marked difference between the behavior of α-brass in anodic polarization and in long-term corrosion shows that it is necessary to make a special study of the behavior of alloys in corrosion conditions, not only in anodic solution.

In conclusion we must note that the results are also of practical interest. If corrosion of brass occurs in conditions of continuous renewal of the electrolyte (flow), when the copper concentration near the electrode is kept low and constant, brass should dissolve uniformly, and its rate should not increase in time. On the other hand, corrosion becomes particularly dangerous when in various parts of a structure (slits, gaps), owing to poor electrolyte circulation, conditions are created which favor pseudoselective solution of brass.

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