DEZINCIFICATION OF α-BRASSES THROUGH ANODIC POLARIZATION IN CHLORIDE SOLUTIONS

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A radiometric method with simultaneous and continuous recording of the radiations from ^{65}Zn and ^{64}Cu γ isotopes was used to determine selective dissolution of zinc from α-brasses in chloride solutions at low anodic current, during cathodic polarization, and during corrosion with oxygen depolarization. The process is limited by a transient stage in the diffusion of zinc from the bulk alloy to the alloy/solution interface.

One of the most dangerous types of brass corrosion is the selective dissolution (SD) of zinc. Considerable data exist on the corrosion and anodic dissolution of α-brasses [1-10]. Some works have shown [3, 5-8] that brass dissolves uniformly whereas others indicate SD of zinc [1, 8, 10].

A theoretical analysis [3] and experimental results for In–Zn and Sn–Zn alloys [11, 12] have demonstrated that one of the possible mechanisms for dissolution of an electronegative component from an alloy is its transient diffusion from the bulk alloy to the alloy/solution interface, the rate of which is proportional to $1/\sqrt{t}$, where t is the time. During anodic dissolution or corrosion this process is supplemented by continuous removal of surface layers so that within a certain time after dissolution begins SD alternates with uniform dissolution, wherein the duration of an SD period decreases the higher the total dissolution rate and the lower the diffusion coefficient of the negative component of the alloy [10, 11, 13]. Theoretical analysis shows that even a hard-to-detect, short-term, initial SD of the negative component should deplete the near-surface zone, which will remain in this state during succeeding uniform dissolution [4, 10, 13, 14]. Existence of such a depleted zone was detected during anodic dissolution of Cu–Zn, Au–Cu, In–Zn, and Sn–Zn alloys [3, 10-12, 14]. Since it is this surface layer that determines an alloy's electrochemical, corrosion, and certain other properties [15], information on its thickness, composition, and structure is of considerable interest. An ionization kinetics study of alloy components during the initial period of dissolution is therefore of great importance in developing an all-embracing explanation of alloy dissolution patterns. Time-dependent partial dissolution rates of α-brass components have either not been examined [1, 2, 5, 7] or do not provide reliable information on the kinetics of the initial dissolution stage due to insufficient sensitivity of methods designed to determine average values after long time periods [4, 6, 8]. In studying the corrosion of α-brass, a highly sensitive radiometric method was used to detect the SD of zinc even in the first 5-10 sec [9]. It is evidently difficult to establish alloy dissolution patterns for such a short period of time. It is thus apparent that the SD kinetics of zinc from α-brass has not been sufficiently investigated.

The objective of this work is to study the kinetics and mechanism of anodic dissolution of α-brass components in chloride solutions under active dissolution conditions. Dissolved Cu and Zn were analyzed radiometrically with automatic, simultaneous recording of the radioactivity of both components. This provided evidence on the kinetics of alloy component dissolution approximately 20-30 sec after dissolution begins [16].

The studies were conducted at 20°C using α-brass samples containing 6 and 30 at.% Zn in 1 N NaCl + 0.01 N HCl in a N_2 atmosphere (during anodic and cathodic polarization) and in air (during corrosion). Cu and Zn in the alloy were tagged with the radioactive isotopes ^{64}Cu and ^{65}Zn. Conditions for irradiating the brass samples in a nuclear reactor, radiometric measurement methods, procedures for calculation of partial dissolution rates of Zn (i_{Zn}) and Cu (i_{Cu}), the selective dissolution coefficient of Zn (Z_{Zn}), and methods for sample preparation and surface treatment have been described earlier [16]. Cathodic and anodic polarizations were conducted potentiostatically and galvanostatically, respectively.

*Yu. A. Stekol'nikov and E. I. Shchenyaev, final-year students, participated in the experimental work.

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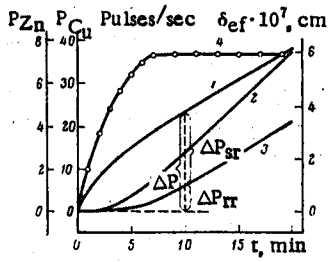

Fig. 1

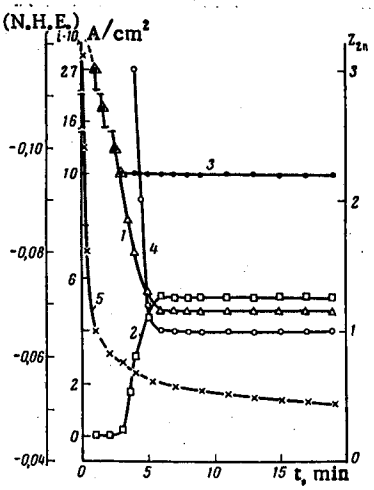

Fig. 2

Fig. 1. Effect of time on dissolution of Cu–Zn (30%) at $i = 1 \cdot 10^{-5}$ A/cm^2: radioactivity of the solution with respect to ^{65}Zn for experimental (1) and calculated (3) curves, with respect to ^{64}Cu (2); and versus thickness of the zinc-depleted zone δ_{ef} (4).

Fig. 2. Dissolution parameters of Cu–Zn (30%) at $i = 1 \cdot 10^{-5}$ A/cm^2; relation of time to dissolution currents of Zn (1), Cu (2), their sum (3), the coefficient Z_{Zn} (4), and potential φ (5).

A theoretical analysis of SD kinetics was simplified through a study of anodic dissolution in the galvanostatic mode, since the removal rate V of the alloy surface layers then remains constant [13].* In addition, the alloy dissolves under practically the same conditions as when undergoing electrochemical corrosion, particularly if the anodic current density without depolarizer coincides with the rate of cathodic depolarizer reduction at zero current potential; then the external anodic current is a direct measure of the corrosion rate and SD behavior should be the same whether through anodic polarization or corrosion.

Let us examine the anodic dissolution pattern of Cu–Zn (30%) alloy under various conditions. Figure 1, which is a plot of radioactivity vs time for a solution containing ^{64}Cu (P_{Cu}) and ^{65}Zn (P_{Zn}) during anodic dissolution, shows that the slope of the P_{Zn} vs time curve decreases in the first six minutes and then becomes constant. Judging from the P_{Cu} vs t curve there is practically no increase in the radioactive Cu content of the solution during the first tens of seconds, which indicates lack of Cu ionization; a gradual rise in slope then occurs. Values for i_{Zn}, i_{Cu}, and Z_{Zn} at various t's were calculated from the P vs t slopes and shown on the respective curves presented in Fig. 2. It is evident from Fig. 2 that in the first 6 min i_{Zn} decreases and i_{Cu} increases; then both remain constant. In the initial dissolution stage at $t \geq 3$ min, the total current ($i_{Cu} + i_{Zn}$) remains constant and equal to the external current density i. This indicates the absence of partial currents due to oxide dissolution [16]. In the first 6 min, Z_{Zn} is substantially greater than one but then decreases to one. Higher values of Z_{Zn} are observed at other i's (Fig. 3) wherein uniform dissolution ($Z_{Zn} = 1$) is achieved earlier as i increases; at $i = 5 \cdot 10^{-5}$ A/cm^2 Z_{Zn} is virtually one. Experimental detection of zinc dissolution from α-brasses must therefore be achieved through measurement of fractional ionization rates at the initial dissolution stage rather than at higher values of i, at which the determination is much more difficult.

Figure 3 shows that the Z_{Zn} vs t curve for the initial period of brass corrosion with oxygen depolarization is quite close to the curve for $i = 1 \cdot 10^{-5}$ A/cm^2 taken in a deaerated solution. It may be presumed that the SD process is identical in both cases.†

*Strictly speaking, V is constant if the external current is much greater than the partial dissolution current of the negative component; such is the case when alloys are low in this component and when both components have the same valence as, e.g., Sn–Zn alloy [12].

†Results of a study on the corrosion of α-brass [9] are difficult to correlate with our data since the corrosion rate was unknown and the tests were carried out in other solutions. The short SD period for zinc noted in this work (5-10 sec) was probably due to a high alloy dissolution rate.

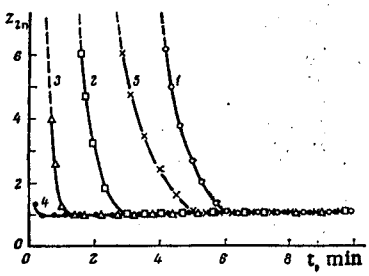

Fig. 3

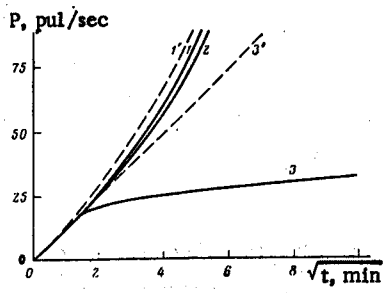

Fig. 4

Fig. 3. Change in Z_{Zn} with time upon dissolution of Cu–Zn (30%) at the following values of i (A/cm^2): 1) $1 \cdot 10^{-5}$; 2) $2 \cdot 10^{-5}$; 3) $3 \cdot 10^{-5}$; 4) $5 \cdot 10^{-5}$; 5) during corrosion.

Fig. 4. Relation of time to radioactivity of ^{65}Zn isotope dissolved from Cu–Zn (30%): 1) during anodic dissolution ($i = 1 \cdot 10^{-5}$ A/cm^2; 2) during corrosion; 3) during cathodic polarization ($\varphi = -0.35$ V). The dashed curves are derived from calculations for: 1') anodic and 3') cathodic polarizations.

The SD of zinc agrees well with the manner in which the potential φ of brass changes with time (Fig. 2, curve 5).

Immediately after anodic polarization begins the ionization rate of zinc is high and the potential of the alloy is probably close to the potential of zinc. If a depolarizer such as hydrogen ions is present, it will be reduced at the electrode at a rate of i_{dp}. As a result, there should be a delay in the initial part of the φ–t curve (not shown in Fig. 2) at which $i_{Zn} \sim i + i_{dp}$. Furthermore, a situation arises where $i_{Zn} < i + i_{dp}$ because of the gradual decrease of i_{Zn} with time. Part of the external current is then expended on shifting φ toward the positive direction (Fig. 2, curve 5) and at t > 1.5 min Cu begins to ionize rapidly (Fig. 2, curve 2).* This relation of φ to t is apparently inexplicable with uniform dissolution and is one indication that the negative component of the alloy dissolves through SD. When pure Cu polarizes anodically under the same conditions its potential (~–0.03 V) is virtually constant with time.

Thus, SD is observed during the initial period of Cu–Zn (30%) dissolution, subsequently changing to uniform dissolution.

What mechanism governs the SD of zinc? It was noted above that the criterion for a mechanism of transient diffusion of a negative component from the bulk alloy to the alloy/solution interface is a linear relation between the partial dissolution rate of the component and $1/\sqrt{t}$ or between its concentration in the solution and $\sqrt{t}$ [11]. The data in Fig. 1 for Zn (curve 1) is transcribed to Fig. 4 in coordinates of P_{Zn} vs $\sqrt{t}$ (curve 1). This relation was linear during the first ~3 min, showing that the SD of zinc took place through a mechanism of transient diffusion. Nonlinearity at t > 3 is probably because the advance rate of the diffusion front becomes comparable with the rate of surface alloy layer removal [11, 12].

It was of interest to study the dissolution of Zn upon cathodic polarization at the point where radiometric data showed that Cu did not dissolve (Fig. 4, curve 3).† Initially, the slope of curve 3 coincided with that of curve 1 (anodic polarization) and then decreased. Both curves also coincided initially with curve 2 (corrosion), i.e., passage of Zn into solution during the initial SD stages independent of φ. The data indicate that the initial dissolution of Zn under the above conditions is controlled by its transient diffusion from the bulk alloy to the alloy/solution interface.

The markedly higher value of i_{Zn} over i observed during the initial period of dissolution (Fig. 2, curve 1) is unrelated to the presence of Zn oxide on the alloy surface. Indeed, the fact that the initial linear sections of the P_{Zn} vs $\sqrt{t}$ curves have the same slope at anodic dissolution, corrosion, and cathodic dissolution is evidence

*Figure 2 shows that a slight positive shift in φ occurs also at t > 6 min, i.e., after dissolution becomes uniform (curve 4). This effect, which is also observed in the case of a copper electrode, is probably due to accumulation of Cu ions in solution.

†In the cathodic polarization we chose a φ more positive than the equilibrium potential of Zn.

TABLE 1. Relation of D in α-Brasses to Polarization Conditions

Cu content in the alloy		Experimental conditions	φ,* V (N.H.E.)	i, A/cm^2	$D \cdot 10^6$, cm^2/sec	$\delta_{ef} \cdot 10^7$, cm
At.%	g/cm^3					
30	2,7	Anodic polarization	−0,105 −0,100 −0,090	$1 \cdot 10^{-5}$ $2 \cdot 10^{-5}$ $3 \cdot 10^{-5}$	8,4±0,6 9,5±0,5 8,7±0,6	5,9±1,0 3,3±0,2 2,4±0,2
		Cathodic polarization	−0,350		8,2±0,6	
		Corrosion	−0,050		8,4±0,6	
6	0,545	Anodic polarization	0,05 −0,045 0,035	$5 \cdot 10^{-6}$ $1 \cdot 10^{-5}$ $3 \cdot 10^{-5}$	3,6±0,2 3,2±0,4 3,0±0,5	7,7±0,1 3,6±0,2 1,8±0,2
		Cathodic polarization	−0,350		3,2±0,6	
		Corrosion	−0,030		3,0±0,6	
0,5	0,045	Cathodic polarization	−0,350		1,2±0,1	

*For corrosion, the values of φ were obtained 30 min after dissolution began.

of Zn dissolution through a mechanism of transient diffusion and not through chemical dissolution of Zn oxide. It should also be noted that the above higher value occurred at the same time as that observed during the initial dissolution stage where φ varied with time; this cannot be explained through dissolution of the oxide. Table 1 lists values for Zn diffusion coefficients (D) calculated from the equation $P = k2C_0\sqrt{Dt/\pi}$ (k is the coefficient for conversion of Zn concentration in the brass C_0 (g/cm^3) to radioactivity) taken from the initial slopes of P_{Zn} vs $\sqrt{t}$ curves [11, 12].

The values of D were used to plot calculated curves of P_{Zn} vs $\sqrt{t}$ through transient diffusion mechanism for SD of a negative alloy component involving removal of alloy surface layers [12, 13].* It is evident from Fig. 4 that the experimental and calculated anodic polarization curves show satisfactory agreement.†

The above relations thus provide a satisfactory description of the experimental curves not only at the beginning but upon transition from SD to uniform dissolution. The deviation of curves 1 and 1' at t > 3 min as well as a considerable decrease in the slope of the experimental cathodic polarization curve with time are evidence of a reduction of D as the diffusion front penetrates the bulk metal. It should also be noted that the SD of zinc upon cathodic polarization produces some movement of the alloy/solution boundary the rate of which V decreases with time; this was not taken into account in plotting curve 3'. A change in V with time also occurs to a certain extent upon anodic dissolution of brass (at $Z_{Zn} > 1$) even under galvanostatic conditions at a given i. Thus, at the very beginning of anodic polarization, when no Cu is dissolving (Fig. 2, curve 2), V probably decreases as a result of a gradual reduction of i_{Zn}; furthermore, when both Zn and Cu are dissolving, some change in V can occur due to the different valences of the ions passing into solution ($n_{Zn} = 2$, $n_{Cu} = 1$) and it is only at $Z_{Zn} \sim 1$ that V can be considered as constant. It is evident that the use of a model is not sufficiently accurate to interpret experimental data for alloys with high negative components. Equation 2 from [12], applied in [13], was based on the assumption that the alloy/solution boundary changes at a constant rate at a given i. At low values of t, however, it reduces to the usual transient diffusion equation (Eq. (4) from ([12]), according to which the rate of boundary movement has no effect on the dissolution rate of the negative component. In accordance

*In calculating the cathodic polarization curve it was assumed that the alloy/solution boundary remained stationary.

†We made no comparison of the experimental values of Z_{Zn} and those calculated from Eq. (3) of [12], as was done for the alloy Sn−Zn (0.1%). This was because the theoretical expression (3) derived in [13] agrees with the accepted estimation of Z [11, 15] only for alloys with a low content of negative component, where we can neglect changes in dissolution rate of the positive component with time and assume it to be equal to the external current.

with this conclusion, initial sections of P_{Zn} vs $\sqrt{t}$ curves coincide for both anodic and cathodic polarization, even with alloys having high Zn contents (Fig. 4), and are governed by the transient diffusion equation.

The selective dissolution of zinc in the initial period of dissolution should produce a zinc-depleted zone on the alloy surface with an effective thickness δ_{ef} [3, 12] of

$$\delta_{ef} = \frac{\Delta m}{C_0}. \quad (1)$$

Let us assume that the total amount of zinc in solution is a result of conjoint dissolution with Cu in proportion to alloy content, and SD. It is then simple to distinguish radiometrically the excess Zn (Δm, g/cm^2) that passed into solution through SD of the zinc-depleted zone. To this end, we calculated the P_{Zn} vs t relation (Fig. 1, curve 3) that governs uniform alloy dissolution, i.e., $Z_{Zn} = 1$ [11], through use of the experimental P_{Cu} vs t curve (Fig. 1, curve 2):

$$P_{Zn} = \frac{A_{Zn} P_{0Zn} m_{0Cu} P_{Cu}}{A_{Cu} P_{0Cu} m_{0Zn}} \cdot \frac{C_{Zn}^{al}}{C_{Cu}^{al}} = k P_{Cu}, \quad (2)$$

where A_{Zn} and A_{Cu} are the atomic masses of Zn and Cu; P_0Zn and P_0Cu are the radioactivities (pulses/sec) of the standard Zn and Cu solutions containing m_0Zn (g) and m_0Cu (g), respectively; and C_{Zn}^{al} and C_{Cu}^{al} are the concentrations of the Zn and Cu in the alloy (at. %).

Through the use of curves 1 and 3 (Fig. 1) we can subtract the radioactivity for uniform dissolution (ΔP_{ud}) from the total radioactivity for a particular time period (ΔP) and easily determined the excess radioactivity that passes into solution as a result of SD (ΔP_{er}): $\Delta P_{er} = \Delta P - \Delta P_{ud}$ and hence to calculate δ_{ef} from (1) as a function of time. Let us bear in mind that $C_0 = N_0^{Zn} A_{Zn}/v_M^{al}$ (where v_M^{al} is the molar volume of the alloy in cm^3 and N_0^{Zn} is the mole fraction of zinc in the alloy) and that $\Delta m = m_0 Zn v \Delta P_{er}/S v_0 P_{0Zn}$ (where S is the electrode area in cm^2 and v_0 and v are the volumes in cm^3 of the standard solution and the solution in the cell, respectively). Then (1) takes the form:

$$\delta_P = \frac{\Delta m}{C_0} = \frac{v_M^{al} m_{0Zn} v \Delta P_{er}}{S A_{Zn} N_0^{Zn} v_0 P_{0Zn}} = k_1 \Delta P_{er} \quad (3)$$

It is evident from Fig. 1 that δ_{ef} first increases and then becomes constant upon reaching steady state ($Z_{Zn} = 1$). Table 1 lists the constant values of δ_{ef}. It is plain that δ_{ef} decreases with an increase in i, which agrees with theoretical analyses [13] and experimental data obtained for In–Zn and Sn–Zn alloys with low percentages of negative component [11, 12]. At $i = 5 \cdot 10^{-5}$ A/cm^2 the value calculated for δ_{ef} from the equations given in [12, 13] does not exceed $1.5 \cdot 10^{-7}$ cm (5 monolayers). This shows that a very small excess of dissolved Zn is difficult to detect with the high background created by the rather rapid onset of uniform alloy dissolution; hence, δ_{ef} is so small that it cannot be computed from the radiometric data.

Results of depleted zone studies and δ_{ef} calculations agree well with the data of Holliday and Pickering on copper enrichment of the surface layer of Cu–Zn (30%) alloy upon anodic polarization, obtained through x-ray spectroscopy using soft radiation [10]. They showed that anodic polarization produced a copper-enriched surface zone the thickness of which increased during the initial growth period and then became constant ($\sim 10^{-6}$ cm). On the basis of these data, the authors arrived at the important conclusion that the formation of such a zone is a necessary condition for transition from SD to the succeeding steady-state, uniform dissolution.

Relations analogous to those cited above were obtained in studies of anodic behavior of brasses with lower Zn contents (6.0 and 0.5%).

It is evident from Table 1 that δ_{ef} and D decrease with a reduction of C_0. In addition, reduction of C_0 substantially modifies the nature of the P_{Zn} vs $\sqrt{t}$ relation during cathodic polarization – the lower the C_0 the later the relation departs from linearity towards lower values of P_{Zn}, probably caused by a reduction of D as the diffusion front moves into the bulk alloy. Thus, although this deviation is observed for Cu–Zn (30%) alloy 3 min after the start of cathodic polarization (Fig. 4, curve 3), for Cu–Zn (0.5%) alloy linearity indicative of limiting, nonsteady-state diffusion (with an immobile alloy/solution interface) is maintained for 100 min.

All these characteristics are probably due to a greater number of vacancies formed during SD in the surface layer of an alloy with 30% Zn than in alloys with lower C_0. A reduction of D with time can be explained by its dependence on vacancy concentration [3]. Indeed, more vacancies are formed in the surface layer initially, due to the high SD rate of zinc, than are dictated by the volume of the alloy. With time, however, the excess diminishes as a result of vacancy diffusion into the bulk alloy and diffusion of surface Cu atoms both along the surface and into the bulk alloy. This also reduces D with time and probably shifts the alloy/solution

boundary to some extent. The i_{Zn} decreases with a reduction of C_0 and consequently lessens the excess of vacancies in the surface layer. As a result, the change of D with time for alloys with very low percentages of negative component is either insignificant, as is observed for Cu–Zn (0.5%), or does not occur at all as in the case of Sn–Zn (0.1%) [12].

We will finally mention results obtained through long-term ionization of Zn from Cu–Zn (30%) during cathodic polarization, when Cu does not dissolve. Analysis of the P_{Zn} vs $\sqrt{t}$ curve (Fig. 4, curve 3) shows that i_{Zn} decreases rapidly with time down to very low values* (e.g., at $\varphi = -0.35$ V, $i_{Zn} = 3 \cdot 10^{-8}$ A/cm^2 after 3.5 h) and steady-state current is not achieved, as was observed earlier for brasses [4] and Au–Cu alloys [14, 17].

All the results of the study on dissolution of α-brasses, including those with high Z_{Zn} values, as well as the manner in which φ changes during the initial period of anodic dissolution and corrosion are convincing evidence of the SD of zinc under these conditions with subsequent transition to uniform alloy dissolution. Experimental data for the initial SD period could be quantitatively interpreted by an equation for nonsteady-state diffusion of Zn from the bulk alloy to its surface. Coincidence of the slopes for the initial linear sections of the P_{Zn} vs $\sqrt{t}$ curves (and values of D calculated therefrom) during anodic polarization, corrosion, and cathodic polarization confirm the conclusion on bulk diffusion as a limiting stage in the ionization of Zn. Use of the model takes into account not only transient diffusion of the negative component but also the effect of continuous removal of surface layers during anodic polarization. We could thus define the mechanism for SD and subsequent transition to uniform dissolution as well as explain the effect of current density on SD kinetics and thickness of the depleted zone.

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*The high sensitivity and selectivity of radiometric measurements in combination with continuous automatic recording of radioactivity of the solution makes this method highly suitable and reliable for plotting i_{Zn} vs t curves at very low values of i_{Zn}.