DEZINCING OF TIN AND ALUMINUM α-BRASSES DURING ANODIC POLARIZATION IN CHLORIDE SOLUTIONS

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During anodic dissolution (AD) of nonalloyed α-brasses, in the initial period (3-6 min) there is selective dissolution (SD) of Zn, which is limited by its nonstationary diffusion in the bulk of the alloy [1-4]. Later SD is replaced by stationary uniform dissolution (UD) of the alloy; dissolution of Zn from the brasses and also of the alloy as a whole is determined by the kinetics of dissolution of the copper component [3-6]. In some conditions, immediately after UD, for example, in prolonged corrosion of α-brass in a closed volume of electrolyte, together with dissolution of Zn and Cu from the alloy, we also observe deposition of Cu from the solution. This type of corrosion is known as pseudoselective dissolution (PSD) [7, 8].

Alloyed α-brasses are widely used in practice [9]. The dezincing of such brasses is less marked than that of nonalloyed ones [10, 11], but to judge by the character of the overall polarization curves, alloying with tin [12] or aluminum [13] does not influence the limiting stage of their AD in steady conditions. However, these brasses have not been sufficiently studied: It is not clear which stage — primary SD or PSD — involves the influence of the alloying additives. It is therefore of interest to study the AD of alloyed brasses and, in particular, the influence of alloying on the primary SD of Zn, since the laws of SD in AD and corrosion may be the same [1, 2].

This article describes an investigation of the kinetic laws of dissolution of the components of tin- and aluminum-alloyed α-brasses in the initial stages of their AD and also in the steady state.

We have studied the α-brasses Cu29.3Zn0.7Sn and Cu28Zn2Al (concentrations are given in atomic percent). The alloys were prepared by the method in [4]. The alloying additives were added to the brass in pure form.*

Our investigations were made by combining electrochemical and radiometric measurements with simultaneous continuous registration of the γ-isotopes Zn^{65} and Cu^{64} in the solution [14]. In the case of tin brass we used a radiometric complex with a minicomputer [15] and a semiconductor (Ce/Li) detector [16] which enabled us to make continuous simultaneous registration of the isotopes Zn^{65}, Cu^{64}, and Sn^{117m} in the solution. From the slopes of the radioactivity—time curves we calculated the partial currents of the corresponding components [14].

Since aluminum cannot be determined radiometrically on account of the short half-life of its isotope, quantitative analysis for Al was made by the atomic absorption method in samples taken from the cell at definite time intervals during AD of nonirradiated aluminum brass. The experiments were performed at room temperature in a cell with separate electrode spaces in a solution of 1N NaCl + 0.01N HCl, deaerated with purified N_2. The (φ, log i) polarization curves were recorded by the galvanostatic method. The potentials are given relative to an N.H.E.

*In practice, use is often made of alloys containing 1 or 2 at.% of Sn, which, as our investigations show, are inhomogeneous. Therefore, we used an alloy with a lower Sn content, which is homogeneous. Alloying was effected with tin enriched with the stable isotope Sn^{116} (96%), because during irradiation in a reactor a specimen of ordinary Sn accumulates the foreign radioisotopes Sb^{125}, Te^{125}, and In^{113}, which may create difficulties in γ-spectrometric analysis.

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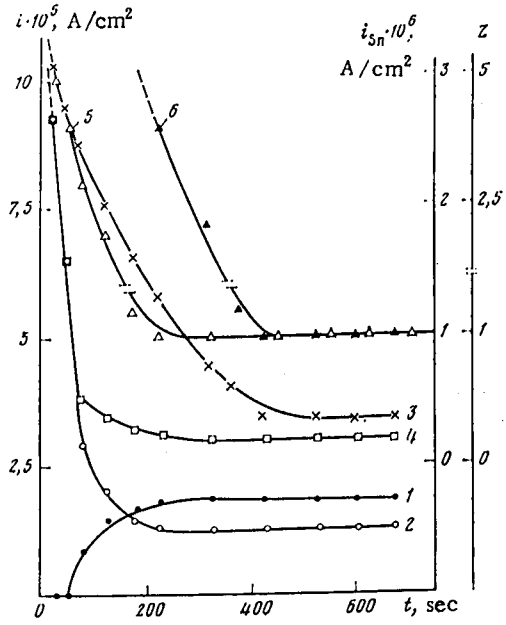

Fig. 1. The dependences of partial dissolution currents of copper (1), zinc (2), and tin (3), and their sum (4), and of the coefficients Z_{Zn} (5) and Z_{Sn} (6) during anodic dissolution (AD) of the alloy Cu-29.3Zn0.7Sn at $i = 3 \cdot 10^{-5}$ A/cm².

Let us consider the anodic behavior of tin brass in the initial period at $i = 3 \cdot 10^{-5}$ A/cm² (Fig. 1). We see that in the first 200 sec i_{Zn} decreases with time and $i_{Cu} = 0$ for 50 sec and then gradually rises. At $t > 200$ sec both quantities become constant. For the first 400 sec i_{Sn} decreases with time, then becomes constant. Starting at $t > 200$ sec, $i_{Cu} + i_{Zn} + i_{Sn} = i$, where i is the external current density.* For the first 200 sec, $Z_{Zn} \gg 1$, and then decreases to $Z_{Zn} = 1$; at $t \leq 400$ sec, Z_{Sn} is greater than unity, and then becomes established at $Z_{Sn} = 1$.† Increased values of Z_{Zn} and Z_{Sn} were also observed at other values of i; as also for unalloyed α-brass [1-3], the transition to UD ($Z_{Zn} = 1$; $Z_{Sn} = 1$) is the earlier, the higher i; when $i \geqslant 5 \cdot 10^{-5}$ A/cm² there is practically no deviation of Z_{Zn} and Z_{Sn} from unity.

Similar (i_{Cu}, t), (i_{Zn}, t), and (Z_{Zn}, t) curves are observed with $t < 3$ min for nonalloyed α-brass [1-3].

As also for nonalloyed α-brass [1, 2, 17], when anodic polarization is imposed on tin brass in galvanostatic conditions, in the initial period there is a sharp shift in φ toward the negative, to a value close to the region of the equilibrium potential of pure Zn [the (φ, t) curve is not given in Fig. 1]. As shown in [17], a similar change in φ is caused by SD of Zn.

Thus, in the initial period of AD, tin brass dissolves selectively on account of preferential ionization not only of zinc but also of tin, and after more prolonged AD (up to 3 h) tin brass, like nonalloyed brass [1-4], dissolves uniformly, i.e., $Z_{Zn} = 1$ and $Z_{Sn} = 1$.

Our investigations of aluminum brass revealed that in the initial period of AD there is also SD of Zn and Al. In time, UD is attained; for example, at $i = 3 \cdot 10^{-5}$ A/cm², $Z_{Zn} = 1$ is established in 3-7 min, and $Z_{Al} = 1$ in 10-15 min.

With the aim of elucidating the influence of alloying on the mechanism of SD of Zn, the experimental (N_{Zn}, t) curves (where N_{Zn} in the Zn radioactivity of the solution) were plotted

*At $t < 200$ sec, $i_{Cu} + i_{Zn} + i_{Sn} > i$. This is due to the initial SD of Zn, which occurs at a higher rate than i owing to reduction of the depolarizer (H^+ ions) [1-3].
†Z_{Sn} and Z_{Al} were calculated by means of the same expression as that used for Z_{Zn} [3, 5], i.e., in relation to Cu.

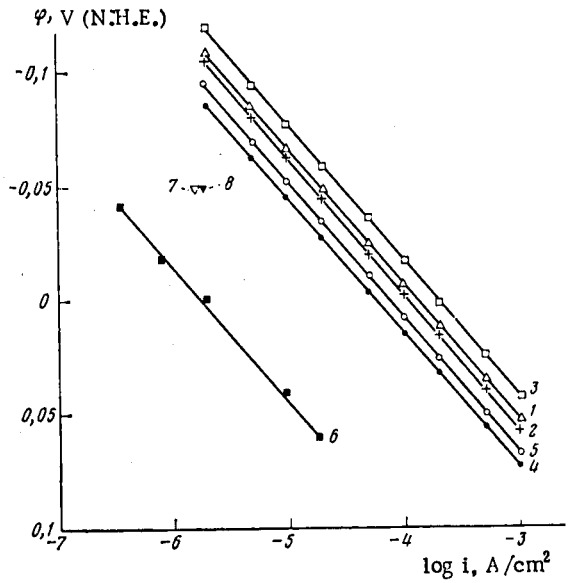

Fig. 2. Stationary partial anodic polarization curves of dissolution of copper: 1) from nonalloyed, 2) tin, and 3) aluminum α-brasses; 4) polarization curve of pure copper; partial polarization curves of dissolution of 5) zinc and 6) tin from alloy Cu29. 3-Zn0.7Sn; partial solution current of Al from alloy Cu28Zn2Al at $i = 3 \cdot 10^{-5}$ A/cm², obtained 7) experimentally and 8) by calculation.

as graphs of N_{Zn} vs $\sqrt{t}$. It was found that these curves have a linear section, for example, at $i = 1 \cdot 10^{-5}$ A/cm² from 20 sec to 400-600 sec. This is evidence that SD of Zn is occurring by a mechanism of bulk diffusion, as also in the case of nonalloyed α-brass [1-3]. From the slope of this section we calculated the mean diffusion coefficients of zinc, $\bar{D}_{Zn}$, which are equal to $2.2 \cdot 10^{-15}$ cm²/sec and $1.9 \cdot 10^{-15}$ cm²/sec for tin and aluminum α-brasses, respectively, and are close to the value of $\bar{D}_{Zn}$ for nonalloyed α-brass [1-3].

Thus, in the AD of alloyed brasses, Sn and Al do not influence the laws of primary SD of zinc; their behavior is typical of an electronegative component, as shown by their SD.

Let us consider the behavior of alloy brasses in stationary conditions. In conformity with [3-5], analyzing the overall anodic polarization curves and the partial polarization curves of solution of the alloy components, we can establish the limiting stage of dissolution both for the individual components and for the alloy as a whole. For alloyed brasses it was found that the Tafel slope of the overall polarization curves is 0.06 V, just as for pure Cu. The partial polarization curves of solution of the components of the alloyed brasses are shown in Fig. 2. We see that the slopes of the partial anodic polarization curves of dissolution of Cu from alloyed brasses (60 mV, curves 2 and 3) coincide with the slope for pure Cu (curve 4) and for dissolution of Cu from nonalloyed α-brass (curve 1). The slopes of the partial curves of dissolution of Zn from tin (curve 5) and aluminum brasses (not shown in Fig. 2) and of dissolution of Sn (curve 6) are also equal to 0.06 V. For Al the experimental value of i_{Al} (point 7) coincides with the theoretical value (point 8) at $i = 3 \cdot 10^{-5}$ A/cm².* These results are definite evidence that the kinetics of dissolution of Zn, Sn, and Al, and also of alloyed brasses, like those of nonalloyed brasses [3, 5], are determined by the behavior of the copper component; the rate of dissolution of the electronegative components is limited by diffusion of their atoms through the copper-enriched surface layer. The observed

*The theoretical value of i_{Al} (point 8) was obtained starting from the condition that $Z_{Al} = 1$ for given i; the experimental value of i_{Al} (point 7) was obtained on the basis of Faraday's law from the quantity of Al going into solution in a given period of time.

shift of the (φ, log i_{Cu}) curves toward more negative φ for alloyed brasses in comparison with the curve for pure Cu is evidently due to an increase in the thermodynamic activity of the surface Cu atoms, as also in the case of nonalloyed brass [5, 18].

Thus the laws of AD of alloyed brasses, both in nonstationary conditions and in UD, are practically indistinguishable from the behavior of nonalloyed brass: In the initial period there is SD of the electronegative components; then UD of the alloy sets in. Consequently, simultaneous occurrence of SD of Zn and Sn, Zn and Al does not distort the laws of primary SD of Zn or its mechanism.

In conclusion, we may note that the results obtained with AD do not shed light on the cause of the reduction in dezincing of the alloyed brasses in comparison with nonalloyed brasses during corrosion. We did not succeed in modeling the behavior of alloyed brasses in the conditions of their corrosion with oxygen depolarization by making polarization measurements, apparently owing to some sort of specific effects (for example, PSD), which appear only when depolarizer is present in the solution in the absence of external polarization. Consequently, to elucidate the mechanism of the influence of alloying additives on the dezincing of brass, it is necessary to investigate the partial processes of solution of all the components of the alloyed brasses in corrosion conditions.

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