OXYGEN FORMATIONS ON THE SURFACE OF LEAD, INDIUM, AND THEIR ALLOYS

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Series of cathodic charging curves, recorded after ten-second polarizations at various specified potentials, are used in order to identify various oxygen containing compounds developing on the surface of lead, indium, and Pb-In alloys during anodic polarization in dilute alkali. The mechanism underlying the formation of such compounds and their role in passivation processes are discussed, due allowance being made for the composition of the alloy and the easy diffusion of its components in the metallic phase.

The corrosion and electrochemical properties of comparatively refractory solid solution (Cu-Ni, Sb-Bi) [1, 2] vary sharply over narrow ranges of composition (1-2 at.%). A measurement of the work function before and after the brief action of a corrosive medium confirms [3] that this variation is associated with a change in the surface composition of the alloys in the electrolyte.

A study of the Bi-Sb system [2] shows that the individual oxides of the components only exist on the oxidized surface of the alloys for specific ranges of composition; this state of affairs is only possible if the internal diffusion of the alloy components is impeded, i.e., if the "resorption" of surface changes in composition is severely retarded.

In order to verify this proposition, we studied a series of In-Pb alloys; these yield an almost continuous series of solid solutions [4] and are characterized by high coefficients of internal diffusion of the components. The smooth change observed in the rate of corrosion of these alloys in 20% H_2SO_4 on passing from In to Pb* supports the foregoing comments as to the negative influence exerted by diffusion processes in the alloy on the possible formation of a protective corrosion structure.

Oxide formations on Pb, In, and Pb-In alloys were studied by a potentiogalvanostatic method in an oxygen-free 0.01 N solution of KOH (pH 11.86). The rate of spontaneous lead dissolution under these conditions was no greater than $3.6 \cdot 10^{-6}$ g-atom/$m^2 \cdot h$ ($7.6 \cdot 10^{-4}$ g/$m^2 \cdot h$), while indium was absolutely stable and no loss of weight could be detected.

Electrodes (cylindrical samples with a working end surface area of 0.05 cm^2) were prepared from indium of the In-00 type and S-1 lead using the method described in [5]. Reproducible results were obtained if the working surface was first brought to a specular luster by flattening on a plate of polished chromium.

The specified potential (φ_{an}) of between -1.50 and -0.34 V (relative to the normal hydrogen equivalent) was usually held for 10 sec by means of a potentiostat, after which the cathodic charging curve was immediately recorded at a current density of $1.4 \cdot 10^{-3}$ A/cm^2.

The number and duration of the arrests formed on the charging curve gave a fair idea of the number of compounds formed and the amount of each of these present; the minimum anodic potential after the holding

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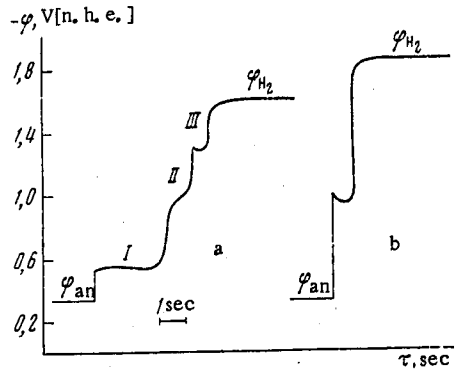

Fig. 1. Charging curves of lead (a) and indium (b) in 0.01 KOH. φ_{an} = anodic polarization potential; φ_{H_2} = potential of hydrogen evolution.

period for which any particular arrest became noticeable on the cathodic curve (i.e., the potential corresponding to the initial formation of the arrest φ_{in}) gave an idea of the thermodynamic potential of formation of the corresponding compound.

Lead. After a holding period at $\varphi_{an} = -0.415$ the cathodic charging curve of lead (Fig. 1a) showed three arrests of potentials of $\varphi_I = -0.544$ V; $\varphi_{II} = -0.962$ V and $\varphi_{III} = -1.326$ V. Using the method described earlier [6] it was found that the potential for the initial formation of the third compound φ_{in}^{III} equalled -0.424 ±0.005 V, in close agreement with the equilibrium potential of formation of $Pb(OH)_2$ (calculated on the basis of thermodynamic data [7] for pH 11.86) in the reaction

$$Pb + 2H_2O \rightleftharpoons Pb(OH)_2 + 2H^+ + 2e. \quad (1)$$

The thickness of the layer* of $Pb(OH)_2$ at $\varphi_{an} = -0.34$ V extends to 8 Å in 10 sec (the density of $Pb(OH)_2$ equals 7.59 g/cm^3 [8]).

The experimentally determined potential φ_{in}^{II} for the arrest II equals -0.452 ± 0.005 V, agreeing with the calculated value of φ_{eq} for the reaction

$$Pb + H_2O \rightleftharpoons PbO + 2H^+ + 2e. \quad (2)$$

The thickness of the PbO layer for $\varphi_{an} = -0.34$ V reaches 4 Å in 10 sec (the density of PbO is 9.53 g/cm^3 [8]). The small amount of lead oxide PbO on the surface is probably associated with a certain dissolution of this in alkalis [9]. There is accordingly no II arrest on the charging curve of lead recorded in stronger alkalis (0.1 N KOH).

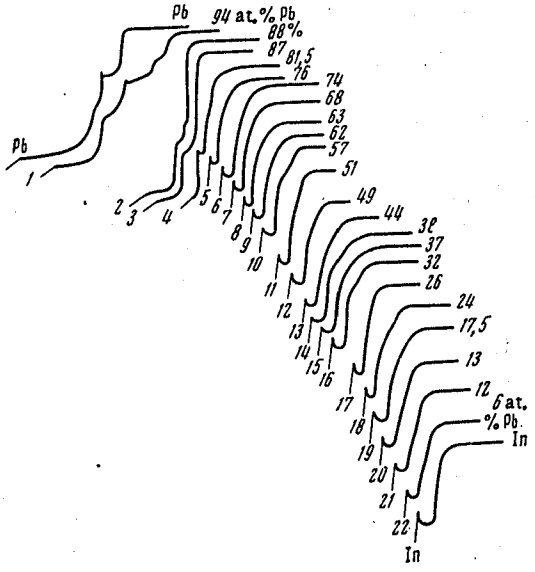

Fig. 2. Oscillograms of Pb, In, and their alloys ($\varphi_{an} = -0.34$ V).

The close agreement between the equilibrium potentials for the formation of PbO and $Pb(OH)_2$ (and also bismuth [5], antimony [6], and copper [10] oxides) calculated from thermodynamic data and the φ_{in} of the arrests on the cathodic charging curves suggests that the properties of the compact oxides and the thin oxide layers observed on the metal surface are very similar. In this case, we may without serious error consider that φ_{in} is equal to the φ_{eq} of the oxide formation process.

Arrest I has $\varphi_{in}^{I} = -0.502 \pm 0.005$ V.

Judging by existing data [7], at such negative potentials lead should not form any oxygen-containing compounds. The first arrest is practically horizontal, i.e., it should correspond to a phase of constant composition. The corresponding amount of electricity ($4.4 \cdot 10^{-3}$ C/cm^2) is sufficient to reduce 120/f monolayers of oxygen (f being the roughness factor). This is three times as great as the total charge of

* Here and subsequently the calculation is based on the earlier [6] assumption that the roughness factor is equal to three, while the oxides are distributed uniformly over the whole surface.

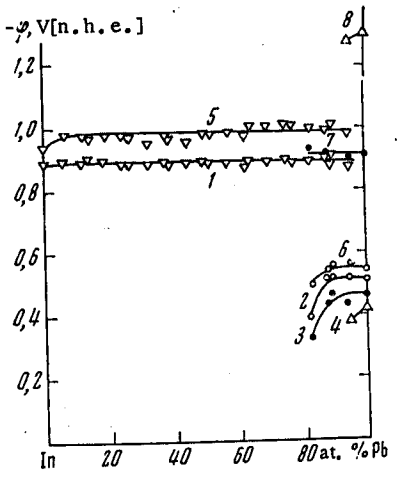

Fig. 3

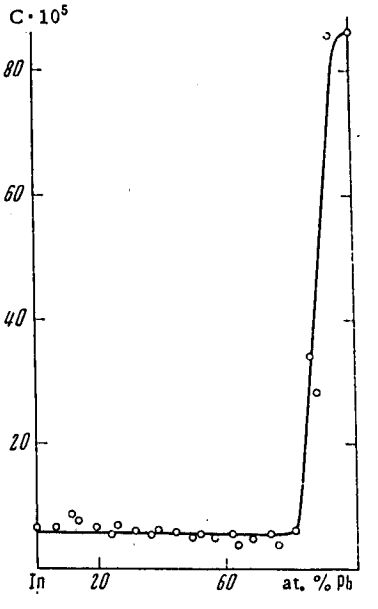

Fig. 4

Fig. 3. Dependence of φ_{in} (1-4) and the reduction potentials (5-6) of the oxides on the composition of the alloy: 1, 5) In_2O_3; 2, 6) Pb_2O; 3, 7) PbO; 4, 8) $Pb(OH)_2$.

Fig. 4. Dependence of the total amount of electricity used in the reduction of oxygen compounds from the surface on the composition of the alloy.

the lead ions, which, judging by parallel corrosion measurments, might pass into solution during the previous anodic polarization. In addition to this, $HPbO_2^-$ ions artificially introduced into the solution (to a concentration of $1.25 \cdot 10^{-3}$ g-ion/liter) are reduced at a smaller negative potential (-0.49 V). Hence the first arrest cannot be explained by reduction of small quantities of oxygen dissolved in the surface layers of the metal [10], nor by the reduction of lead ions which have passed into solution.

We might well believe that the first arrest is the result of the penetration of a potassium ion into the lead, with the formation of a solid solution or intermetallic compound [11]. This phenomenon is quite possible in the present case for hydrogen evolution potentials of -1.6 V. Then the intermetallic compound of potassium may decompose at φ_{in}^{I} with the formation of $Pb(OH)_2$, as occurs in the case of Pb_3Na [11]. At a potential of $\varphi_I = -0.544$ V, however, the hydrate of lead oxide is reduced as in reaction (1). The latter is thermodynamically possible even at φ_{in}^{I} (since $\varphi_{eq}^{III} = -0.424$ V), but it evidently experiences kinetic hindrances. Thus $Pb(OH)_2$ is reduced at two potentials (φ_I and φ_{III}), which may be presumably associated with the different structures of the hydroxide obtained by the direct oxidation of lead and by the decomposition of the intermetallic compound.

However, this explanation for the nature of the first arrest is not the only one possible. An increase in the time of anodic polarization at φ_{in}^{I} should reduce the length of the first arrest in view of the possibility of $Pb(OH)_2$ being reduced at this potential. Actually an increase in the time from 10 sec to 5 min increases the amount of electricity expended in the first arrest from $4.4 \cdot 10^{-3}$ to $49.2 \cdot 10^{-3}$ C/cm^2. The latter is possible if two conditions are satisfied simultaneously: 1) the rate of decomposition of the intermetallic compound at φ_{in}^{I} is much greater than the rate of reduction of $Pb(OH)_2$; 2) the amount of the intermetallic compound is so great that it is sufficient for the formation of the hydroxide over a period of 5 min.

It would appear more reasonable to suppose that the first arrest corresponds to the reduction of lead suboxide, the existence of which was mentioned in [8, 9], although no published data as to the work of formation of Pb_2O are to be found. The calculated thickness of the proposed layer of Pb_2O (for a density of 8.342 g/cm^3 [8]) reaches ~100 Å in 10 sec at $\varphi_{an} = -0.34$ V. Subsequently we shall regard the first arrest as being associated with the reduction of Pb_2O.

In accordance with the results obtained, we must therefore assume that the oxides formed on the surface of the lead are reduced with considerably different overvoltages. The reduction of Pb_2O at $i = 1.4 \cdot 10^{-3}$ A/cm^2 requires $\Delta\varphi = 0.042$ V; PbO $\Delta\varphi = 0.51$ V; and $Pb(OH)_2$ $\Delta\varphi = 0.873$ V. In view of this, both the formation and the reduction of the oxides take place in the following order: Pb_2O, PbO and $Pb(OH)_2$. This is quite feasible when the oxides are disposed on the surface, not in layers, but in individual "outgrowths" [12]. Otherwise it is difficult to conceive the initial reduction of the relatively thick (up to 100 Å) layer of Pb_2O, lying underneath a layer of PbO and $Pb(OH)_2$.

Indium. The cathodic charging curve of the indium electrode (Fig. 1b) shows one arrest corresponding to the reduction of a certain compound at -0.940 V. The φin of this compound is -0.884 ± 0.005 V.

At this potential it is possible for In_2O_3 to be formed by the reaction

$$2In + 3H_2O \rightleftharpoons In_2O_3 + 6H^+ + 6e,$$

the calculated equilibrium potentials of which (for pH 11.86) [7] equals -0.890 V.

The onset of the reduction of InO_3 is accompanied by a considerable additional polarization, reaching as much as 150 mV, as indicated by the presence of a maximum preceding the reduction of In_2O_3 on the charging curve. Similar maxima observed earlier [6] may have been associated with hindrances to the decomposition of the oxide lattice in its reduction.

In contrast to the lead oxides, a change of φ_{an} from -0.87 to -0.34 V does not alter the thickness of the In_2O_3 layer, which remains practically constant and equal to 3 Å.

Such a slight thickness (determined by calculation) indicates that the oxide only covers the surface in individual regions [12]. The fact that the thickness of the In_2O_3 layer remains independent of φ_{an} is probably associated with the extremely slow formation of this oxide. An increase in the time of anodic polarization at $\varphi_{an} = -0.34$ V from 10 sec (the holding period which we usually adopted) to 5 min showed that the amount of reduced oxide In_2O_3 remained unchanged ($q = 4.10^{-3}$ C/cm^2). Yet the amount of PbO and $Pb(OH)_2$ increases from $0.6 \cdot 10^{-3}$ to $3 \cdot 10^{-3}$ C/cm^2, and Pb_2O from $4.4 \cdot 10^{-3}$ to $49.2 \cdot 10^{-3}$ C/cm^2. This indicates the highly protective properties of In_2O_3 (low ionic or low electron conductivity, or both together).

Lead–Indium Alloys. Figure 2 illustrates some oscillograms (with an indication of the compositions) for each of the alloys of the Pb-Sn system studied, these being obtained after 10 sec of anodic polarization at $\varphi_{an} = -0.34$ V. According to the character of the cathodic charging curves, the whole system may be divided into two regions.

The first (mixed) region includes lead-base alloys containing 100-81.5 at.% Pb, on the surface of which all the lead oxides (Pb_2O, PbO, and $Pb(OH)_2$) may be formed; starting from 94 at.% Pb or under, indium oxide may be formed as well. This may be seen from Fig. 3, which shows the change taking place in the potential of the initial formation (curves 1-4) and reduction (5-8) of the oxides on varying the composition of the alloys.

The second region embraces alloys from 81.5 at.% Pb to pure indium, and is characterized by the presence of solely In_2O_3 on the surface.

None of the alloys examined had any other oxides on their surface but those already formed on the pure lead and indium. No mixed oxides occurred in this system, in contrast to the Bi-Sb system of alloys [2].

It is an interesting fact that In_2O_3 is formed on the surface of all the alloys studied. The Pb_2O and PbO appear on alloys containing more than 81.5 at.% Pb, and $Pb(OH)_2$ only on the alloy with 96 at.% Pb. An analogous effect takes place in the Cu-Ni system.

The variation in the total amount of oxygen combined with the surface of the alloys is illustrated in Fig. 4. The amount of oxygen falls sharply from pure Pb to the alloy containing 81.5 at.% Pb, this change being associated with a reduction in the quantity of lead oxides, which are predominant on the surface of the alloys in this region. The amount of oxygen on all the other alloys, however, remains practically constant, indicating a constant and very small (~ 3 Å) amount of In_2O_3, since only this oxide is formed on the alloys in this region.

The sharp reduction in the quantity of lead oxides on the alloy surfaces as the indium content increases may be explained by using earlier [13] developed ideas, to the effect that groups (assemblies) of

atoms of the corresponding alloy component (sufficient to form the oxide of this component) have to be present at a single point on the surface of the alloy.

A calculation based on the principles of [13] shows that the minimum assembly required for the formation of the hypothetical Pb_2O (which constitutes the chief surface constituent on the alloy) should contain 14 lead atoms, i.e., it must be extremely large. For comparison, we may note that the formation of Sb_2O_4 on the surface of Bi-Sb alloys would require an assembly of four antimony atoms, which for the formation of Bi_2O_3 on alloys of the same system six bismuth atoms would be needed [13].

Such a large number of lead atoms lying together in one place on the surface of the alloys is only possible when the indium content is very low. This clearly explains the sharp fall in the amount of lead oxides on passing from pure lead to the Pb-In alloys, and the impossibility of these being formed on alloys containing less than 81.5 at.% Pb.

At all points at which, as a result of the oxidation of the lead (under conditions in which it is unable to form an oxide phase), indium atoms come to the surface, In_2O_3 is formed. The small amount of this oxide on the indium-rich alloys (and on indium itself) indicates the validity of the oft-reiterated opinion that the oxides are formed, not in the form of a continuous layer, but in that of individual "outgrowths" and in places at which the structure of the surface is favorable toward this configuration. The preparation of the alloy surfaces ensured a low roughness coefficient, so that the number of asperities promoting the formation of indium oxide should have been small. It may well be that in the present case the roughness factor (which we did not determine directly) was smaller than three, and possibly close to unity.

It is reasonable to assume that the surface of the alloys was slightly enriched with indium (this being the component with the greater stability under present conditions) relative to the main volume. This surface enrichment, like the enrichment of the surface with copper in the Cu-Zn system [14], evidently proceeds up a certain constant composition, and this is why there is a constant amount in In_2O_3 on the alloys between 0 and 81.5 at.% Pb. The increase in the total amount of oxygen in the alloys which begins at 81.5 at.% Pb (Fig. 4) shows that change in the surface composition of even low-melting-point alloys may well occur if, after a brief anodic polarization (10 sec), the cathodic charging curve establishing these changes is recorded immediately. The diffusion of the atoms in the alloy cannot then render the composition of the main volume and the surface of the alloy uniform. Nevertheless, the change in the composition of the surface is not particularly sharp (1-3 at.%), while the total content of lead oxides varies widely, over a range of some 20 at.%.

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LITERATURE CITED

1. I. A. Makhnovetskaya and V. V. Skorchelletti, Zashchita Metal., 2, 617 (1966); A. M. Borshchevskii, V. V. Skorchelletti, and T. I. Mikhaleva, Zh. Priklad. Khim., 39, 1429 (1966).
2. A. M. Borshchevskii and V. V. Skorchelletti, Zashchita Metal., 2,46 (1966).
3. V. N. Lepeshinskaya, V. V. Skorchelletti, and V. N. Monastyrev, Zh. Priklad. Khim., 38, 1556 (1965); V. V. Skorchelletti, I. A. Makhnovetskaya, and S. S. Kotova, Zh. Priklad. Khim., 41, 651 (1968); V. V. Skorchelletti, I. A. Makhnovetskaya, and Yu. A. Kharlamov, Zh. Priklad. Khim., 42, 1558 (1969).
4. M. Hansen and K. Anderko, Constitution of Binary Alloys, Vol. 1 [Russian translation], Metallurgizdat, Moscow (1962).
5. V. V. Skorhelletti and A. M. Borshchevskii, Zh. Priklad. Khim., 37, 87 (1964).
6. A. M. Borshchevskii and V. V. Skorchelletti, Zashchita Metal., 1, 624,630 (1965).
7. W. Latimer, Oxidized States of the Elements and Their Potentials in Aqueous Solutions [Russian translation], IL, Moscow (1964).
8. Handbook of Chemistry, Vol. 2 [in Russian], Goskhimzdat, Moscow (1963), p. 194.
9. G. Remi, Course of Inorganic Chemistry, Vol. 1 [Russian translation], Mir, Moscow (1963).
10. A. M. Borshchevskii, V. V. Skorchelletti, and T. I. Mikhaleva, Zh. Priklad. Khim., 39, 1427 (1966).
11. B. N. Kabanov, I. G. Kiseleva, and I. I. Astakhov, Elektrokhimiya, 7, 955 (1972).
12. J. Benare, Oxidation of Metals, Vol. 1 [Russian translation], Metallurgiya, Moscow (1968).
13. V. V. Skorchelletti and A. M. Borshchevskii, Zashchita Metal., 4, 430 (1968).
14. A. M. Borshchevskii and V. V. Skorchelletti, Zashchita Metal., 5, 554 (1969).