ELECTROCHEMICAL IMPLANTATION AND ITS RELATION TO CERTAIN PROBLEMS IN THE CORROSION OF METALS

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The results of an investigation into the mechanism and kinetic characteristics of the electrochemical implantation of metals are presented. It is shown that implantation constitutes a structure-sensitive process. The rate of this process depends on the microstructural state of the electrode in both the initial and final stages. Intermetallic compounds are formed as a result of electrochemical implantation. This imparts new properties to the cathode surface.

Electrochemical implantation processes have recently been more and more extensively studied, chiefly at the instigation of Soviet electrochemists [1].

The difference between implantation and other electrochemical processes lies in the fact that, in the actual act of the electrochemical reaction, a chemical compound is formed between the incoming element in the electrode metal. The potential at which implantation occurs is displaced in the positive direction relative to the precipitation potential of the pure phase. In systems with a weakish interaction this displacement equals tens or hundreds of millivolts (for example, in the implantation of tin into gold [2]), while in systems comprising elements which interact vigorously with each other the potential displacement may account to 1.5 V or over. In this respect the implantation of metals into another metal is analogous to the electrochemical formation of amalgams and other liquid alloys. However, in contrast to the rates of formation of liquid alloys, implantation depends considerably on the structural state of the electrode, and is determined by the concentration of vacancies and other structural defects in the surface layer of the electrode, since the act of implantation may, as a rule, only take place when the penetrating metal falls into a vacancy or other defect of the solid surface. In the classification of electrochemical processes the implantation of elements thus occupies a special place between electrocrystallization (electrodeposition) and the formation of liquid metallic solutions.

Among the various problems associated with the study of implantation, two are directly concerned with metal protection: the problem of electrochemically creating protective layers of intermetallic compounds on metal surfaces, and the problem of cathodic corrosion on metal electrodes. These both arose long before the appearance of the first papers on implantation. Thus indications as to the possibility of cathodically depositing protective coatings of aluminum or beryllium intermetallic compounds appeared even in the 1920s [3], while the first papers on the cathodic sputtering of lead and certain other metals appeared still earlier [4]. However, only very recently have there been any detailed experimental investigations into electrochemical implantation and theoretical calculations of the kinetic laws governing this process in certain particular cases.

The study of electrochemical implantation includes three main problems. Firstly there is the thermodynamic analysis of the compounds formed during implantation, aimed at predicting how compounds are formed as a result of implantation in a specified system under specific conditions. Secondly there is the study of implantation kinetics, and thirdly the study of the electrochemical, mechanical, corrosion, and other properties of the compounds formed as a result of implantation. The latter part of the investigation is important if it is impossible to predict the properties of the intermetallic compounds formed in advance, for example, if implantation occurs at lowish temperatures, under conditions in which metastable phases not shown in the phase diagram are likely to be formed.

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It is well known that intermetallic compounds often possess extremely valuable properties which are absent from their constituent elements. By forming intermetallic compounds we may increase the heat, scale, and corrosion resistance of the material and impart magnetic, catalytic, semiconducting, or superconducting properties.

It is often required to impart some of these properties simply to a thin outer layer of the metal. The use of implantation enables us to create layers of intermetallic compounds of the surface of the cathode while keeping the properties of the interior unaltered. Objects of practical value may be obtained in this way [5]. By implanting boron into molybdenum the surface becomes almost as hard as a diamond. Beryllium on being implanted in copper improves the strength, flexibility, hardness, and corrosion resistance without harming the electrical conductivity. Silicon on being implanted into tungsten, rhenium, niobium, and molybdenum increases their corrosion resistance. In other cases such as, for example, the cathodic implantation of sodium into lead, intermetallic compounds actively interacting with water are created, and this leads to the catastrophically rapid decomposition of the cathode (pulverization).

The difference between the implantation potential and the precipitation potential of the pure phase of the penetrating element is determined by the free energy of the intermetallic compound formed on implantation. Practically all intermetallic compounds possess a more or less extensive range of homogeneity, and hence every intermetallic compound is characterized not by a single specific potential of formation but by a more or less extensive range of potentials. If the components interact weakly, their activity also varies very little in the range of existence of a particular compound, and the range of potentials over which the compound is formed is quite narrow. In the case of strong interaction the range of formation of any one intermediate phase may extend over several tenths of a volt, and the activity of the components in the compound will then vary by many orders of magnitude, as occurs in the implantation of alkali and alkaline-earth metals.

For many intermetallic compounds of alkali and alkaline-earth metals with solid metals the stoichiometric composition is already known [6]; however, information as to their free energy of formation or standard potentials has only recently started accumulating. We shall here pay special attention to the most widely studied compound of Na with Pb.

After aging in order to bring it into a stable state, an alloy containing 27 at. % Na approximately corresponds to the composition* $NaPb_3$ and should react at the electrode thus:

$$NaPb_3 \rightleftharpoons Na^+ + 3Pb + e^-, \tag{1}$$

while the equilibrium potential

$$\varphi = \varphi^0 + \frac{2{,}3RT}{F} \lg a_{Na^+}. \tag{2}$$

Experiments give the equilibrium potential of the $NaPb_3 - Na^+$ system for unit activity of the Na^+ ions† (i.e., the standard potential φ^0) as −1.32 V [7, 8]. According to Eq. (2) φ falls by 60 mV when the activity of the Na^+ ions falls by a factor of 10, independently of the activity of the OH^- ions (Fig. 1) [8]. The maximum free energy of the compound $NaPb_3$ calculated from the standard potential equals −135 kJ/mole. This is almost twice the free energy of the compound $NaHg_3$ (−77 kJ/mole). On the other hand, the standard exchange current i_0 in the $NaPb_3/Na^+$ system (~10^{-3} A/cm^2 [8, 9]) is four orders of magnitude smaller than that of sodium amalgam (for −1.86 V it is ~10 A/cm^2 [10]).

Other compounds of Na with Pb (and at least five are known [6]) have other equilibrium potentials (Fig. 2) [7, 11]. The compound NaPb has approximately $\varphi^0 = -2$ V. Thus the compound $NaPb_3$ should be formed during implantation in the potential range from −1.3 V to almost −2 V. It may be shown by calculation that the activity of sodium in this compound varies by 11-12 orders of magnitude over its range of existence (6% concentration). Evidently the richer the compound in lead the greater is the negative value of its free energy per sodium atom.

Some evidence exists as to the standard potentials of compounds formed by K with Pb and also by Na and K with Cd, Hg, etc. The equilibrium potentials φ^0 and the free energy of formation F^0 of several

*The correspondence is only approximate, since in this range of concentrations there is a β-phase which is usually treated as a solid solution of sodium in the hypothetical compound $NaPb_3$. We shall here refer to this phase as the "compound" $NaPb_3$.

†We consider that the activity of the metal ion equals the product of its concentration and the mean activity of the electrolyte ions.

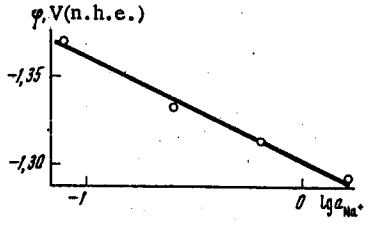

Fig. 1

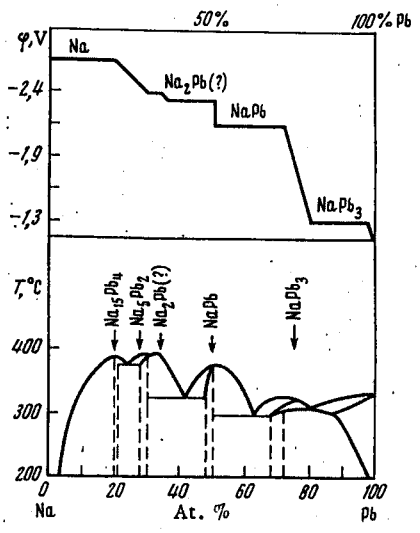

Fig. 2

Fig. 1. Equilibrium potential of the $NaPb_3 - Na^+$ system as a function of the logarithm of the activity of the sodium ions in a solution with a pH of 13. Slope of straight line 59 mV.

Fig. 2. Phase diagram of the Na – Pb system and equilibrium potentials φ of the intermetallic compounds of this system.

intermetallic compounds calculated by means of the equation $F^0 = F_{Me^+} - \varphi^0 \cdot 96.48$ [9, 12] are presented below:

Composition	$NaHg_2$	NaPb	$NaHg_6$	$NaCd_2$	$NaPb_3$	$NaCd_6$	KCd_{13}
ϑ, V	—2.0	—2.0	—1.92	—1.4	—1.32	—1.25	—1.1
F_0, KJ /mole	—69	—69	—76.5	—127	—135	—141	—176

When studying the implantation of alkali metals in aqueous solutions, and also the properties of the intermetallic compounds so formed, the method most widely used is that of chronopotentiography (plotting anodic and cathodic charging curves) [1]. In order to determine the amount of alkali metal penetrating into the electrode, chemical analysis [36] and x-ray structural [2] methods are also employed. Spectral methods may also be used, for example, flame photometry.

The implantation process may conveniently be considered as taking place in two stages. In the first stage the ions of the metal being implanted are released from their hydrate shell, and after discharging enter into a chemical bond with the surface layer of the electrode atoms. The second stage involves the passage of the implanted atoms into the interior of the electrode and the corresponding crystallization phenomena.

The possibility of implantation taking place in the lattice of a metal with close packing of the atoms is, as a rule, kinetically associated with the existence of structural defects on the surface of the metal; at such defects the atom of the penetrating element is bound to the atoms of the electrode metal far more strongly than on an atomically smooth surface. The energy gain associated with the formation of bonds between the penetrating atom and the atoms of the electrode metal is the greater, the greater the number of these bonds which are formed. Hence for not very negative potentials the most probable event is the discharge of the implanted atom in a vacancy on the surface of the electrode. When the potential moves in the negative direction, other surface defects, characterized by smaller coordination numbers, play a greater and greater part; finally, for very negative potentials (approaching the equilibrium potential of the pure penetrating metal) any part of the electrode surface becomes a site suitable for implantation.

The velocity of the first stage is usually high, only it may at first be smaller than the diffusion velocity, so that starting from a certain instant the velocity of the whole process should be limited by the second stage, i.e., by the rate at which the implanted metal passes into the interior of the electrode by diffusion. It was found that under certain conditions the rate of solid-phase diffusion could be very considerable even at room temperature. Thus it was observed in [13] that when sodium penetrated into lead

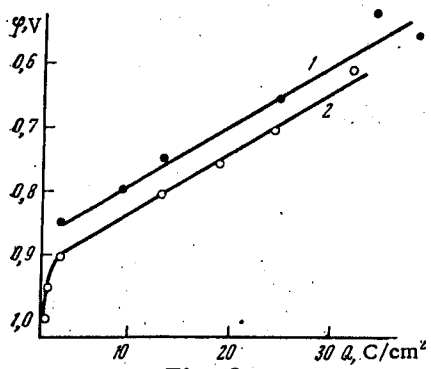

Fig. 3

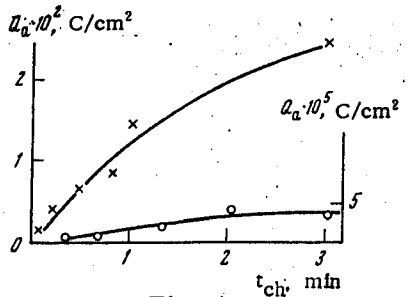

Fig. 4

Fig. 3. Amount of cathodically implanted lithium as a function of the potential of solid gallium at 26°C (1) and lithium gallium at 34°C (2) on implantation from a solution of 0.6 N $LiClO_4$ in propylene carbonate. Time of implantation 4 h. The potentials are given relative to the normal lithium electrode.

Fig. 4. Amount Q_a of anodically ionized sodium as a function of the duration of cathodic polarization at a lead electrode: left) 0.5 N $NaNO_3$ in dimethylformamide; right) 1 N $NaNO_3$ in water.

at room temperature the volumetric diffusion coefficient was at least 10^{-13} cm^2/sec.

The concentration distribution of the penetrating element with respect to electrode depth should have the same character as in reactive diffusion [14]. On the surface of the electrode there is a layer of the intermetallic compound containing the greatest proportion of the implanted element; behind this are layers of less enriched intermetallic compounds, and still deeper layers of primary solid solution. At the boundaries between the layers the concentration of the implanted element changes sharply. The rate of the second stage of implantation increases with increasing chemical potential of the implanted element on the surface of the electrode, while the chemical potential, in turn, varies with electrode potential in the manner required by the Nernst equation, subject to the existence of electrode – electrolyte electrochemical equilibrium.

In the case of implantation into solid metals from melts, the crystallization of the intermetallic compounds is farily rapid (owing to the high temperature) and thick, well-formed layers of intermetallic compounds are created. Implantation from melts has been used for a long time in producing surface layers with special properties on various objects, for example, borides or beryllides. The kinetics of implantation at the second stage have already been calculated for layers of this kind. These calculations showed that the square of the amount of implanted material varied linearly with the electrode potential and the logarithm of the activity of the implanted ions in the solution or melt. A parabolic dependence of the rate of implantation on potential was obtained experimentally when studying the implantation of lead into platinum from various melts [15].

Implantation at lower temperatures is characterized by a lower velocity of the crystallization processes. Conditions are accordingly created for the formation of nonequilibrium phases; this occurs, for example, in the implantation of sodium into lead [13].

However, in those cases in which hardly any metastable phases are formed, the kinetics of implantation may be calculated even at room temperature. Thus it was shown that, for implantation into the surface of a liquid metal, diffusion control led to a linear dependence of the rate of implantation on the potential. A relationship of this kind was found experimentally when studying the discharge kinetics of alkali ions on liquid mercury [16] and tin [17] cathodes.

It may be shown that a linear dependence of the rate of implantation on the electrode potential should also be observed when the rate of implantation is limited, not by diffusion, but by the chemical reaction leading to the formation of the intermetallic compound. Such a relationship was observed experimentally when studying the penetration of lithium into gallium from a nonaqueous solution [18] (Fig. 3). The rates of penetration into liquid and solid cathodes differ very little in this case, thus confirming the existence of chemical control.

Cathodic implantation may lead to considerable changes in the mechanical and electrochemical properties of the cathode metal. We may mention the displacement of the zero-charge potential of a metal when alkali metals are passed into it. For an alloy of lead with 1% sodium, the zero-charge potential was determined by an ac method in [19] by reference to the minimum differential capacity of the double electric layer. It was found that the zero-charge potential of this alloy was −0.85 V (n. h. e.), i.e., ~0.2 V in the negative direction relative to the zero-charge potential of pure lead in the same solution or a solution of NaF [20]. On increasing the sodium content of the lead this displacement increases.

The overvoltage corresponding to the reduction of the NO_3^- ion was very low on an Na—Pb intermetallic compound [21]. On mercury under similar conditions the process takes place at an overvoltage some 0.7 V higher; this is apparently associated with the convective removal of a large proportion of the intermetallic compound from the surface of the electrode into the interior of the drop, and also possibly with the lower negative free energy of formation of mercury intermetallic compounds (as compared with the intermetallic compounds of such metals as lead).

The great chemical strength of intermetallic compounds enables them to be formed at such low negative potentials that the implantation of alkali metals is very extensively employed in the electrochemistry of metals. For example, potassium passes into zinc from concentrated alkali even at the stationary potential [22].

The effect of the implantation of alkali metals on the hydrogen overvoltage of Pb, Ag, Sn, Zn, Cd, and other metals is already well known [23].

At potential more negative than −2.2 V, metals become pulverized in strong alkali solutions; many investigations have been undertaken into this over a long period [4, 24, 25]. In the older papers it was indicated that this effect took place by virtue of the decomposition of the intermetallic compound in water, with the evolution of hydrogen.

On comparing implantation from aqueous and nonaqueous solutions, results which (in our own opinion) bear witness to the chemical interaction of the implanted metal with water are obtained [26]. The amount of sodium penetrating into lead from a solution of $NaNO_3$ in dimethylformamide over a short period was three orders of magnitude greater than from an aqueous solution at the same potential (Fig. 4). The possibility of large quantities of alkali metal accumulating at the cathode in the case of dimethylformamide may be explained as being due to the absence of any chemical decomposition of the intermetallic compound by water. Accordingly no pulverization of the cathode occurs when sodium is implanted from a nonaqueous solution.

The subsequent fate of metal pulverized in an aqueous solution depends on its properties. Metals having a standard potential well to the negative side of the equilibrium potential of the hydrogen electrode in the same solution will be dissolved, with the evolution of the equivalent amount of hydrogen. Dissolution will occur very rapidly in view of the highly-dispersed nature of the pulverized metal. Such metals include aluminum [27], magnesium [28], zinc, manganese, etc. However, it is by no means impossible that some of these metals will not become pulverized, but pass straight into solution as a result of the chemical interaction of the intermetallic compound with water, for example:

$$NaAl+H_2O+2OH^-=Na^++AlO_2^-+2H_2$$

More electropositive metals may be oxidized by traces of dissolved oxygen and other oxidizing agents, while in the absence of these highly-dispersed lyophobic colloids will be formed; these will coagulate if this effect is not prevented by the adsorption of surface-active substances (stabilizers) also in solution.

The range of metals interacting by the implantation mechanism is very wide. At the present time evidence exists as to the implantation of the following elements in various metals: H, Li, Na, K, Cs, Be, Mg, Ca, Sr, Ba, Cd, B, Ti, Tl, Si, O, Mn, I. Also extensive is the range of metals into which various elements may be implanted: Cu, Ag, Au, Mg, Zn, Cd, Hg, Al, Ga, In, Tl, Sn, Pb, Sb, Bi, W, Te, Fe, Ni, Pt, Mo. We also note that alkaline-earth and alkali metals, and possibly Cd and Tl, may be implanted into metals of group VIII, since these are adsorbed at potentials several tenths of a volt to the positive side of the equilibrium potential of the adsorbed metal in the solution in question [29]. There are some indications that a cathodic compounding of alkali metals with iron may also take place [30], while the adsorption of sodium (or more probably its implantation) is considered as a likely intermediate stage in the evolution of hydrogen on platinum [31] and nickel [32] in alkalis. There are cases of the implantation of lead into platinum [33], manganese into bismuth [34], boron into molybdenum [5], and also silicon into tungsten, niobium, and molybdenum [35].

These data by no means exhaust all cases of the electrochemical implantation of one element into another.

It has been considered, for example, that transition elements do not interact with alkali elements. In particular there are no data relating to the chemical interaction of alkali metals with molybdenum. The great difference in the melting and boiling points, in fact, constitutes a serious obstacle to the occurrence of this process at high temperatures. However, the difference in the electronegativities of these metals is high enough (for sodium 0.90, for molybdenum 2.09) for their interaction to be possible. In this case electrochemical implantation is the only way of obtaining intermetallic compounds. The occurrence of implantation at potentials more positive than the equilibrium potentials of the free alkali metals means that chemical interaction takes place between the alkali metals and molybdenum [36].

Thus electrochemical implantation is related to metal-protection problems in two ways. The implantation of alkali metals from aqueous solutions may lead to the catastrophically fast breakdown of the cathodes (pulverization). When other metals are implanted, intermetallic compounds possessing various valuable properties (including increased corrosion resistance) may be obtained. Despite the fact that the implantation process is, as a rule, limited by diffusion in the solid phase, considerable rates of implantation may even be obtained at room temperature.

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