CATHODIC IMPLANTATION OF ALUMINUM IN VANADIUM

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The authors investigate the cathodic implantation of aluminum in vanadium from solutions of aluminum bromide in xylene. Implantation begins to occur at an appreciable rate at the potential for separation of an aluminum phase, and continues in parallel with the latter process. As well as a solid solution of aluminum in vanadium, cathode implantation can form one or two intermetallic compounds.

In cathodic electrochemical implantation, the discharging cation interacts with the material of the cathode, leading to the formation of intermetallic compounds or a solid solution [1]. Interest attaches to the cathodic implantation of polyvalent metals in transition metals, because this can form intermetallic compounds with valuable properties. In some cases it appears that deposition of a thin layer of intermetallide on the metal surface is sufficient to cause appreciable changes in its properties. Therefore cathodic implantation is very promising for this purpose.

We have investigated the cathodic implantation of aluminum in vanadium. It is known that the system Al–V forms four intermetallic phases, $Al_{11}V$, Al_6V, Al_3V, and Al_8V_5. At room temperature, the solubility of aluminum in vanadium is 25% [2].

Aluminum is an active metal, and its standard potential is very negative (−2.31 V in alkaline solution [3]). Therefore, as in the case of alkali metals, when we try to effect cathodic implantation of aluminum from aqueous solutions a considerable fraction of the current must be expended on simultaneous discharge of hydrogen ions. On the other hand, electrodeposition of aluminum, even from nonaqueous electrolyte solutions in which the equilibrium potential of aluminum is easily reached, is in many cases much more difficult than deposition of alkali metals from similar solutions. For example, aluminum perchlorate is soluble in a number of organic solvents, but, in contrast with nonaqueous solutions of alkali metal perchlorates, it does not give a metallic deposit on electrolysis [4].

Thus it was necessary to choose a nonaqueous electrolyte from which aluminum would be deposited fairly easily in pure form. It was found that aluminum can be deposited only from a limited range of solutes and solvents – aluminum halides and organoaluminum compounds as solutes, and ethyl bromide, amines or amides, ether, aromatic hydrocarbons (benzene, toluene, and xylene) or mixtures of these substances as solvents [5]. Most of these compounds are expensive, unstable, or dangerous to handle. In our conditions it appeared that the most accessible and promising solution was one of aluminum bromide in xylene. According to [6-10], a freshly prepared solution of aluminum bromide in xylene has an electrical conductivity between $1 \cdot 10^{-5}$ and $1 \cdot 10^{-4}$ $\Omega^{-1} \cdot cm^{-1}$; with the passage of time the conductivity increases 70-fold. The aluminum is precipitated with a current yield of 55-65% of the theoretical value, and the rest of the energy is expended on side processes, on the nature of which authors disagree.

We have used anhydrous aluminum bromide synthesized from the elements and also a commercial preparation of "ch.d.a." ["analytic"] grade, together with "ch." ["pure"] grade p-xylene. Any of the three xylene isomers could have been used as the solvent, because aluminum bromide causes isomerization and a mixture of the isomers is formed in any case. The solution concentration was optimal [7] (about 25 mole % $AlBr_3$).

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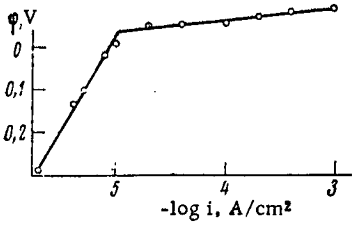

Fig. 1

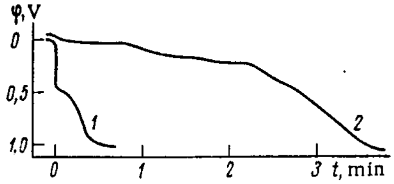

Fig. 2

Fig. 1. Polarization curve for vanadium in 40% solution of aluminum bromide in xylene.

Fig. 2. Anodic chronopotentiograms with $I_a = 0.01$ mA/cm². Preliminary cathodic polarization of vanadium: 1) $t_c = 2h$, $\varphi_c = 0.05$ V; 2) $t_c = 2$ min, $\varphi_c = -0.1$ V.

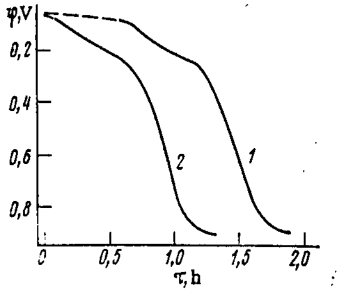

Fig. 3

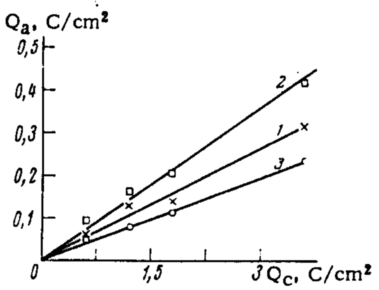

Fig. 4

Fig. 3. Anodic chronopotentiograms with $I_a = 0.05$ mA/cm². Preliminary cathodic polarization of vanadium: $t_c = 1$ h, $\varphi_c = -0.1$ V. 1) Immediately after switching off cathode current; 2) one hour after switching off cathode current. Dashed curve shows arrests due to ionization of metallic aluminum.

Fig. 4. Quantity of anodically ionized aluminum vs quantity of cathodically passed electricity. 1) From metallic aluminum phase; 2) from intermetallide; 3) from solid solution.

Since aluminum bromide strongly absorbs water and hydrolyzes, the solution unavoidably contained some HBr, which according to the literature data does not hinder the separation of aluminum, but reduces the cathodic polarization [10]. The resulting electrolyte could be used to separate aluminum for a month (passing an average of 5-10 C per day). After this the solution became resinified and separation of aluminum practically ceased. Solution not used in electrolysis and stored for several months retained its ability to separate aluminum as if freshly prepared. Some demixing (separation of a thin clear layer) was observed only after prolonged electrolysis (2-3 weeks in the stated conditions).

Electrolysis was effected with an A1000 aluminum anode and a vanadium cathode in the form of a rod, plate, or foil. Before an experiment the vanadium was electropolished in a mixture of perchloric and acetic acids [11]. The potential of the vanadium electrode was measured relative to aluminum in the same solution (φ_{Al}). In this case the usual reference electrodes could not be used, because most inorganic salts are insoluble in xylene, while the aggressiveness of aluminum bromide toward water and many solvents prevented us from using a bridge.

The polarization curve in Fig. 1 shows that aluminum separates with a low overvoltage which does not increase much with the current density. The stationary potential of vanadium relative to an aluminum electrode in equilibrium with complex ions of aluminum in xylene solution was equal to 0.90-0.95 V.

The main method of investigation of the processes occurring on the electrode was to record chronopotentiograms. After the vanadium electrode had been subjected to cathodic polarization for a given time, the anode current was switched on and the changes of potential with time were recorded. If cathode polarization forms intermetallic compounds, there should be arrests at the corresponding potentials **on the anodic potential–time** curve, with lengths governed by the amount of compound formed. Dissociation of the solid solution corresponds to rather slow shift of potential with time toward the positive.

In the course of our investigations we found that if cathodic polarization is effected at potentials more positive than the potential for separation of aluminum in the form of a phase, cathodic implantation takes place, but only very slowly. The current density does not exceed 0.01 mA/cm^2 and falls with time. The shape of the anodic chronopotentiogram indicates the formation of only a small amount of solid solution (Fig. 2, curve 1).

The anode curve is more interesting when the potential for separation of aluminum as a phase is reached during cathodic polarization (Fig. 2, curve 2). In this case, as well as the arrest corresponding to ionization of the separating aluminum, the curve also has other rather broad sections in the region between the potentials of aluminum and vanadium, although the shapes of the curves are not always exactly reproduced. In some cases, on the anode curve we can distinguish two arrests characteristic of intermetallic compounds, lying 0.11 and 0.18 V to the positive side of the potential of the arrest of crystalline aluminum, and also a region of solid solutions. In other cases one of the arrests is not found; in some cases, beside the aluminum arrest there is only a region of solid solutions.

The slow shift of potential during imposition of the anode current might be due not only to ionization of implanted aluminum but also to unknown processes in the solution. To prove that in our case there is really cathodic implantation of aluminum in vanadium, we can adduce the following facts. 1) If a vanadium electrode on which a layer of intermetallide or solid solution has been formed is replaced in the same solution by a pure vanadium electrode, the latter will have the potential (without current) characteristic of pure vanadium. 2) If the original vanadium electrode is washed free of solution and replaced in the solution, it again acquires its original potential in the region between the potentials of aluminum and vanadium.

It follows that the shapes of the anodic chronopotentiograms must be due to processes occurring on the electrode, and not in the solution, and the formation of a surface vanadium–aluminum alloy can be regarded as proved. In contrast to the usual case of cathodic implantation, the interaction between the aluminum and the vanadium occurs in parallel with separation of aluminum in the form of a phase. This fact can be explained either by parallel occurrence of cathodic implantation and separation of aluminum, or by diffusion of separated aluminum into the vanadium. In the former case the amount of separated aluminum should increase with the cathodic polarization time. In the latter case only the formation of a layer of aluminum on the electrode surface is important, and further diffusion of aluminum into the vanadium should occur without cathodic polarization. The following facts support the former hypothesis. The length of the arrests corresponding to the total quantity of intermetallide and solid solution is the same whether we record the anodic chronopotentiogram immediately after cathodic polarization or after an interruption (Fig. 3). This means that diffusion of aluminum from the deposited phase layer of aluminum into the vanadium does not play an important part in the process, and that formation of an intermetallide or solid solution occurs only during cathodic polarization.

As we see from Fig. 4, the quantities of anodically ionized intermetallide and solid solution (and also the quantity of anodically ionized metallic aluminum) increase in proportion to the quantity of cathodically passed electricity. This fact, together with the virtual absence of diffusion of aluminum into the electrode without cathodic polarization, favors the idea that cathodic implantation and separation of an aluminum phase occur in parallel.

We can apparently represent the overall process as follows. Formation of an alloy of aluminum and vanadium occurs with relatively high overvoltage and reaches an appreciable rate during simultaneous deposition of aluminum in the form of a phase, which occurs with a low overvoltage. The separated aluminum forms a loose layer which does not hinder the simultaneous implantation process. A similar case was observed when manganese was implanted in bismuth: Electrodeposition of a manganese phase occurs in parallel at an appreciable rate [12].

The total quantity of anodically ionized aluminum is 20-30% of the quantity of cathodically passed electricity. This is two or three times less than the current yield quoted in the literature [7] for the separation of aluminum as a phase. The explanation may be that part of the aluminum is chemically dissolved by interacting with HBr formed by partial hydrolysis of the aluminum bromide. From the data in Fig. 3 we can estimate the rate of chemical solution of aluminum as about 0.2 C/cm^2·h, leading to almost complete disappearance of the arrest due to ionization of metallic aluminum on curve 2, which was recorded 1 h after the end of cathodic polarization. In addition, some of the aluminum is not extracted by the anode current and remains in the interior of the electrode owing to diffusion limitations. This can be seen from the fact that when the anode current is switched off, aluminum diffuses from the interior of the electrode to the aluminum-depleted surface layer, and the electrode potential gradually shifts toward negative values.

Thus our results lead us to the conclusion that, as suggested, cathodic implantation of aluminum into vanadium from aluminum bromide solution in xylene actually does take place. Cathodic implantation begins to occur at an appreciable rate on reaching the potential for deposition of aluminum as a phase, and takes place in parallel with the latter process. As well as a solid solution of aluminum in vanadium, one or two intermetallic compounds can also be formed during cathodic implantation.

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ADSORPTION OF CALCIUM AND BARIUM CATIONS ON A Pt/Pt ELECTRODE IN ALKALINE SOLUTIONS

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By measuring the electrical conductivities of solutions, the authors study the dependences of the adsorption of calcium cations ($\Gamma_{Ca^{2+}}$) and barium cations ($\Gamma_{Ba^{2+}}$) on the potential (φ_r) in alkaline solutions on a Pt/Pt electrode. They find that when $\varphi_r = 0$, $\Gamma_{Ca^{2+}} = 20\ \mu C/cm^2$ in $2 \cdot 10^{-3}$ N $Ca(OH)_2 + 3 \cdot 10^{-3}$ $Ca(ClO_4)_2$ solution, and when $\varphi_r = 0$, $\Gamma_{Ba^{2+}} = 22.5\ \mu C/cm^2$ in 10^{-3} N $Ba(OH)_2 + 4 \cdot 10^{-3}$ N $Ba(ClO_4)_2$; as the potential shifts toward the anodic side to $\varphi_r = 0.8$ V, they increase. In this range of φ_r, the values of $\Gamma_{Ca^{2+}}$ and $\Gamma_{Ba^{2+}}$ are independent of the direction of potential change. By means of charging and potentiodynamic curves the authors show that Ca^{2+} and Ba^{2+} ions do not appreciably alter the quantity of adsorbed hydrogen on platinum in alkaline solutions; the quantity of strongly bound hydrogen is reduced, but at the same time the quantities of hydrogen with medium or low binding energy increase somewhat. Adsorption of calcium and barium is accompanied by strengthening of the bonds of oxygen to platinum.

Adsorption of calcium and barium cations on a Pt/Pt electrode in alkaline solutions has been investigated [1] by means of radioactive indicators. It was found that* at $\varphi_r = 0.3$-0.4 V, on a reduced electrode the potential

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* The symbol φ_r denotes potentials referred to a reversible hydrogen electrode in the same solution.

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