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ANODIC DISSOLUTION OF NICKEL IN ELECTROLYTES BASED ON DIMETHYL SULFOXIDE AND ITS MIXTURES WITH WATER

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The anodic behavior of Ni in acid perchlorate solutions of DMSO were studied. It was found that the rate of anodic dissolution of Ni (i_a) in solutions of DMSO is several orders of magnitude lower than in other solvents (H_2O, DMF). It was suggested that the inhibition of the anodic reaction is associated with chemisorption of solvent molecules. It was established that i_a increases substantially when chloride ions and H_2O molecules are introduced into the solution, which is due to displacement of passivating DMSO molecules from the Ni surface by these particles. When the critical potential is reached, the dissolution of Ni proceeds with the formation of pitting. Under these conditions an increase in the Cl^- ion and H_2O content leads to a stronger activation of the electrode.

The limited number of systematic investigations on the mechanism of corrosion-electrochemical behavior of metals in various solvents [1, 2], the complexity of the nature of the interaction of molecules of the organic solvent with components of the medium [2, 3] and surface atoms of solid metals [4-12], as well as methodological difficulties that arise in conducting correct investigations in many nonaqueous media [13], are causes of the fact that the theoretical bases of the influence of the nature of the solvent on processes of dissolution and passivation of metals are as yet largely unformulated.

In this work the role of the solvent was investigated for the reaction of anodic dissolution of nickel in perchlorate solutions of DMSO containing various additions of chloride ions and water. It was calculated in this case that a comparison of the data on the kinetics of the ionization of nickel in a nonaqueous aprotic solvent (DMSO), differing sharply from water in solvating [3] and adsorption [6, 10, 14, 15] properties, with the data obtained in its mixture with H_2O and in other solvents [17], will permit the detection of certain principles of the influence of solvent molecules on the processes of anodic dissolution and passivation of nickel.

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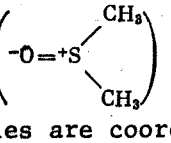
The method of preparation of the solutions and the performance of electrochemical measurements in nonaqueous solutions was described in [13]. The working samples in the form of cathodic deposits, possessing a readily reproducible surface, enriched with the face (100) (Fig. 1a), were produced by electrodeposition of nickel on a platinum base according to the procedure described in [16]. Nickel was determined in solution by the method of atomic-absorption spectrometry. The topography and composition of the surface layer of nickel were investigated with a scanning electron microscope and by x-ray spectral microanalysis. The potentials are presented relative to a saturated aqueous calomel electrode.

An analysis of the solution showed that at all the investigated potentials the anodic current i_a is equivalent to the rate of dissolution of nickel with the formation of Ni^{2+} ions. In anhydrous ($C_{H_2O} \leqslant 0.01$ mass %) perchlorate solution at potentials from −0.15 to +0.10 V, the rate of dissolution is low and depends little on the potential. More positive than some critical potential σ_p, the static anodic current density increases sharply (Fig. 2, curve 1). Measurements of the nonstatic current density indicate a change in the nature of the anodic process. Actually, until this value is exceeded, any sharp increase in σ leads only to a transitory flareup of the anodic current, followed by a fall to low static value, which is the usual for passive metals. If a potential more positive than σ_p is set, however, then after the initial flareup, a further monotonic rise in the current is observed, approaching the already mentioned limiting static value, which is usually characteristic of a process of surface activation. In this case the dissolution of the metal loses its uniform character, and pits are formed (Fig. 1b), which gives a basis for considering φ_p as the potential of pit formation.*

The introduction of additions of water into the perchlorate solution causes a substantial increase in i_a, especially in the range 0.3-3.0 M H_2O (Fig. 3, curve 1). At the same time, a large dependence of the rate of dissolution on the potential appears (Fig. 2, curves 2 and 3). Increasing the H_2O content at a constant composition of the remaining components of the medium leads to a contraction of the region of uniform dissolution of nickel as a result of a negative shift of φ_p. At a water concentration from 0.01 to 0.7 M, the following equation is correct: $\varphi_p = 0.02 - 0.03 \log C_{H_2O}$. As a result, by introducing water into the solution at a constant value of the potential ($\varphi = -0.10$ V), a transition from uniform (at low value of C_{H_2O}) to local dissolution of nickel (at sufficiently high C_{H_2O}) with an already discribed change in the nature of the curves of i_a vs τ can be observed. The passive state of nickel can be disrupted by the introduction into solution not only of water, but also of chloride ions. In the latter case the anodic curves (φ vs $\log i_a$) are strongly shifted in the negative direction along the potential axis. At comparable concentrations, chloride ions provide for a several orders of magnitude stronger acceleration of the anodic process than water (Fig. 3), as well as a large negative shift of φ_p. At Cl^- concentrations from 0.001 to $5 \cdot 10^{-2}$ g-ion/liter, the following function is in effect: $\varphi_p = -0.34 - 0.12 \log C_{Cl^-}$, which is evidence of strong activation of the nickel surface by chloride ions.

Thus, in contrast to the cases investigated earlier, of the dissolution of nickel in dimethylformamide and acetonitrile solutions [17] and of chromium in methanol solutions [18], where the introduction of the critical amounts of water produced a transition of the metal from the active to the passive state, in dimethyl sulfoxide solution the introduction of water leads to a depassivation of the metal. Such an unusual influence of the organic solvent and water can be explained if we take into consideration the structural peculiarities of the DMSO molecules  [19] and the nature of its interaction with the metallic cations. The DMSO molecules are coordinated with most metal cations (including nickel cations) by means of the oxygen atom, on which the excess negative charge is localized [20-22]. The formation of a Me-O bond leads to a substantial weakening and loss of the double character of the bond in the $O^-=S^+$ polar group [22]. On the other hand, in a number of studies [5, 6, 10, 14] the possibility of strong chemisorption of DMSO molecules on metallic surfaces has been established.

*In the case of sufficient exposure of the electrode in the region $\varphi > \varphi_p$, pits pass through the nickel and reach the platinum base (Fig. 1c). In these sites the electronic microprobe and scanning microscope permit the detection of nonmetallic inclusions on the surface of the substrate — complex compounds of silicon and sometimes aluminum oxides, typical of the platinum used. The possibility of the formation of pits in organic perchlorate solutions has been noted for a number of metals [5, 10].

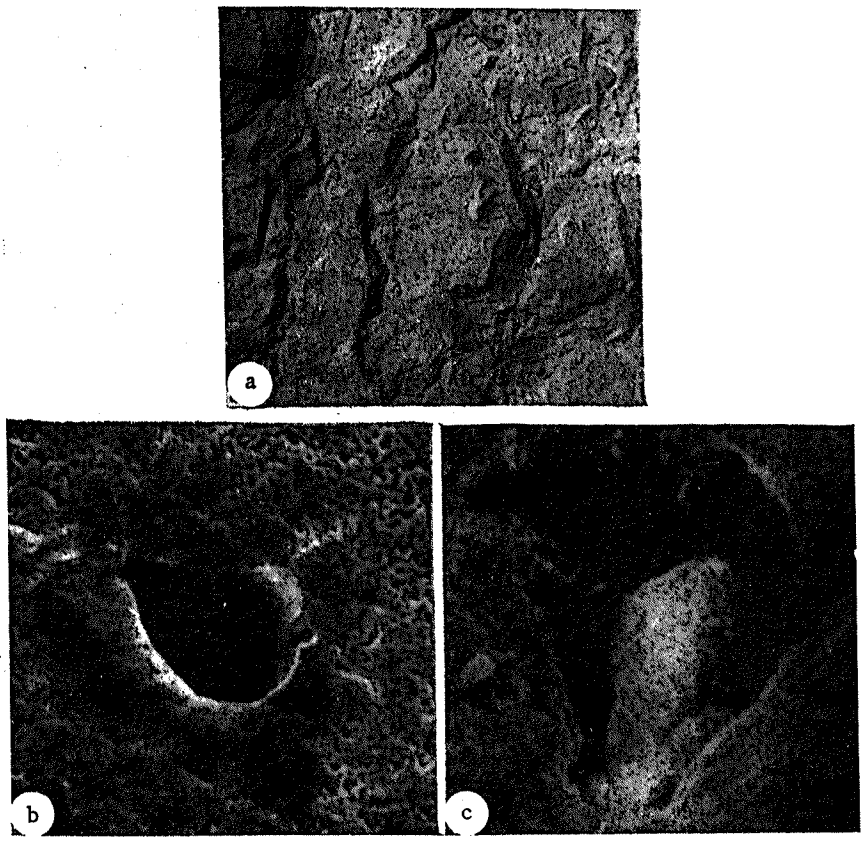


Fig. 1. Electron micrograph of the electrode surface: a) platinum–carbon replica of the initial surface (×20,000); b) pitting (×1680) formed at φ = 0.15 V, in DMSO + 1 M $NaClO_4$ + $1 \cdot 10^{-3}$ M $HClO_4$ + $1 \cdot 10^{-2}$ mass % H_2O; c) pitting (×2000) formed at φ = 0.10 V, in DMSO + 1 M $NaClO_4$ + $1 \cdot 10^{-3}$ M $HClO_4$ + 0.5 mass % H_2O.

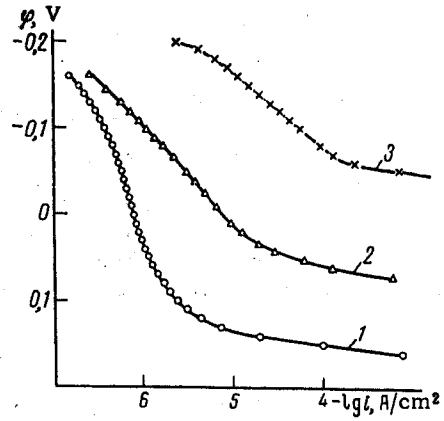


Fig. 2

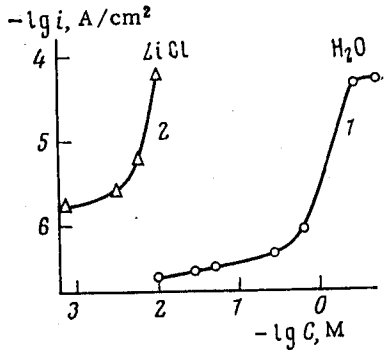


Fig. 3

Fig. 2. Polarization curves of the dissolution of nickel in DMSO + 1 M $NaClO_4$ + $1 \cdot 10^{-3}$ M $HClO_4$ as a function of the water concentration (mass %): 1) $1 \cdot 10^{-2}$; 2) 1.0; 3) 5.0.

Fig. 3. Dependence of the anodic current density on the water concentration (1) and chloride ion concentration (2) in DMSO + 1 M $NaClO_4$ + $1 \cdot 10^{-3}$ M $HClO_4$ at φ = –0.10 V.

Considering these data, it can be assumed that the adsorption of DMSO molecules on nickel is accompanied by a splitting out of an oxygen atom from the molecules of the organic solvent (or a strong deformation of the O=S bond), as a result of which a compound of the type of $(Me-O)_{ads}$, responsible for passivation, is formed on the surface. The catalytic influence of the H_2O molecules and chloride ions in DMSO solutions is evidently associated with the direct interaction of these particles with nickel atoms with the formation of electrochemically active surface complexes, for example, $(NiOH)_{ads}$ and $(NiCl)_{ads}$, which participate in various stages of ionization of the metal [23-26].* It should be assumed here that in the region of potentials in which there is a passivation of nickel on account of its interaction with adsorbed molecules of the organic solvent, the passivating influence of the oxygen of water is not yet capable of appearing. Thus, the kinetics of the anodic dissolution of nickel in the investigated solutions should be entirely determined by competitive adsorption of molecules of both solvents and the surface-active anion on the surface of the electrode.

In contrast to DMSO and organic solutions that do not passivate nickel (DMF, AN), the interaction of the solvent with metal cations occurs in most cases through the nitrogen atom, on which a certain excess negative charge of the polar group N≡C is localized [27]. It can be assumed that in the adsorption of such solvents, the interaction of the surface nickel atoms with charged nitrogen atoms does not lead to the formation of particles capable of retarding the ionization process, and passivation becomes possible only in the presence of a definite amount of oxygen of water. The competing influence of the passivator (H_2O) and activator (halide ions) in such solvents is manifested in an opposite influence of these particles on the potential of pitting: with increasing C_{H_2O}, the latter becomes more positive, while with increasing C_{Cl^-} it becomes more negative [5, 18, 28, 29]. In DMSO solutions, both additives catalyze the process of dissolution of nickel, displacing φ_p in the negative direction. A more detailed consideration of the role of the solvent molecules and anions in the processes of dissolution and passivation of nickel in the investigated media will require an investigation of the competitive adsorption of the components of the solution on the surface of nickel.

CONCLUSIONS

1. The possibility of passivation of nickel in anhydrous dimethyl sulfoxide solutions was established. It was hypothesized that the passivation is a consequence of adsorption interaction of the surface atoms of nickel with the oxygen atoms of dimethyl sulfoxide.

2. The passive state of nickel is disrupted in the presence of small quantities of H_2O and chloride ions. On the basis of the dependence of the rate of anodic dissolution on the composition of the solution, it was concluded that the determining factor in processes of dissolution is competitive adsorption of solvent molecules and catalysts on the anodic process (H_2O, Cl^-) on the nickel surface.

3. When a definite potential is reached in anhydrous perchlorate solutions of DMSO, there is a local activation of passive nickel, which is facilitated in the presence of water and chloride ions. Pits are formed on the surface of galvanic deposits of nickel primarily at sites corresponding to nonmetallic inclusions in the platinum substrate.

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*The acceleration of anodic dissolution with increasing C_{H_2O} cannot be explained by a stronger solvation of Ni^{2+} ions in water-rich mixtures of DMSO–H_2O. The activity of the metallic cations in DMSO is several orders of magnitude lower than in H_2O [3], i.e., DMSO possesses substantially greater solvating capacity in comparison with water.

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SODIUM SALTS OF ORGANIC ACIDS AS INHIBITORS OF THE CORROSION OF ALUMINUM AND ITS ALLOYS

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It was shown that sodium oleate in nonalkaline solutions effectively inhibits both the anodic and the cathodic reactions of aluminum. Its joint use with dinitrobenzoate ensures an effective suppression of pitting corrosion of aluminum.

Pitting on aluminum and its alloys is the main form of corrosion breakdown in neutral and weakly alkaline solutions. For its prevention, it is recommended that salts of certain organic acids be introduced into the corrosion medium [1, 2].

In this work we investigated the inhibition of the corrosion of aluminum (AV 000) and its alloys (AMg6, V95, D16) by salts of benzoic (BN), 3,5-dinitrobenzoic (DBN), phthalic (PN), and oleic acids.

A mechanically polished electrode, degreased with acetone and set up horizontally, with a working surface of 0.5 cm^2, was exposed for 1 h before the beginning of the polarization measurements to establish the potential E_{st}. The potentiodynamic curves were taken at a rate of displacement of the potential 2 mV/sec with a model 170 electrochemical system of the PAR (United States) and recorded on a two-coordinate automatic recording device. The potentials were measured relative to a silver chloride electrode and recalculated to the normal hydrogen scale.

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