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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Electrochemical Deposition of Tellurium from $TeCl_4$ Solutions in Aprotic Solvents

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Abstract—Electrolysis of 0.01–0.1 M $TeCl_4$ solutions in dimethyl sulfoxide, dimethylformamide, and acetonitrile was studied in the temperature range 20–60°C. The microscopic structure of cathode deposits was analyzed.

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The electrochemical deposition of tellurium has been studied in most detail in acid [1, 2] and alkaline [1, 3] aqueous solutions containing hydrated cations $[Te(H_2O)_n]^{4+}$ and oxo anions TeO_3^{2-}, respectively. The instability of water at elevated electrode potentials and the tendency of tellurium(IV) salts to undergo hydrolysis result in a number of side electrochemical and chemical reactions, which leads to difficulties in obtaining pure cathode deposits of tellurium.

Use of organic solvents makes it possible, in some cases, to eliminate these drawbacks and to obtain tellurium in a wide range of potentials from solutions of simple salts [4, 5].

This study, concerned with the electrochemical deposition of tellurium from organic aprotic solvents, continues the systems analysis of the electrochemical behavior of metals in the nonaqueous medium specified [6, 7].

EXPERIMENTAL

Electrode processes were studied in 0.01–0.1 M $TeCl_4$ solutions in dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and acetonitrile (AN) in the temperature range 20–60°C. The organic solvents were of chemically pure grade, and $TeCl_4$ was synthesized by the procedure described in [8]. A PI-50-1.1 potentiostat with a standard electrochemical cell, platinum auxiliary electrode, and silver-chloride reference electrode was used.

Polarization curves were measured at a potential sweep rate of 2.0 mV s^{-1}. The cathode processes were studied using a graphite rod with a diameter of 6 mm and lateral surface insulated with a fluoroplastic tape. The anode processes were examined with tellurium press-fitted in a fluoroplastic cartridge. Before each experiment, graphite samples were trimmed with a fine-grained emery paper, polished with a velvet cloth, and washed with ethanol. To study the morphology of cathode deposits, the electrolysis was carried out with a soluble tellurium anode. Tellurium was deposited onto the edge surface of the graphite rod. The morphology of the anode surface was examined on a cleaved surface of metal lumps. In all cases, the electrolysis was carried out at a constant potential without stirring until a coating with an average thickness of 5 μm was obtained. The resulting cathode deposits remaining on a graphite sample, and anodically etched tellurium plates were washed with an appropriate aprotic solvent and acetone, dried in air at 60°C, and examined with a REMMA-102-02 scanning electron microscope.

A 200–300-mV plateau is observed in the cathodic polarization curves obtained in DMSO (Fig. 1a) and DMF (Fig. 1b) solutions, which points to a strong polarization of tellurium. In acetonitrile solutions (Fig. 1c), the polarization is less noticeable. In addition, the currents in AN considerably exceed those in DMSO and DMF at equal cathode potentials. This is primarily attributable to the fact that the donor numbers (DN) of DMSO and DMF markedly exceed the donor numbers of AN (DN_{SbCl_5} for DMSO, DMF, and AN are 29.8, 27.0, and 14.1, respectively [9]). Therefore, the stability of solvated tellurium(IV) cations in dimethyl sulfoxide and dimethylformamide

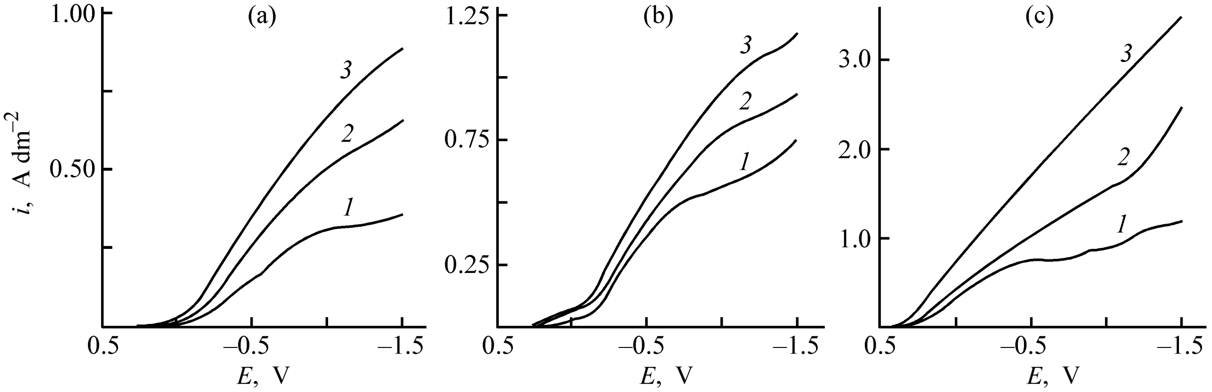

Fig. 1. Cathodic polarization curves obtained in $TeCl_4$ solutions in (a) dimethyl sulfoxide, (b) dimethylformamide, and (c) acetonitrile at different temperatures (c_{TeCl_4} = 0.05 M). (*i*) Current density and (*E*) potential; the same for Fig. 3. Temperature (°C): (*1*) 20, (*2*) 40, and (*3*) 60.

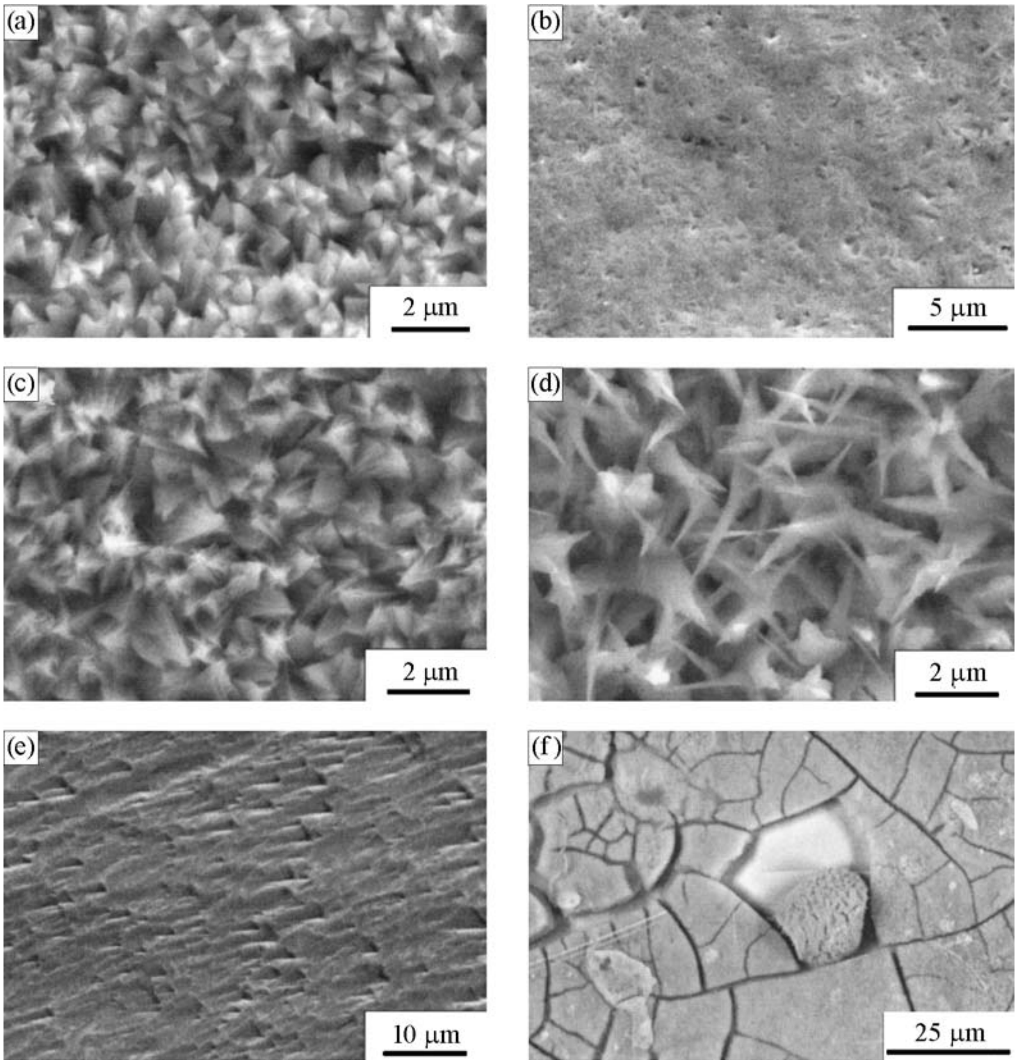

Fig. 2. Morphology of (a, d) tellurium cathode deposits on a graphite substrate and (e, f) tellurium surfaces after anodic dissolution in 0.005 M $TeCl_4$ solutions in (a, d, e) DMSO, (c, f) DMF, and (d) AN at different potentials. Potential (V): (a) –0.5; (b)–(d) –1.0; (e, f) 1.0. Magnification: (a, c, d) 10000; (b) 5000; (f) (COMPO mode) 1200.

solutions is higher than that in acetonitrile solutions. Furthermore, the solvents specified strongly differ in viscosity: 2.003, 0.796, and 0.328 cP for DMSO, DMF, and AN, respectively [9], which is also an important factor of electrode polarization.

The increase in the cathode currents with temperature does not exceed 25% per 10° (Fig. 1). This indicates that the cathodic deposition of tellurium occurs under the diffusion control. As the concentration of $TeCl_4$ increases from 0.01 to 0.1 M, the cathode currents grow virtually proportionally.

In deposition of compact tellurium from DMSO, DMF, and AN solutions, comparatively solid and uniform coatings (Fig. 2) are formed. At low cathode potentials, crystallites with distinct configuration (Fig. 2a) are formed. As the potential (current density) increases in the DMSO medium, there occurs a kind of flattening and branching of the crystallites (Fig. 2b), which is manifested in that the coating becomes smoother and more lustrous. The tendency toward smoothing of the surface of a tellurium coating with increasing cathode potential (current density) is also observed in DMF solutions. However, this is mostly due to a decrease in the size of the crystallites and to an increase in their packing density (Fig. 2c). In AN, no smooth films are deposited (Fig. 2d). In this case, as the cathode potential increases, the crystallites decrease in size and coarsely crystalline dark gray coatings turn into finely crystalline black velvety crystals.

As demonstrated by the results of the study, the nature of a substrate chemically indifferent toward tellurium affects the morphology of a cathodic deposit only slightly. For example, the microscopic structure of the tellurium coating and the shape and sizes of crystallites on titanium and graphite samples differ only slightly in identical solvents at close cathode current densities (potentials).

The anodic dissolution of tellurium in DMSO and DMF solutions, as well as the cathodic deposition, occurs with polarization (Fig. 3, curves *1* and *2*). At potentials of 0.3–1.5 V, the anode currents depend virtually linearly on potentials, which points to an unhindered dissolution of tellurium.

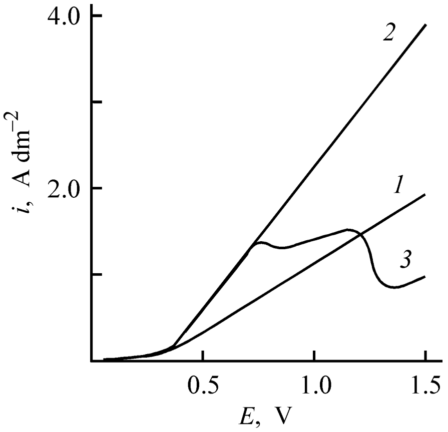

Fig. 3. Anodic polarization curves obtained on tellurium in 0.005 M $TeCl_4$ solutions in (*1*) DMSO, (*2*) DMF, and (*3*) AN at 40°C.

Comparison of the initial surface tellurium with that after the anodic dissolution in DMSO solutions of $TeCl_4$ (Fig. 2e) shows that crystallites are etched-out in electrolysis. In this case, the surface becomes corrugated, but single-phase. In DMF solutions, a new phase appears in electrolysis on the tellurium surface (Fig. 2f), as indicated by electron-microscopic studies in the COMPO. According to the energy-dispersion X-ray microanalysis, this phase contains chlorine. Thus, the anodic dissolution of tellurium in DMF occurs via formation of a solvated salt film. A similar pattern is observed in acetonitrile solutions. However, the film formation in DMF does not passivate the anode, as can be seen from the shape of the polarization curve (Fig. 3, curve *2*), whereas in AN, tellurium is passivated (Fig. 3, curve *3*).

CONCLUSIONS

(1) In dimethyl sulfoxide and dimethylformamide solutions of $TeCl_4$, the cathodic deposition of tellurium occurs with an appreciable polarization.

(2) Smooth films are formed on a graphite substrate in dimethylformamide, and smooth and lustrous coatings, in dimethyl sulfoxide. In acetonitrile, tellurium is deposited in the form of velvety coatings.

(3) In dimethyl sulfoxide solutions of $TeCl_4$, there occurs uniform electrochemical dissolution of tellurium, without accumulation of anodic products on the surface. This makes it possible to use soluble anodes in deposition of tellurium films in dimethyl sulfoxide.

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