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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Morphology of Tellurium Electrolytically Deposited in a Pulsed Mode

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Abstract—Morphology of tellurium deposits produced by pulsed electrolysis of 0.005–0.05 M $TeCl_4$ solutions in dimethyl sulfoxide was studied. The effect of the $TeCl_4$ concentration and pulsed current parameters on the structure of electrolytically deposited tellurium films was examined.

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Pulsed electrolysis is one of the most efficient ways to form the structure of metal and alloy deposits [1–4]. This is also a promising method for obtaining nanosize dispersed materials [1, 5, 6]. Most of studies of the pulsed deposition mode refer to aqueous solutions, and only those carried out in the very recent years, to organic [4, 7] or aqueous-organic solvents [1]. Some of organic solvents and, especially, aprotic solvents are distinguished by high donor properties and electrochemical stability [6], as well as by indifference toward numerous metals. This enables deposition of metals at high potentials and provides formation of a stable morphology of deposits, without side cathodic reactions.

This study, devoted to deposition of tellurium by electrolysis of $TeCl_4$ in an organic aprotic solvent dimethyl sulfoxide (DMSO) with a pulsed current, proceeds with systematic analyses of the electrochemistry of tellurium [8] and other metals [6, 7] in a nonaqueous medium.

EXPERIMENTAL

Tellurium was deposited in a 50-cm^3 thermostated three-electrode glass electrolyzer in a 0.005–0.05 M solution of $TeCl_4$ in DMSO at temperatures of 20–60°C. Tellurium tetrachloride was synthesized by a procedure described in [9] and dissolved in DMSO of chemically pure grade. The edge of a graphite rod 6 mm in diameter served as the working electrode. Its nonworking surface was insulated with a fluoroplastic tape. Prior to each experiment, the working surface of the electrode was trimmed with fine emery paper, polished with a velvet fabric, and washed with isopropanol. The role of the anode was played by lump tellurium in a fluoroplastic basket with a platinum current lead. The potentials are given relative to a saturated silver chloride electrode placed in a glass vessel with a saturated quinoline solution of KCl and connected to the electrolyzer by a Luggin–Haber capillary. An IPC-Pro potentiostat was used in electrolysis in steady-state and pulsed modes. The potential pulses used were of rectangular shape, the pulse and pause widths, τ_{pu} and τ_{pa}, were 0.02–5.0 s. The deposits obtained were washed, without being removed from the graphite electrode, with DMSO and then with isopropanol, dried in air at 60°C, and examined with REMMA-102-02 and EVO 40XVP scanning electron microscopes.

It has been shown previously that a steady-state electrolysis of $TeCl_4$ in dimethyl sulfoxide solutions yields smooth and shining tellurium films [8]. However, dispersed tellurium starts to be formed in a 0.05 M solution of $TeCl_4$ in DMSO at $E_c > |–1\ V|$. It was found that use of a pulse mode makes it possible to obtain tellurium films at more negative potentials (up to –2.0...2.5 V). At the same time, the sizes of crystalline grains constituting a film and their configurations and packing modes are strongly different. For example, the size of crystallites formed in the dc mode is 0.7–1.1 μm (Fig. 1a), and that for the pulsed mode, 0.2–0.4 μm (Fig. 1b). Possibly, this is due to adsorption of electron-donor DMSO molecules

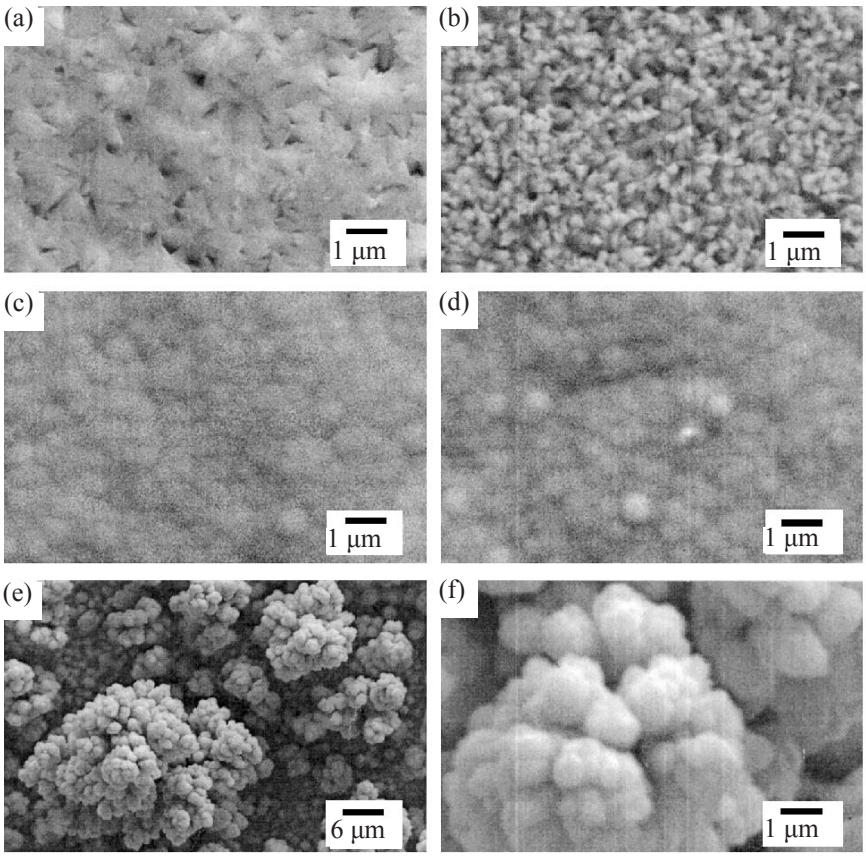

Fig. 1. Morphology of tellurium electrolytically deposited in (a) steady-state and (b) pulsed electrolysis modes (τ_{pu} = 2 s, τ_{pa} = 5 s). *E* (V): (a, b) –0.75, (c), –1.25, and (d–f) –2.5.

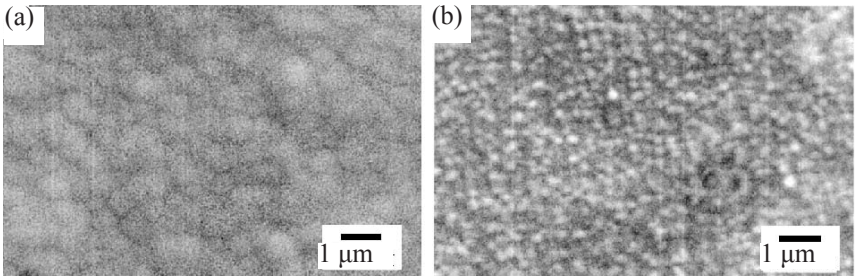

Fig. 2. of tellurium deposited in a pulsed mode from (a) 0.05 and (b) 0.005 M $TeCl_4$ solutions in DMSO (*E* = –2.0 V; τ_{pu} = 2 s, τ_{pa} = 5 s).

on active centers during a pause between pulses, which favors appearance of new nuclei during the subsequent pulse. This is also favored by the diffusion of tellurium ions toward the cathode in the absence of an external current. These conditions lead to nucleation in any new cycle and, accordingly, to a decrease in the crystallite size.

As the cathodic potential increases from –0.75 (i_{av} = 0.123 A dm^{-2}) to –1.25 V (i_{av} = 0.24 A dm^{-2}) at constant pulsed current parameters, temperature, and solution concentration, the size of crystallites becomes approximately two times larger (Figs. 1b, 1c). An also noticeable change is observed for the configuration of grains, which become rounded and densely packed. This can be attributed to a rise in the average cathode current density upon an increase in the potential. In addition, the influence exerted by dimethyl sulfoxide becomes more pronounced because its molecules are localized near the electrode surface upon discharging of tellurium solvates:

$$[Te(DMSO)_n]^{4+} + 4e \rightarrow Te_{ad} + n\text{DMSO}.$$

The subsequent increase in the cathodic potential

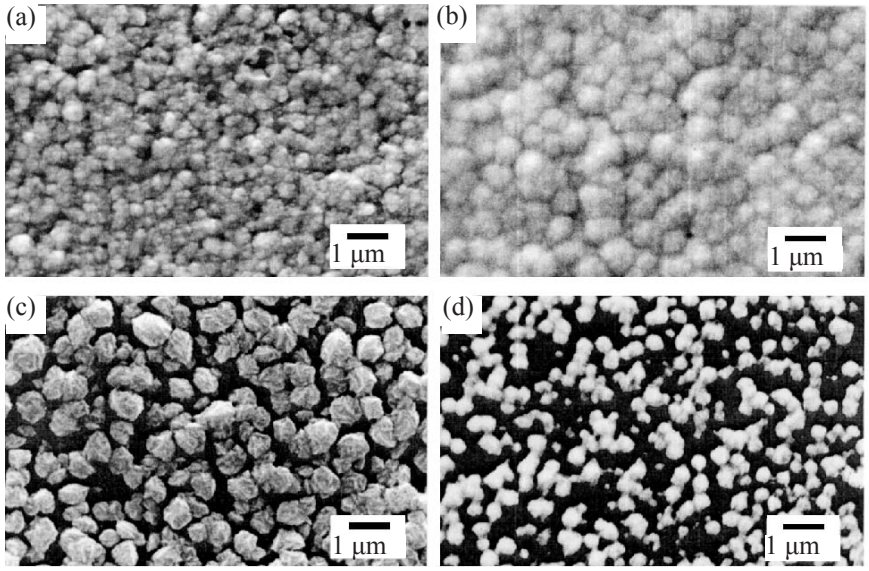

Fig. 3. Morphology of tellurium deposited in a pulsed mode (E = –2.0 V). Electrolysis duration (s): (a–c) 1000 and (d) 200. τ_{pu}/τ_{pa} (s/s): (a) 1/5, (b) 0.2/0.5, and (c, d) 0.02/0.05.

to –2.5 V (i_{av} = 0.46 A dm^{-2}) has almost no effect on the crystallite size (Fig. 1d), but gives rise to dendrites along the perimeter of the cathode edge (Figs. 1e, 1f), which occurs because the limiting diffusion current is reached.

Variation of the electrolyte temperature within the range 20–60°C has no significant effect of the grain size and morphology of the deposits.

In the case of a pulsed current, the size of deposit particles is strongly affected by the $TeCl_4$ concentration. For example, the grain sizes in deposits obtained from 0.05 and 0.005 M solutions under otherwise identical conditions are 0.5–0.8 and 0.1–0.3 μm, respectively (Fig. 2). The possible reason is that, as the content of ions decreases, the concentration polarization becomes stronger, as also does the throwing power of the electrolyte.

It is known that the morphology of crystallites can be controlled by varying pulsed current parameters (width and repetition frequency of pulses) [3]. It was found that, as the pulse width is reduced from 2 (Fig. 2a) to 1 s (Fig. 3a) at a constant pause duration of 5 s, the particle size decreases from 0.5–0.8 to 0.3–0.6 μm. Such a noticeable change is due to the prevalence of the nucleation rate over that of nucleus growth as a result of passivation of crystallization centers and a more uniform distribution of the $TeCl_4$ concentration at the cathode surface during the pause.

The pulse repetition frequency exerts a specific influence in deposition. As the frequency increases from 0.143 Hz (τ_{pu} = 2 s, τ_{pa}= 5 s) (Fig. 2a) to 1.43 (τ_{pu} = 0.2 s, τ_{pa} = 0.5 s) and 14.3 Hz (τ_{pu} = 0.02 s, τ_{pa} = 0.05 s) (Figs. 3b and 3c), the size of crystallites remains nearly unchanged, but morphological deviations appear. The grains become more faceted and the packing density noticeably decreases. This is due to a decrease in the adsorption of highly polar DMSO molecules and to diffusion of the reactants.

In aqueous solutions at high pulsed current frequencies, the morphologies of deposits formed in the steady-state and pulsed modes differ only slightly [3]. Apparently, the same will occur in organic aprotic solvents. As evidence in favor of this conclusion can serve the noticeable increase in the crystallite size in a prolonged growth of a film under the influence of a high-frequency pulsed current. If, for example, the deposition duration is made shorter, the crystallite size in the deposit must accordingly decrease. Indeed, as the electrolysis duration is diminished by a factor of 2 (f = 14.3 Hz), the crystallite size decreases from 0.5–0.8 μm (Fig. 3c) to 0.1–0.6 μm (Fig. 3d), as in the case of a steady-state electrolysis.

CONCLUSIONS

(1) Compared with a steady-state electrolytic deposition of tellurium, that in a pulsed mode makes

it possible to obtain tellurium films at more negative potentials (up to –2.0...2.5 V) and to make the crystallite size 2–3 times smaller.

(2) The size of crystallites in the tellurium deposit can be diminished by lowering the $TeCl_4$ concentration from 0.05 to 0.005 M and by reducing the pulse width from 2 to 1 s at a constant pause duration of 5 s. Conditions in which tellurium deposits with grain sizes of 0.1 to 1 μm can be obtained are recommended.

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