Electroplating With Tungsten From Pyrosulphate-Containing Oxide Melts.

V. Malyshev, A. Gab, I. Astrelin, M. Gaune-Escard*
National Technical University of Ukraine “Kyiv Polytechnical Institute”
Peremoga ave, #4, 03056, Kyiv, Ukraine
*Ecole Polytechnique Universitaire de Marseille
CNRS UMR 6595, IUSTI, Dept. Mecanique & Energetique, Technopole de Chateau-Gombert, 5 Rue Enrico Fermi, 13453 Marseille cedex 13, FRANCE

Electromotive forces (EMFs) of the following electrochemical circuits were measured:

Pt, $O_2|Na_2WO_4$- $Na_2S_2O_7||Na_2WO_4$-$0.2W0_3|O_2$, Pt, (1)
$W|Na_2WO_4$-$Na_2S_2O_7||Na_2WO_4$-$0.2WO_3|O_2$, Pt. (2)

The decrease in the activity of O^{2-} ions upon the introduction of $S_2O_7^{2-}$ ions in a chloride-tungstate melt is confirmed by the increase in the equilibrium potential of the oxygen electrode with an increase of the $S_2O_7^{2-}$ concentration. In the presence of $S_2O_7^{2-}$ ions in a Na_2WO_4 melt, the formation of $W_2O_7^{2-}$ takes place:

The EMF of a circuit (2) was measured in a $Na_2S_2O_7$ concentration range from 1.0 to 10.0 mol %. At a pyrosulphate concentration lower than 1.0 mol %, tungsten insubstantially corrodes (at a corrosion rate of 3 to 5 x 10^{-7} g/(m^2 h)). At a $Na_2S_2O_7$ concentration higher than 1.0 mol %, the corrosion is not practically observed. An equation for the attained steady-state potential of a tungsten electrode can be written in the form of equilibrial potential:

$$4W_2O_7^{2-} + 6e \leftrightarrow W + 7WO_4^{2-} \qquad (3)$$

According to voltammetric data the proportionality of the limiting current to the concentration of sodium pyrosulphate, the constancy of the $i_{p/2}$ /$V^{1/2}$ratio, and the value of the mass-transfer constant, which is 8.3 to 9.5 x 10^{-5} cm/s for the steady-state waves, indicate the fact that the electrode process is limited by the diffusion of electrochemically active particles to the electrode. Ditungstate ions, become electrochemically active in the summary electrode process (3). Under the steady-state conditions, the slope of the *E—log(*i_d - I) dependence varies from 38 to 42 mV at different $Na_2S_2O_7$ concentrations, while the number *n* of electrons, which are transferred in the electrode process, is 5.8 ± 0.3. This means that the charge transfer stage Eq. (3) is reversible. The number of electrons, which is determined from the half-widths of the peaks in non-steady-state voltammograms according to Matsuda-Ayabe criterion for the $Na_2S_2O_7$ concentrations lower than 10 mol % and the polarization rates from 0.04 to 0.2 V/s, equals 5.9 to 6.1.

A condition of the good cohesion between a coating and a substrate is the more positive value of the substrate's free-corrosion potential compared to the deposition potential. Therefore, for estimating the possibility of applying tungsten coatings to various substrates, we measured steady-state potentials of copper, nickel, St3 steel, stainless steel, and titanium in the chosen electrolytes. In a Na_2WO_4-$Na_2S_2O_7$ melt, the steady-state potentials of all the electrodes are much more positive than the deposition potential of tungsten, and good adherent coatings can be obtained on all of them.

Tungsten coatings in a Na_2WO_4- $Na_2S_2O_7$ melt form at a sodium pyrosulphate concentration from 1.5 to 10.0 mol %. Above this limit, along with tungsten, its bronzes form, and the deposit soon begins to grow as dendrites.

Continuous tungsten coatings were obtained at a temperature from 1023 to 1123 K and a current density of up to 40 A/dm^2. At a temperature below 1023 K, only thin (up to 15 or 20 µm) tungsten layers are formed. At a current density higher than 40 A/dm^2, highly dispersed tungsten powders with a specific surface area of 40 to 50 m^2/g form.

Adherent, continuous, and nonporous coatings were obtained from the above electrolytes at temperatures of 923 and 1173 K and current densities of 1 to 15 and 3 to 25 A/dm^2, respectively. The grains size in the deposit has a minimum depending on the current density, and above 25 A/dm^2, the crystallites become substantially larger, while the surface grows rougher. Finally, the deposit transforms into dendrites. At a current density lower than 2.5 A/dm^2, the corrosion rate of a substrate is too large, and no adherent coating is formed. The deposition rate of tungsten in the studied range of current densities is 20 to 45 µm/h in an oxide electrolyte. The current efficiency of a tungsten coating is up to 95%. As the duration of electrolysis increases, the current efficiency drops.

In oxide melts, the coatings were obtained also on steels St3, 15X, 45, 40X, and 30XFA (according to the Russian State Standard GOST 1050-74), instrumental steels Y7, Y10, and P6M5 (according to GOST 1435-74), hard alloys BK6 and BK20 (according to GOST 19265-73), and copper-or nickel-plated titanium.

Profilometric investigation shows that, as the deposit thickens, its single-phase fine-crystalline structure transforms into a coarser one. We tried to prevent the formation of a coarse-grain structure by applying reversal conditions of electrolysis. The duration ratio of the cathodic to anodic period was varied from 15 to 50 at a duration of the anodic period from 0.5 to 3.0 s, and the anodic current density was changed from 20 to 50 A/dm^2. The following conditions are optimal for a Na_2WO_4—5 mol % $Na_2S_2O_7$ electrolyte at 1173 K: i_c = 15 A/dm^2, i_a = 30 A/dm^2, τ_c = 25 s, and τ_a = 1.5 s. In this case, relatively smooth coatings of a thickness of up to 0.5 mm were obtained at the cathode.

The microhardness does not change across the coating and equals 460 to 485 kgf/mm^2. The diffusional area of 5 to 20 µm, revealed with the x-ray spectral microanalysis of the cross sections of a specimen, indicates that there is a mutual diffusion of the elements of the coating and the substrate, which provides the proper adherence of the coating. The continuity of the transition from the coating to the substrate was confirmed by stereoscanograms of spallings of the specimens, which concurrently showed a pronounced columnar structure of the deposit.

The specimens of steel 45 with a tungsten coating were thoroughly tested in a friction pair with a quenched steel 45 counterbody. As a result of the plating, the wear resistance increased by a factor of 4.5 to 5.7.

The specimens of steel 45 with tungsten coatings were tested for abrasive resistance in an electrocorundum 100-µm fraction at a load of 52 ± 0.25 N. Due to the coating, the abrasive resistance increased 2.5 to 4.3 times.

This work was supported in part by Ministry of education and science of Ukraine in the framework of Ukrainian-France program “Dnipro” by the project No M/353-2003.