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EXTENDED ABSTRACT

Plasma electrolytic oxidation of metals*

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Abstract: The results of investigation of the plasma electrolytic oxidation (PEO) process on some metals (aluminum, titanium, tantalum, magnesium and zirconium) were presented. The whole process involves anodizing metals above the dielectric breakdown voltage, when numerous micro-discharges are generated continuously over the coating surface. For characterization of the PEO process, optical emission spectroscopy and real-time imaging were used. These investigations enabled the determination of electron temperature, electron number density, spatial density of micro-discharges, the active surface covered by micro-discharges, and the dimensional distribution of the micro-discharges at various stages of the PEO process. Special attention was focused on the results of a study of the morphology, and the chemical and phase composition of oxide layers obtained in the PEO process on aluminum, tantalum and titanium in electrolytes containing tungsten. Physicochemical methods: atomic force microscopy (AFM), scanning electron microscopy (SEM-EDS), X-ray diffraction (XRD) analysis, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy served as tools for examining the obtained oxide coatings. In addition, the application of the obtained oxide coatings, especially the application of TiO₂/WO₃ coatings, in photocatalysis was discussed.

Keywords: plasma electrolytic oxidation; micro-arc oxidation; micro-discharges; oxide coatings; optical emission spectroscopy.

Plasma electrolytic oxidation (PEO), also called micro-arc oxidation (MAO) or anodic spark deposition (ASD), is an economic, efficient, and environmentally benign technology capable of producing a stable oxide coating on the surface of lightweight metals (aluminum, magnesium, zirconium, titanium, tantalum, *etc.*) or metal alloys.^{1,2} The oxide coatings have controllable morphology and composition, excellent bonding strength with the substrate, good electrical and ther-

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mal properties, high microhardness, and high-quality wear and corrosion resistance.

The PEO process is coupled with the formation of plasma, as indicated by the presence of micro-discharges on the metal surface, accompanied by gas evolution.^{3,4} Various processes, including chemical, electrochemical, thermodynamic, and plasma-chemical reactions, occur at the discharge sites, due to increased local temperature (10^3 to 10^4 K) and pressure ($\approx 10^2$ MPa). These processes are responsible for modifying the structure, composition, and morphology of obtained oxide coatings. The oxide coatings formed by the PEO process usually contain crystalline and amorphous phases with constituent species originating from both the metal and electrolyte.

Micro-discharge phenomena are important characteristics of the PEO process. Given the liquid environment, optical emission spectroscopy (OES) is the most convenient technique for characterization of the micro-discharges appearing during the PEO process. OES in the visible and near UV spectral region was not only used for identification of species present in the investigated systems, but also for determination of important parameters of these systems.⁵⁻¹¹ The results of relative line intensity measurements of species originating in the substrate or in the electrolyte were employed to determine the electron temperature.^{5,6,8} Spectral line shape analysis of the hydrogen Balmer lines was used to estimate the electron number density.^{5,9} The molecular vibrational temperature was determined from the $B^2\Sigma^+ - X^2\Sigma^+$ emission transition of AlO,¹⁰ and the $B^1\Sigma^+ - X^1\Sigma^+$ emission transition of MgO.¹¹ Real-time imaging showed that the spatial density of micro-dischargers was the highest in the early stage of the PEO process, while the percentage of oxide coatings area covered by active discharge sites decreases with PEO time.^{7,9,12}

The results of an investigation of the PEO process on aluminum, titanium, and tantalum in tungstate electrolytes (12-tungstosilicic acid, 12-tungstophosphoric acid, and sodium tungstate) were presented in the lecture,¹²⁻¹⁶ because tungsten-containing oxide layers have extensive catalytic, semiconducting, and corrosion-resistant properties. It was shown that the outer layer of oxide coatings formed by PEO in tungstate electrolytes was tungsten bronze. In addition, it was shown that PEO of titanium in 12-tungstosilicic acid is an economic and efficient process for forming TiO_2/WO_3 coatings with enhanced photocatalytic activity, compared to that of pure TiO_2 .¹⁶

ИЗВОД

ПЛАЗМА ЕЛЕКТРОЛИТИЧКА ОКСИДАЦИЈА МЕТАЛА

СТЕВАН СТОЈАДИНОВИЋ

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У овом предавању су приказани резултати истраживања плазма електролитичке оксидације (PEO) метала (алуминијума, титана, тантала, магнезијума и цирконијума). Процес се заснива на анодизацији метала изнад напона диелектричног пробоја оксидног слоја и карактерише га појава микропражњења на целој површини метала. Представљени су резултати истраживања феномена PEO методама оптичке емисионе спектроскопије и праћењем догађаја у реалном времену. Овим истраживањима је омогућено одређивање електронске температуре плазме формиране на местима микропражњења, електронске густине плазме, просторне густине микропражњења, активне површине обухваћене микропражњењима и димензионалне дистрибуције величина микропражњења у различитим етапама PEO процеса. Посебна пажња је фокусирана на резултате истраживања морфологије, хемијског и фазног састава оксидних слојева добијених PEO процесом на алуминијуму, танталу и титану у електролитима који садрже волфрам. Карактеризација добијених површина је вршена физичко хемијским методама: AFM микроскопијом, SEM-EDS микроскопијом, рентгенском структурном анализом, фотоелектронском и Рамановом спектроскопијом. Дискутована је и примена добијених оксидних структура, нарочито примена TiO_2/WO_3 структура у фотокатализи.

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