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Comparison of structural, mechanical and corrosion properties of $(Ti_{0.68}W_{0.32})O_x$ and $(Ti_{0.41}W_{0.59})O_x$ thin films, deposited on TiAlV surface by electron beam evaporation

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ABSTRACT

In this paper, comparative studies of the structural, mechanical and corrosion properties of TiO_2-WO_3 thin films, with different contents of WO_3, have been investigated. The thin films were formed using the electron beam evaporation method, on the Ti6Al4V surface. After the deposition process both thin films were additionally annealed at 1073 K in a computer-controlled Nabertherm tubular furnace in an ambient atmosphere.
The structural characteristics of the thin films obtained, before and after the annealing process, were examined using SEM and XRD measurements. The mechanical properties of the coatings were determined by nanoindentation measurements. The corrosion properties of the thin films were determined by an analysis of the voltammetric curves.
The results obtained show that the layer with the higher content of tungsten – $(Ti_{0.41}W_{0.59})Ox$ annealed at 1073 K is characterised by the best mechanical and corrosion properties from all tested samples. The hardness obtained for this sample was equal to 14.9 GPa, and was about four times higher than the value obtained for the same sample before the annealing process, and almost one and half times higher than the value obtained for the annealed sample with a lower content of tungsten. In addition, the value of corrosion current density for this sample was equal to $6.02 \cdot 10^{-9}$ A/cm^2 and was lower than the value obtained for the same sample before the annealing process. This indicates that after the annealing process the mechanical and corrosion properties of the $(Ti_{0.41}W_{0.59})O_x$ thin film improved, as compared with the layer with the lower content of tungsten, for which the corrosion properties after the annealing process degraded.

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1. Introduction

Titanium dioxide, also known as titania, is one the most investigated transition metal oxides due to its remarkable chemical, optical and electronic properties that make it suitable for a variety of applications, such as energy conversion and storage, especially photovoltaics [1], photocatalysis [2], optical coatings [3], gas sensors [4] and biomedical uses [5]. Along with its useful applications, TiO_2 provides the benefits of low toxicity, good chemical stability, and ease of fabrication [5]. But, like everything in balanced nature, it also has its own insufficiencies. The most representative are: low hardness, poor wear resistance, low tribo-corrosion performance [6], low corrosion resistance in hot, concentrated and low pH solutions [7] and low resistance to oxidation in high temperatures [8].

In the previous decade a large number of publications appeared concerning titanium dioxides coupled with other oxides, such as: tungsten trioxide (WO_3) [9], to improve titanium dioxide's thin film properties and make it more chemically and thermally stable [10].

Tungsten trioxides (WO_3) exhibit nontoxic, stable, and native n-type semiconductor properties. WO_3 has hydrophilic [11], gasochromic [12] and photochromic properties [13]. It is also characterised by good resistance to photocorrosion in acidic aqueous solutions [14]. Owing to its properties, WO_3 thin films have a wide variety of applications especially in gas/chemical sensors [15], optical devices [16], pseudo-capacitors [17], electrochromic devices [18], photochromic sensitivity [19], optical absorption [20], hole injection/transport layer in organic-inorganic optoelectronic devices [21] photochemistry [22], lithium-ion batteries [23], photocatalytic activity [24], solar cells [25], thermal stabilizers [26], fuel cells [27] etc.

The mixed oxide system formed by TiO_2 and WO_3 has gained relatively high attention in the literature. It seems that such systems may benefit from the combination of the best properties of their pure

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components, and a modification of the structure of the whole system can be expected. This includes changes in the bulk as well as the surface properties.

In 1991, Hashimoto and Matsuoka first reported that an amorphous TiO_2-WO_3 film, produced by the electron beam deposition method, exhibits a longer lifetime and higher thermal stability than do pure oxides films [28]. Mixing TiO_2 and WO_3, makes the structural changes of the whole system occur at a higher temperature than in its pure oxide components.

In 2001, Tatsuma et al. [29] described the anticorrosion properties of TiO_2-WO_3 thin film deposited on stainless steel substrate. The bactericidal effects of the TiO_2-WO_3 films were reported in [30].

The wide range of applications means that TiO_2-WO_3 thin films are working in different, sometimes adverse environments. Therefore, the corrosion resistance and mechanical properties of TiO_2-WO_3 thin films play a significant role as regards their durability. Unfortunately, there are no studies concerning the structural, corrosion and mechanical properties of TiO_2-WO_3 thin films. Most publications have focused on the photocatalitycal, electrochromic and gas sensing properties of TiO_2-WO_3 thin films [31] in the whole composition range of the coating system, including pure oxides.

The purpose of this work was to study the structural, mechanical and electrochemical properties of TiO_2-WO_3 thin films, with two different contents of WO_3, formed by using the electron beam evaporation method, on the Ti6Al4V surface.

2. Materials and methods

2.1. Experimental design

2.1.1. Specimen preparation

Ti6Al4V titanium alloy (Table 1) was used as the substrate material. Before preparing the thin films, the titanium alloy surfaces were polished using Stuers RotoPol 21 grinding and polishing apparatus. The surface of the samples was polished with emery papers and diamond suspension up to 0.05 μm to a "mirror image".

2.1.2. The TiO_2-WO_3 thin film preparation

Thin films with various material compositions of mixed TiO_2-WO_3 oxide thin films were evaporated using a typical box coater equipped with an electron beam evaporation system [32]. Prior to deposition the 400 L vacuum chamber was evacuated with rotary and diffusion pumps to a base pressure of 1.5×10^{-5} mbar. The WO_3 and Ti_3O_5 pellets (99.99 at.% purity) were placed in a molybdenum crucible and the electron beam parameters were 6 kV acceleration voltage and approx. 100 mA of beam current. The different material compositions of each sample were obtained due to the change of content of the WO_3 and Ti_3O_5 pellets in the crucible. The distance from the evaporation materials to the substrates was 50 cm. During deposition an additional oxygen flow of 100 ml/min was introduced to the chamber to ensure the full oxidation of the evaporated materials. Additionally, substrates were rotated during deposition at a speed of 30 rpm.

After the deposition process both samples were additionally annealed at 1073 K in a computer-controlled Nabertherm tubular furnace with an accretion temperature of 200 K/h. The annealing process was conducted in an ambient atmosphere.

Table 1
Composition of Ti6Al4V titanium alloy.

	Components, wt.%						
	C	Fe	N	O	Al	V	Ti
Standard	0.08	0.25	0.05	0.20	5.50–6.75	3.5–4.5	Balance
Analysed	0.08	0.09	0.05	0.20	5.83	4.08	Balance

2.2. Analysis of surface characteristics

The surface morphology and elemental composition of the thin films were investigated with the aid of a FESEM FEI Nova NanoSEM 230 scanning electron microscope equipped with an energy dispersive spectrometer (EDS). Surface and cross section images were obtained at the same magnification of 200 k using a "through-the-lens" (TLD) secondary electron (SE) detector. The EDS used for the measurements was calibrated for quantitative analysis, while in such case it is accurate for qualitative analysis from approximately 0.1 at.% and for quantitative analysis from approx. 1 at.% of element content. The distribution of each element (titanium, tungsten) in the thin films was also investigated.

The structural properties of both thin films were determined based on the results of the X-Ray Diffraction (XRD) method. For the measurements, an Empyrean (PANalytical) diffractometer with a PIXel3D detector and a Cu lamp (40 kV, 30 mA) employing Bragg-Brentano reflecting geometry parafocusing optics was used.

2.3. Mechanical characterisation

The hardness measurements of the obtained thin films were performed using a nanoindenter manufactured by CSM Instruments (Switzerland) equipped with a diamond Vickers indenter. The hardness was calculated using the method proposed by Oliver and Pharr [33]. A number of measurements were carried out for various depths of nanoindentation (from 80 nm to 700 nm). In order to measure the "film-only" properties and minimise the impact of the substrate, a method of nanoindentation measurement approximation was implemented [34].

2.4. Corrosion tests

The corrosion behaviour of titanium alloy and alloy with thin films was examined using a three-electrode cell set-up in a sodium chloride solution. In this set-up, the titanium alloy and titanium alloy with surface modification were used as a working electrode, while a platinum and Ag/AgCl electrode with a Luggin capillary were used as counter and reference electrodes, respectively. The applied potential window for corrosion study was from −150 mV to 1000 mV (versus open circuit potentials – OCP) at a scanning rate of 1 mV/s. Prior to each polarization experiment the samples were immersed in the electrolyte for 1 h while monitoring the open circuit potential to establish steady state conditions. The measurements were carried out by means of an Autolab EcoChemie System of the Autolab PGSTAT 302N type equipped with GPES software in aerated solutions at room temperature. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined from the extrapolated data of the cathodic and anodic parts of the potentiodynamic polarization test or a Tafel plot.

3. Results and discussion

3.1. Structural characterisation of the TiO_2-WO_3 thin films

The material composition of coatings deposited in processes with the changed content of the WO_3 and TiO_2 pellets was measured using x-ray microanalysis, and the amount of tungsten was equal to 32 at.% and 59 at.%, respectively. Therefore, in the paper, prepared thin films are denoted as $(Ti_{0.68}W_{0.32})Ox$ and $(Ti_{0.41}W_{0.59})Ox$, respectively. The performed investigations showed that the distribution of each element in the $(Ti_{0.41}W_{0.59})Ox$ thin films was homogenous. The EDX spectra showing the lines from the Ti and W elements are presented in Fig. 1 for each thin film. It is clearly seen that in the case of the $(Ti_{0.68}W_{0.32})Ox$ coating the W L_α line in the EDS spectrum is considerably lower than for the $(Ti_{0.41}W_{0.59})Ox$ thin film, which testifies to the lower content of tungsten.

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