CHARACTERIZATION OF TUNGSTEN/TITANIUM CARBIDE COATINGS DEPOSITED BY CATHODIC ARC DEPOSITION FOR HYDROGEN EVOLUTION

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ABSTRACT

In this investigation, the use of thin films of tungsten-titanium carbide as electro-catalysts for the evolution reaction of hydrogen (HER) was evaluated. Thin films, with a different number of layers, were deposited on titanium substrates by cathodic arc deposition. The samples were structurally characterized by X-ray diffraction (XRD) and the surface roughness was analyzed by Atomic Force Microscopy (AFM). The HER kinetics were analyzed with 0.5 M sulfuric acid as an electrolyte on films supported on titanium substrates. With EIS together with AFM, the relationship between surface roughness and the electrochemical response was determined, indicating that as the number of layers increases, the capacitive activity increases and the grain size decreases, associating with the generation of hydrogen production. It was concluded that the coatings generate catalytic activity when subjected to 1000 voltammetric cycles.

Keywords: Hydrogen, Coating, Voltammetry, Roughness.

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INTRODUCTION

Tungsten-titanium carbide films are nano-composite material.^{1,2} In this case, the selected materials are metal-ceramic based on carbides due to their metallic and covalent bonds that provide excellent mechanical and electrical properties.^{3,4} These materials have been studied independently, that is, as tungsten carbide and titanium carbide.^{5,6} To deposit thin films are used different processes, one of the most used is the sputtering (PVD, Physical Vapor Deposition) which allows a wide range of materials, especially transition metal carbides, that can be deposited achieving a variation of their properties.^{7,8} The PVD technique allows greater ionic current density which allows modifying the microstructure of the films and obtaining denser layers with low roughness.^{9,10}

Some materials used as a cathode for the production of hydrogen are still in a stage of development.¹¹⁻¹³ The cost in the production of energy from fuel cells still cannot compete with the costs of electricity production by conventional methods.^{14,15} The use of expensive manufacturing materials and processes, and the need to create a new infrastructure for the generation, transport, and distribution of hydrogen, are some of the main aspects for which the use of this technology has not been widely implemented.¹⁶

The formulated analytical methodologies can determine the properties of the catalyst without the production of hydrogen, but once said catalyst has been applied to the electrode and the assembly has been manufactured, it is necessary to use electrochemical techniques for its characterization in operation as a cell.^{17,18} Among the electrochemical techniques stand out the curves of cyclic voltammetry and electrochemical impedance spectroscopy. These techniques are used to study the kinetics of electro-catalysts, establishing a macroscopic relationship between current density and anodic and cathodic over-potentials, and the electrolyte adjacent to the electrode.^{19,20} Therefore, thin-film coatings allow having materials with good electro-catalytic properties because they have advantages for their implementation as cells due to their stability in acid media and their low production costs.²¹⁻²⁴

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The objective of this research work is to improve the catalytic activity for the evolution reaction of hydrogen, by means of the design of tungsten carbide titanium electrodes obtained the magnetron sputtering technique varying different periods of growth.

EXPERIMENTAL

Thin films of titanium-tungsten carbide were shaped, varying the number of bilayers, on titanium substrates by means of cathodic arc deposition. As source materials, titanium and tungsten targets were used. Using a 1000 l/s diffusion pump backed by a mechanical pump, the chamber pressure was $1.5 \cdot 10^{-6}$ mbar. As a pre-treatment for the bilayers, the silicon substrates were cleaned by cathodic arc deposition for 15 minutes under an argon atmosphere, chamber pressure of $4.6 \cdot 10^{-3}$ mbar and negative bias of -200 V. After cleaning and to improve the adhesion of the coatings a titanium layer with a thickness of 20 nm was deposited by means of cathodic arc deposition with a bias voltage of 10 V and pure Ar atmosphere at $4.6 \cdot 10^{-3}$ mbar. Subsequently, during the initial 5 minutes, a gradual flow from 0 to 100 sccm, the total pressure of $1.3 \cdot 10^{-2}$ mbar and a temperature of 300 °C, is introduced into the C_2H_2 chamber. Titanium films were formed within 10 minutes with the following conditions: argon flux 50 and 70% open conductance valve. For the deposit of TiWN, a power of 350 W on titanium and 420 W on tungsten continues to be applied, with a bias polarization of -10 V; substrate temperature of 300 °C.

Information about crystallinity and changes in crystal lattice arrangements were obtained from diffraction patterns as a function of materials. The changes in the phases of the crystalline network were characterized by X-ray diffraction (DRX) using a Philips X-ray diffraction equipment, configured in Bragg-Brentano mode ($\theta/2\theta$) and Cu/K radiation ($\lambda = 1.5405 \text{ \AA}$).

The surface morphology of the coatings was characterized by the technique of atomic force microscopy (AFM). An AFM Asylum Research MFP-3D® device was used in tapping mode. Using the Scanning Probe Image Processor (SPIP®), the roughness values of each of the films were estimated.

For the electrochemical study, an AUTOLAB PGSTAT 204 (Metroh-Autolab) with an EQCM module was used. The test was carried out using a three-electrode electrochemical cell: Ag/AgCl reference electrode, Pt counter electrode, and TiWC coated titanium disk surface as a working electrode. The work area was 1 cm^2 . The electrolytic solution used in the analysis was H_2SO_4 at 0.5 M. In measurements by electrochemical impedance spectroscopy (EIS), the following parameters were taken: frequency from 100 kHz to 10 mHz, 5 points per decade and sinusoidal disturbance 1 mV, in the open circuit potential (OCP). Initially, a time of 8000 seconds was established; the time necessary to stabilize the corrosion potential, then the tests were carried out using EIS. Subsequently, the measurements were made with the following conditions: potentiodynamic range from 0 to -3V and scanning speed of 5 mVs^{-1} . The results of the electrochemical tests were the average of three measurements with the aim of guaranteeing the reproducibility of the experiment.

RESULTS AND DISCUSSION

Figure-1 shows the diffractograms related to the titanium substrate and films $n=1$ and $n=40$, respectively. Fig.-1a) corresponds to the substrate. A stable phase of titanium -alpha (PDF 01-071-4632) is evidenced in a system of the hexagonal crystal structure with network parameters of a and $b = 2.97 \text{ \AA}$ and $c = 4.72 \text{ \AA}$, and a calculated density of 4.41 g/cm^3 . By refining Rietveld, the refinement of the crystalline structure was minimized the difference of the intensities observed and calculated, identifying the following crystallographic planes (100), (101), (110) and (201).^{25,26} Figure-1a) and Fig.-1b), respectively, show the X-ray diffraction patterns for $n = 1$ and $n = 40$ layers deposited on titanium substrates. For the coating $n = 1$ diffraction peaks are observed in $2\theta = 37.03^\circ$ with plane (001), 41.47° (111), 43.52° (111), 49.93° (200), 70.20° (220), 73.02° (220), 76.87° (110), 88.67° (331).²⁷ These orientations correspond to a BCC structure related to the δ -WC phase (space group 225-Fm3m).²⁸ The information obtained is correlated with the JCPDF files 00-020-1309 and identifying a parameter of $4.23 \text{ \AA}$.²⁹ For films $n = 40$, Fig.-1c), there are two diffraction peaks with greater intensity at 71.70° (220) and 42.20° (111). This increase in peak intensity is due to the miscibility of the structural phases favoring the growth of the crystallographic grains and preferential orientation.³⁰

Fig.-1: XRD in Coatings Obtained by RF Magnetron Sputtering. Titanium Substrate, Coating Layers $n = 1$ and Coating Layers $n = 40$.

The topography of the films can be seen in Fig.-2. The area analyzed in the types of samples was $22.5 \mu\text{m} \times 22.5 \mu\text{m}$ with a Z scale around 750 nm. The study allowed establishing the values of roughness and grain size by software (SPIP®).³¹ The grain size values are around $129.5 \pm 5 \text{ nm}$ for layer $n = 1$ and $68.6 \pm 2 \text{ nm}$ in layer $n = 40$. On the other hand, the roughness values were determined at $14.1 \pm 0.2 \text{ nm}$ for layer $n = 1$ and $6.5 \pm 0.2 \text{ nm}$ for layers $n = 40$. From these results, it is possible to infer the surface regularity of the coatings. This superficial regularity is attributed to the increase in the number of layers because the bombardment of Ar^+ ions on the films stimulates nucleation due to the reduction of the modulation period.³² The decrease in grain size and the formation of more compact microstructures decrease the total surface roughness and increase the density of the films.

Fig.-2: Micrograph Obtained by AFM, for Tungsten Carbide Titanium Layers. (a) $n = 1$ and (b) $n = 40$.

Figure-3 shows the electrochemical impedance spectroscopy of the films (working electrodes) varying the number of layers. The semicircles differ in the capacitive deformation due to the difference between the numbers of layers.³³ The system has two representations one at high frequencies related to the resistance of the solution, which is similar for $n = 1$ and $n = 40$, and the other at low frequencies where there is a noticeable change in the diameter of the semicircle for the system $n = 40$. The increase in diameter is related to the greater generation of hydrogen due to the kinetic processes and the total impedance parameters of the system. These results show the relationship between systems with the highest number of layers with the ease of electrochemical reactions. Additionally, when correlating the results with the values of surface roughness determined by AFM, it was found that for the layer system $n = 40$ there is a decrease in the roughness due to the effect of reduction in the pore size, which affects the increase of hydrogen production. Therefore, the roughness and the electrochemically active surface are related to bubbling, since, for the $n = 1$ system, the grain size value is twice as large as for the $n = 40$ coatings.³⁴ The

bubble generation zones are located between the valleys of the grains. In conclusion, to increase the production of hydrogen, films with surfaces of low roughness are necessary.

Fig.-3: Nyquist Diagrams for Coatings Immersed in Sulfuric Acid as an Electrolytic Medium

Figure-4 shows the cycle-voltammetric curves of the coatings $n = 1$ and $n = 40$ using as electrolyte a solution of H_2SO_4 . The cycle-voltammetric study was developed with a potential range of -0.1 to 1 V vs RHE and a scanning speed of 5 mV/s.^{35,36} The results allow establishing that at voltages higher than -0.2 V and lower than -0.7 V, the current intensity increases significantly due to the decomposition of the water of the electrolyte with the evolution of oxygen and hydrogen, respectively. The cyclic voltammetry shows that the maximum working voltage range is 1 V with a current of 10 mA/cm². For $n = 1$ coatings show lower over-potentials, this indicates that the absorption of the species is not favored, giving an overlap response at the beginning of the decomposition of the water. Additionally, at 1000 cycles a displacement towards lower over-potentials is observed which infers the existence of areas with high topographic variation and therefore creates bubble entrapment preventing the production of oxygen. Moreover, for the film with $n = 40$ an adequate response to the phenomenon of adsorption was established, indicating that the process is controlled by an electrode surface. Due to repetitive measurements up to 1000 cycles adequate stability and reproducibility are established. An interesting aspect is a rearrangement in the tungsten carbide titanium $n = 40$ coating structure, due to the interfacial conditions that generate controlled conditions and the catalytic activity improves with respect to the $n = 1$ coating. These results are established by the increase in current density when applied over-potential is lower. Additionally, the curve at 1000 cycles is parallel and is taken as similar to the system evaluated with $n = 40$, therefore the kinetic parameters are similar for the two types of coatings evaluated.

Fig.-4: Potentiodynamic Curves to Determine the Degree of Hydrogen Production on the Surface of the Tungsten-titanium Carbide Coatings

CONCLUSION

Electrodes (coatings) were obtained as catalysts by determining the rates of chemical reactions and their surface stability. By means of XRD, the films were characterized structurally and it was established that the greater the number of layers, the greater the grain size and the preferential orientation. With EIS together with AFM, the relationship between surface roughness and the electrochemical response was determined, indicating that as the number of layers increases, the capacitive activity increases and the grain size decreases, associating with the generation of hydrogen production. The bubbles do not remain on the surface due to the smaller grain size, so it can be concluded that with respect to the potentiodynamic curves it is considered that titanium tungsten carbide coatings with $n = 40$ are suitable for the production of hydrogen.

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