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Hydrogen insertion in titanium carbide based thin films (nc-TiC_x/a-C:H) - comparison with bulk TiC_x

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A B S T R A C T

Nanocomposites composed of titanium carbide nanosized grains embedded in an amorphous hydrogenated carbon matrix (nc-TiC_x/a-C:H) are prepared by hybrid Magnetron Sputtering - PECVD process using a titanium metal target and gaseous C_6H_6. By controlling the benzene flow rate, thin films with different carbon content are obtained. The structures of nc-TiC_x/a-C:H materials are analyzed by X-ray diffraction, X-ray photoelectron and Raman spectroscopic methods. The electrochemical hydrogen insertion, as studied by cyclic voltammetry, strongly depends on the carbon content in the thin films. The correlation between the hydrogen insertion ability and the structure of materials are discussed. Furthermore, we show that the hydrogen insertion in these thin films reaches values much more significant than in bulk substoichiometric titanium carbide obtained by reactive sintering.

1. Introduction

Due to global environmental issues like depletion of natural resources or climate change, electrochemical energy devices such as batteries, fuel cells and capacitors could emerge as powerful complement to conventional energy sources, and highly active catalysts are thus in demand. Bulk transition metal carbides, like titanium carbide, have attracted attention as electrocatalysts that could replace noble metals of high price and limited supply [1–3]. It is worth noting that research on bulk nanocomposites has gained considerable momentum due to their ability to enhance electrochemical activity opening the way to the realization of Pt-free fuel-cell with TiC-C composite [4]. TiC presents a large range of composition from $TiC_{0.55}$ to $TiC_{0.98}$ [5–7] and can also be considered for hydrogen storage [8–10]. In these works, the effect of the stoichiometry and of the crystallographic lattice have been studied showing that hydrogen can be electrochemically inserted in the substoichiometric titanium carbide of formula $TiC_{0.6}$, but not in $TiC_{0.9}$ and that long-range ordering of carbon vacancy is responsible of hydrogen insertion. Indeed, the hydrogen diffusion is possible mainly when $TiC_{0.6}$ carbide presents the trigonal ordered structure, of space group R-3m, consisting in alternately empty and full (111) carbon atomic planes [6,7], but not in the disordered structure of space group Fm-3m. Another recent study by Ding et al. [11] confirmed theoretically by first-principles calculations that hydrogen storage in substoichiometric titanium carbides is possible.

As thin film material, titanium carbide combines high hardness, good toughness and low friction coefficient and many studies were devoted to the synthesis and the characterization of these films [12–18]. Most of these coatings are deposited by plasma assisted Physical Vapour Deposition (PVD) and in particular by the sputtering of a pure Ti cathode in the presence of Ar and hydrocarbon gas (methane, benzene or acetylene) as a source of C. This process often described as reactive sputtering should rigorously be classified as hybrid PVD-PECVD (Plasma Enhanced Chemical Vapour Deposition) because coating is formed by sputtered Ti and C from the target surface and also by plasma induced deposition of hydrocarbonaceous radicals at the substrate [19,20]. Moreover, carbon atoms can combine themselves to form a solid deposit, which is not the case during the reactive sputtering with nitrogen or oxygen. Usually the growth process in sputtering is carried out far from equilibrium hence producing metastable phases. While thermodynamics predicts the appearance of free amorphous carbon at the TiC grain boundaries above the C solubility limit, previous results have shown free carbon phase appearing even for low C contents [18,21]. The formation of amorphous carbon phase induces nanocomposite microstructures in which nanosized metal carbide grains are embedded in an amorphous hydrogenated carbon matrix denoted nc-TiC or nc-TiC_x/a-C:H when hydrocarbon is used as reactive gas [15,18,22]. Although it is possible to reveal the nanocomposite structure with TEM and HIKE XPS, it is difficult quantifying the phase fractions and structural dimensions [23]. The mechanical and electrical properties of the films are determined by the C/Ti ratio but also by the size of the TiC_x grains and the relative fraction of the a-C:H matrix. Pure a-C:H thin films belong to the diamond-like carbon (DLC) family which are also relevant

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materials as electrochemical electrodes [24], and recently Ti-C thin films were investigated as for electrochemical transducers [25]. So, nanocomposite thin films containing substoichiometric titanium carbide are potential candidate for electrochemical applications and this work is dedicated to the synthesis by hybrid PVD-PECVD of nc-TiC_x/a-C:H thin films, to their characterization and to the investigation of their electrochemical hydrogen storage properties in comparison with bulk TiC_x obtained by reactive sintering.

2. Experimental

2.1. Deposition process

The apparatus was an industrial coating machine (HEF TSD 400) operated as a hybrid PVD-PECVD process. The sputtering cathode is a titanium plate, (450 × 175 × 8 mm,) equipped with a balanced magnetron. The discharge gas was argon (Air Liquide, France) with various C_6H_6 (Riedel de Haën, Germany) additions. Table 1 provides the main impurities of the target and of the operating gas. The distance between the substrate and the target was 80 mm. The base pressure prior to film deposition was kept below 7.0×10^{-4} Pa. The substrates were steel pellets (diameter = 25 mm) for the XRD and XPS analysis and stoichiometric TiC pellets (diameter = 10 mm), obtained by sintering of a commercial powder (Cerac, USA), for the electrochemical measurements. Before deposition, substrates were mirror polished with SiC papers and degreased with alcohol. Before each deposition, the chamber and the substrates were heated in vacuum for 1 h 30 min at 130 °C, then the cathode and the substrate surfaces were cleaned by argon ion etching for 10 min with 10 kW DC power on the cathode and a pulsed bias voltage of −300 V on the substrate at 1 Pa. During the deposition process, the power on the Ti target was maintained to 10 kW and a continuous bias voltage of −75 V was applied on the substrate. All the experiments were carried out for 10 min, with a 25 sccm argon flow rate (corresponding to 0.3 Pa in pressure) and a variable benzene flow rate (Q). In order to identify the gaseous species, optical emission spectroscopy (OES) has been conducted, using an Avantes Avaspec-3648 spectrometer. The spectra were measured in the range 240–760 nm with a resolution of 0.25 nm.

2.2. Characterization techniques

The crystalline phases of the films were identified by XRD with a Siemens D5000 diffractometer, (using the Cu $K_{\alpha 1}$ radiation, $\lambda = 1.5406$ Å) equipped with a back monochromator, within the $2\theta = 33$–48° range, with steps of 0.07° and an exposure time of 1.4 s, in a chamber maintained thermostatically at a steady temperature of 20 °C. The X-ray patterns were indexed with the DIFFRAC+ EVA software (Bruker AXS) containing the PDF database. Microscopic observations were carried out using a Philips XL30 SEM in secondary electron (SE) mode. Film composition was estimated using an X-ray photoelectron spectrometer (Kratos Axis Ultra). The X-ray source was the monochromated Al K_α line. An Ar^+ ion beam with a voltage of 4.0 kV was used to etch the surface layer of about 5 nm. The elemental peaks used to obtain atomic concentrations were Ti2p, C1s and O1s. Carbon content was calculated using relative sensitivity factors provided by the manufacturer (Kratos modified Wagner Factors). Raman spectroscopy was used to investigate the structure of a-C:H films. Raman analyses were performed with a Jobin Yvon spectrometer (model 64,000) in backscattering mode, using the 514.5 nm line of an argon ion laser.

Table 1
Main impurities in the target and in the processing gases.

	Main impurities	
	Element	Content
Ti target	C	≤0.1%
	Fe	≤0.3%
	H	≤0.015%
	N	≤0.03%
	O	≤0.2%
Ar	H_2O	≤3 ppm
	O_2	≤2 ppm
	C_nH_n	≤0.5 ppm
C_6H_6	H_2O	30 ppm
	HCl	0.4 ppm
	NH_3	0.2 ppm

Electrochemical measurements were carried out at room temperature, i.e., 25 °C, in a standard three-electrode cell. An Autolab PGSTAT30 potentiostat was used, controlled by GPES and FRA 4.9 softwares (EcoChemie, Netherlands). The solution was a 1 M H_2SO_4 aqueous solution (Aldrich and Millipore Milli-Q+ water). It was deaerated by bubbling pure argon gas (Alphagaz 1, Air Liquide, France), prior to measurements, to remove dissolved oxygen, and argon gas was continuously blown on the solution surface during the experiments. The reference electrode was a K_2SO_4 saturated Hg/Hg_2SO_4 electrode. Potentials were recalculated vs. SHE (standard hydrogen electrode, i.e., +0.65 V were added). The counter-electrode was a platinum disk (10 mm in diameter) and the working electrode, WE, consisted in the TiC_x thin films in a Teflon holder, with an effective surface area of 0.126 cm^2 (4 mm in diameter). The WE was mounted on a rotating disk electrode system EDI 101 (Radiometer-Analytical, France) and set at a rate of 2000 rpm. Electrochemical tests were conducted on the samples 7 days +/− 1 day after their deposition.

3. Results

3.1. Thin film deposition

In the deposition conditions, the main emitting species identified by OES measurements were excited states of Ti, Ti^+, Ar and H. Fig. 1 presents the evolution of the emission of Ti^*, Ti^{+*}, Ar^*, H^* with their respective major lines at 520.5, 374.7, 749.7 and 657.8 nm as a function of the C_6H_6 flow rate Q. From 0 to 30 sccm the intensity of H^* and Ar^* remained quite constant, while those of Ti^* and Ti^{+*} decreased slowly. For higher benzene flow rates, Ar^* intensity slightly decreased, H^* increased, while Ti^* and Ti^{+*} decreased rapidly. Fig. 2 presents the evolution of the titanium target voltage (absolute value) as a function of Q. This voltage increased with Q and reached a maximum for Q = 30 sccm. For reactive magnetron sputtering, the target poisoning by a

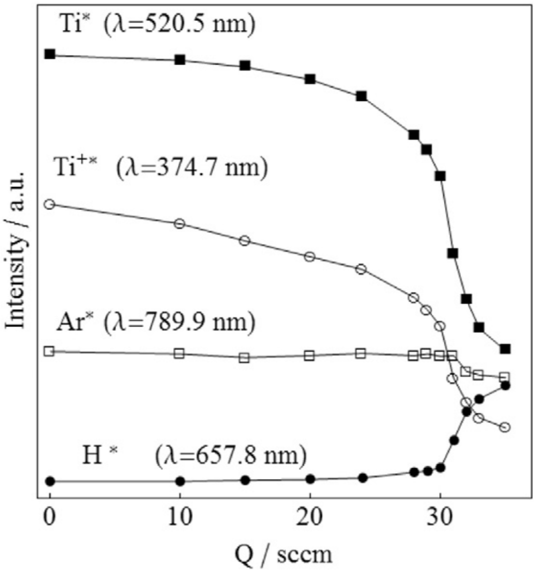

Fig. 1. Emission variation of Ti^*, Ti^{+*}, Ar^*, H^* vs C_6H_6 flow rate.