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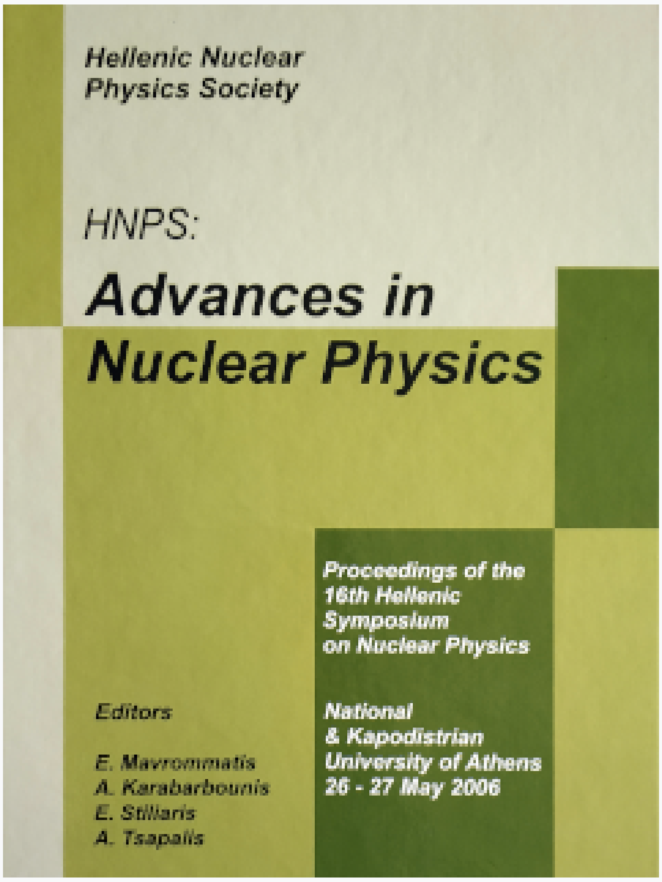

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APPLICATION OF ION BEAM ANALYSIS FOR THE CHARACTERIZATION OF SiC- AND DLC-THIN FILMS

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ABSTRACT

Three series of protective coatings (thickness ca. 200-300 nm) were prepared on the surface of Ti-Al-V alloy (TA6V): silicon carbide (SiC) films produced by ion sputtering (I), silicon carbide films and subjected to Dynamic Ion Mixing (DIM) during the deposition procedure (II) and Diamond Like Carbon (DLC) films produced by ion beam deposition (III). The chemical composition (Si, C and O) of the films was determined using ion beam analysis techniques. The silicon, carbon and oxygen depth distribution was determined by proton Rutherford backscattering spectrometry (p-RBS) and using the resonances at 4.265 and 3.035 MeV of the $^{12}C(\alpha,\alpha)^{12}C$ and $^{16}O(\alpha,\alpha)^{16}O$ interactions respectively. The ratio of Si:C was found to be close to the stoichiometric one. The corrosion resistance of the coated samples was tested under strong aggressive conditions (5M HCl at 50 ^oC). The investigation following the corrosion attack showed that the thickness of the films remained practically unchanged. Only slight diffusion and dissolution effects were observed indicating the good quality of the produced thin films.

INTRODUCTION

In recent years there is a wide use of coatings for the improvement of the mechanical properties and the corrosion resistance of metallic components [1-3]. Amorphous coatings produced at moderate temperatures, which not considerably deteriorate the properties and structure of the metallic substrate, are especially interesting for this purpose [4].

Silicon carbide (SiC) is a ceramic material combining high chemical stability, excellent oxidation and corrosion resistance as well as excellent tribological properties, strength and hardness [1, 5]. Among the various techniques applied for the preparation of SiC-coatings, the ion sputtering combined with dynamic ion mixing (DIM) was found to be especially suitable for the preparation of rather thick dense layers (up to few μm) showing enhanced adhesion to the substrate [5]. The increased adhesion can mainly be attributed to the DIM inducing the formation of an intermediate layer of graded composition through the bombardment of the coating by heavy ions (e.g. Ar^+, Kr^+, Xe^+) of few hundred keV energy. Furthermore Diamond-Like Carbon (DLC) coatings are of growing interest due to their potential biocompatibility and several techniques as plasma and ion beam deposition have been developed for deposition of these coatings [6].

The objective of this study was the preparation, characterization and investigation of the corrosion behaviour of thin SiC and DLC coatings on the surface of a Ti-Al-V alloy (TA6V).

The TA6V alloys are important materials finding many biomedical and engineering applications. Among the biomedical applications their use as dental and orthopaedic implants is of extreme importance whereas their successful utilization in the aeronautic engineering is also well known [7].

EXPERIMENTAL PART

i) Preparation of the coatings and corrosion tests

The substrates used in this work were disks of a commercial titanium alloy TA6V of 16.1 mm diameter and 1.1 mm thickness.

The preparation of the coatings took place at the Laboratory of Physical Metallurgy (LPM) of the University of Poitiers (France) [1, 5]. Three series of thin films (thickness ca. 200-300 nm) were prepared on the surface of a Ti-Al-V alloy (TA6V). The SiC films were produced by ion sputtering at room temperature. A water-cooled SiC target was bombarded with 1.2 keV Ar^+ ions (beam intensity: 80 mA, sputtering angle: 45^o). A part of the SiC coated samples was additionally subjected to Dynamic Ion Mixing (DIM) with 160 keV Ar^+ ions (Sample series II). The Diamond-Like Carbon (DLC) films were prepared by deposition using a Penning ion source (Sample series III).

The corrosion resistance of the prepared coatings was investigated by electrochemical techniques in 5M HCl at 50 ^oC using rapid and slow scan measurements by an AUTOLAB Potentio-Galvanostat (ECO CHEMIE, Netherlands). A saturated calomel electrode used as a reference electrode and a graphite one as an auxiliary electrode for all measurements. In all cases the sample surface exposed to the corroding medium was 1 cm^2 [8].

i) Characterization of the coatings

The phase composition and the structure of the coatings were investigated by X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Transmission Electron Microscopy (TEM) at LPM [4], where also their micro-hardness, wear and density were measured [5].

Information on the elemental distribution and thickness of the coatings was obtained by Rutherford backscattering spectrometry (RBS) at the 5.5 MV Tandem Accelerator of the NCSR Demokritos/ Athens using protons of 1.75 MeV (scattering angle: 170^o, solid angle: 2.54×10^{-3} sr), whereas the oxygen and carbon profiling was performed using alpha particles of 3.035 and 4.265 MeV respectively (scattering angle: 171^o, solid angle: 0.34×10^{-3} sr). The beam current on the target during the measurements did not exceed 10 nA, while the beam spot size was 1.5×1.5 mm^2. The analysis of the data was performed using the simulation code RUMP [9]. The overall uncertainty of the determination was estimated to be ca. 10%.

SEM/EDS examinations of the samples before and after the corrosion tests was performed at the University of Thessaloniki using a JEOL JSM 840A electron microscope equipped with an OXFORD ISIS 300 EDS microanalyser.

RESULTS AND DISCUSSION

The investigation of the coatings by XRD and TEM lead to the conclusion that the films prepared at room temperature were amorphous [4, 10]. The average density of the SiC films was estimated to be ca 3.50 g/cm^3 [5]. In the case of the samples of series II treated by DIM crystallization initiation was also observed [4].

The RUMP simulation of the spectroscopic data obtained by the sample bombardment by 1750 keV protons as well as by 3035 and 4265 keV α-particles revealed information about the thickness and the composition of the coatings. The peaks corresponding to C, O and Si can be observed in Figs. 1a and 1b presenting the α-RBS spectra of a Series I sample before and after the corrosion test. From these figures it is obvious that the silicon distribution is not influenced by the corrosion attack.

The thickness of the SiC coatings was found to be ca. 300 and 280 nm respectively for the Series I and II samples. The Si:C ratio for the Series I samples was found to be ca. 1.2, indicating that the composition of the films was quite close to stoichiometry and gradually approaches the stoichiometric one (1:1) as the crystallization of the SiC proceeds (Series II samples). Coatings treated by DIM had a lower oxygen content and reduced thickness. This could possibly be explained by the additional formation of solid silicon oxide, which, as indicated by the density measurements, also reduces the porosity.

The highest corrosion resistance and best tribological properties were exhibited by the amorphous coatings (Series I and III). The evaluation of the corrosion parameters (corrosion current (i_{corr}) and potential (E_{corr})) showed that these coatings were very stable in both rapid and slow scan tests. This is most probably ought to absence of grain boundaries and crystal imperfections [10, 11].

Figs. 2a and 2b present SEM images of the surface of the Series I sample before and after the corrosion attack (slow scan, long term corrosion study). Homogeneous surface composite layers without pores were observed in both cases indicating the stability of the film. The EDS showed that the silicon concentration in the corroded samples was the same as in the initial ones. Electrochemical tests performed in other corrosive media (e.g. H_2SO_4) showed that the most important parameter determining the corrosion resistance of the SiC layer is its thickness [1].

CONCLUSIONS

The Ion Beam Analysis techniques are valuable tools for the characterization and investigation of thin protective coatings on the surface of technical materials. The determination of the elemental distribution of the coating constituents prior and after a corrosive or oxidative attack can provide important information about the quality and protective action of the coating.

All SiC and DLC coatings investigated during this work showed enhanced corrosion resistance. This is also related with their structure. However, the amorphous coatings (Series I and III samples) being free from grain boundaries and structural imperfections exhibited higher corrosion resistance compared to the crystalline one. The limited porosity and the thickness of the protective films are also of especial importance and increase the protective action of the coating.

Acknowledgements

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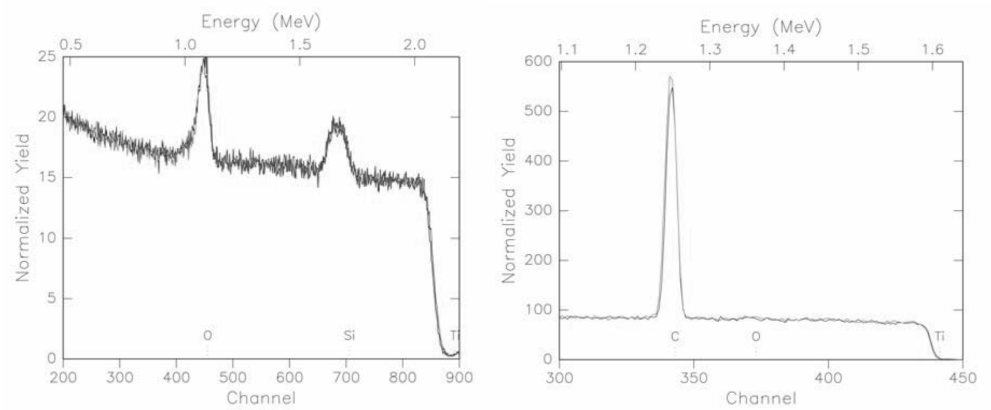

Fig.1. α-RBS spectra of Series I samples before (black) and after (red) the corrosion tests, a)E_α 3035 keV and b) E_α 4265 keV.

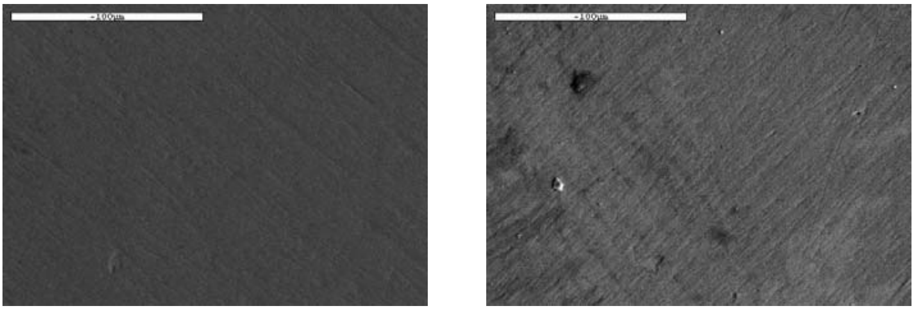

Fig.2. SEM images of a sample of the series I (a) before and (b) after the corrosion test.