ELECTRON BEAM DEPOSITED TANTALUM CARBIDE FILM ON TITANIUM

A. Latini, S. M. Barinov, D. Ferro, J. V. Rau, R. Scandurra

Abstract

Tantalum carbide (TaC) thin films were electron beam deposited on a roughened surface of pure titanium using a hot-pressed TaC ceramic target. The as-deposited film retained the stoichiometry of the TaC target, but after exposure to 750°C in vacuum the TaC film transformed to Ta_2C and developed cracks. The intrinsic hardness of the as-deposited film was obtained via mathematical extrapolation from the multiple hardness measurements of the film/substrate system under varying indentation loads. The hardness thereby obtained is 12.4 GPa - somewhat lower than the hardness reported for bulk TaC. The degree of the reduction of hardness was significantly lower than that revealed for titanium carbide EB deposited films. Possible reasons of the hardness lowering are discussed. TaC films could find a potential application to protect titanium parts of orthopedic devices.

Keywords: coating, tantalum carbide, electron beam deposition, titanium implants

INTRODUCTION

Titanium and titanium-base alloys have found wide application in orthopedics due to their relatively low elasticity modulus and enhanced corrosion resistance compared to more convenient metallic materials intended for implantation into the human body [1]. Some examples are joint replacement parts for the hip, knee, spine, dental implants, etc. [2]. Titanium successfully complies with the biocompatibility of the implant [1]. The major disadvantage of titanium is that some transient oxides can be formed on its surface in the environment of body fluids. Resulting from tribo-chemical reactions, these oxides can produce wear debris, which leads to an adverse cellular response and even to lysis of the surrounding tissue. Therefore, the surface of titanium implants could be protected against the oxidation. The most recognized method consists of formation of a thin layer of a biocompatible ceramic phase at the surface. Continuous research has been directed towards calcium phosphate coatings, some recent results were outlined in [3]. The current method for depositing of calcium phosphates is the plasma-spraying process. Problems with the plasma-sprayed coatings include poor adhesion strength and alterations in both the structure and the phase composition of the film [3,4]. Some refractory nitrides and carbides are considered to be good candidatures for the surface modification of the titanium implant due to their resistance to oxidation and high hardness level. Titanium nitride was demonstrated to also possess a high bioactivity for osteointegration [5].

The films of nitrides and carbides can be obtained using physical or chemical vapor deposition methods avoiding some disadvantages of plasma spraying. Various

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physical deposition methods to cover titanium with ceramic films, in particular of refractory carbide film, are continuously being researched [6,7]. For example, feasibility of the electron beam deposition (EBD) to produce the calcium phosphate films on titanium has been proved [8]. Relatively little is known about the EBD of carbides on titanium. Hardness of the EB deposited TiC film on titanium has shown to be 10-20 GPa compared to 30 GPa for bulk TiC, probably due to carbon diffusion from the film into the substrate [9]. The hardness level depends on the substrate preheating temperature, decreasing from 20 to 10 GPa with an increase of the preheating temperature from 200 to 800°C [9]. As an alternative, Ti can be covered by tantalum carbide films. The activation energy of carbon self-diffusion in tantalum carbide 497 kJ/mol exceeds significantly that for titanium carbide, 399 kJ/mol [10]. Therefore, the EBD tantalum carbide film is expected to retain high intrinsic hardness of the stoichiometric TaC. The present study was aimed at the investigation of the deposition and the hardness of the EBD TaC films on titanium.

EXPERIMENTAL

To prepare the targets for EBD, TaC powder (98% pure) was hot pressed into 18 mm diameter pellets. The pellets were placed into a refractory crucible and then inserted into a water-cooled electron beam gun (EVI-8, Ferrotec). The gun has a magnetic lenses system that allows a 270° deflection of the beam for avoiding contamination of the evaporating material with tungsten of the emitting filament. The substrate was heated under a vacuum of $5 \cdot 10^{-2}$ mbar in the chamber with a high-power halogen lamp. The deposition process was performed at the accelerating voltage -3.5 kV and the emission current of 130 to 200 mA. The pattern of the electron beam was circular, to ensure uniform consumption of the evaporating material. The deposition was performed at the optimized substrate preheating temperature of 500°C for several minutes. Temperature was measured with a thermocouple (an error ± 10°C). No significant spitting of the target was observed. Before the deposition, the titanium substrate was sandblasted with a SiC abrasive powder to provide surface roughness R_a $1.6 \cdot 10^{-9}$ m, necessary for best cell adhesion to the surface of implanted device.

The thickness of the film was evaluated by scanning electron microscopy (SEM) observation of the cross-section of the samples (LEO 1450 VP microscope) with an absolute error of ± 10 nm. The deposition speed was monitored by a quartz microbalance. The SEM apparatus was coupled with X-ray energy dispersive system (EDS). X-ray diffraction measurements were performed with a Philips X'Pert PRO apparatus (Cu K_α irradiation, λ = 1.54056 Å, graphite monochromator, JCPDS cards # 35-0801 (TaC); # 73-1321 (Ta_2C), and # 88-2321 (Ti)).

The hardness of the composite film/substrate system was measured with a Leica VMHT apparatus equipped with a standard Vickers pyramidal indenter. The loading and unloading speed was $5 \cdot 10^{-6}$ m/s, time under the peak load being 15 s. Indentations were made with 5 loads ranging from 0.098 to 19.6 N. To separate the hardness, H_c, of the film/substrate system on its constituents from the film (H_f) and the substrate (H_s), a Jönsson and Hogmark model based on an area law-of-mixture approach was used [11]. Furthermore, the indentation size effect was taken into account [12,13]. The reasonable expression for the H_c in this case is

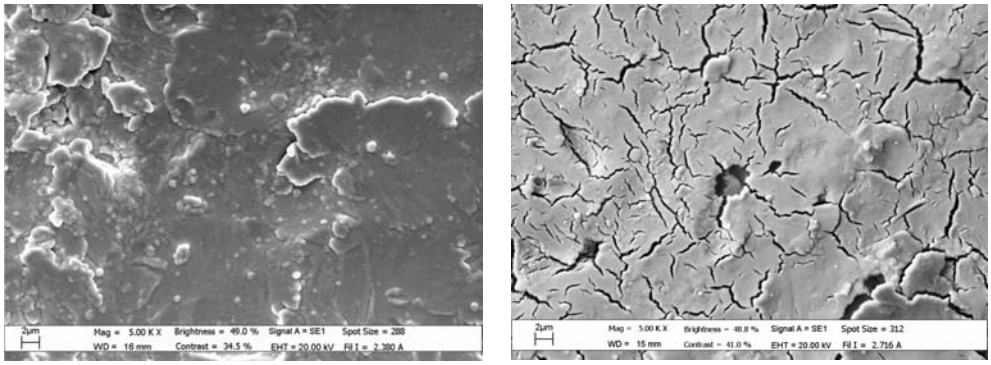
$$H_c = H_{s0} + [B_s + 2ct(H_{f0} - H_{s0})]/D \qquad (1)$$

where $c \cong 0.5$ for brittle hard film on a more ductile substrate [11]; H_{s0} and H_{f0} are intrinsic hardness of substrate and film, respectively; t is film thickness; D is imprint diagonal, and

B_s is the coefficient which can be determined from a separate experiment with the hardness of substrate. To calculate the intrinsic hardness of the film, special attention was paid to choose correctly the indentation depths, d, where the model is adequate. According to the estimations, the d/t ratio must be in the range from 1 to 5 [9]. Such an approach was employed because of difficulty to obtain reproducible and reliable nanoindentation data for the rough film. To evaluate H_{s0} and B_s values, experiments with the titanium substrate were performed. The experimental plot hardness of substrate, H_s, versus inverse of imprint diagonal, 1/D, was well approximated by a linear regression. Evaluated from this were plot values of H_{s0} and B_s equal to 1.84 GPa and $5.38 \cdot 10^{-6}$ GPa.m, respectively.

RESULTS AND DISCUSSION

SEM micrograph of the as-deposited film is shown in Fig.1a. The film is rough, partly due to the roughness of the sandblasted surface of the substrate. There are droplets of 0.2 to 2 μm size on the surface of the film originated from the expulsion of the target. Numerous are both the large grains, of tens to hundreds micrometers size, and the droplets are surrounded with slit-like pores. Cross-sectional SEM observations revealed the averaged thickness of the film as equal to 503 ± 10 nm.



a b

Fig.1. SEM micrographs of as-deposited (a) and heat-treated at 750°C (b) films.

Figure 2 shows the X-ray diffraction patterns for the as-deposited films and the films heat-treated at 750°C (the temperature being lower than that of phase transformation in Ti) in vacuum 10^{-3} mbar for 2.5 hours. Main peaks (111) at 2θ 34.9° (reference intensity 100) and (200) at 40.5° of TaC are present in the diffraction pattern recorded from as-deposited film. According to the EDS data, the Ta/C atomic ratio in the film is close to the stoichiometric value of 1:1. The peaks are broadened, indicating an ultrafine microstructure of the film. The apparently ultrafine grains of the film are constituents of a rather coarse grained microstructure of the coating as visible in Fig.1a. The rather strong line (200) of TaC with the expected intensity 70 (according to JCPDS card #35-0801) becomes of low intensity, probably due to the textured microstructure of the coating. After the heat treatment, the peaks located at 2θ 33.3°, 36.4°, 50.0° and 59.6° were identified as (100), (002), (102) and (110) peaks of Ta_2C. The peaks from stoichiometric TaC were not evidenced. Other intensive lines located at approximately 38.4° and 40.1° are, respectively, (002) and (101) peaks from titanium substrate. The former can coincide with the (101) diffraction line of Ta_2C which is located at 38.1° (intensity 11). The appearance of titanium lines in the pattern obtained from the heat-treated sample could be explained by the loss of

the continuity of the coating. The EDS measurements confirmed qualitatively the composition of the film differs from the stoichiometric one.

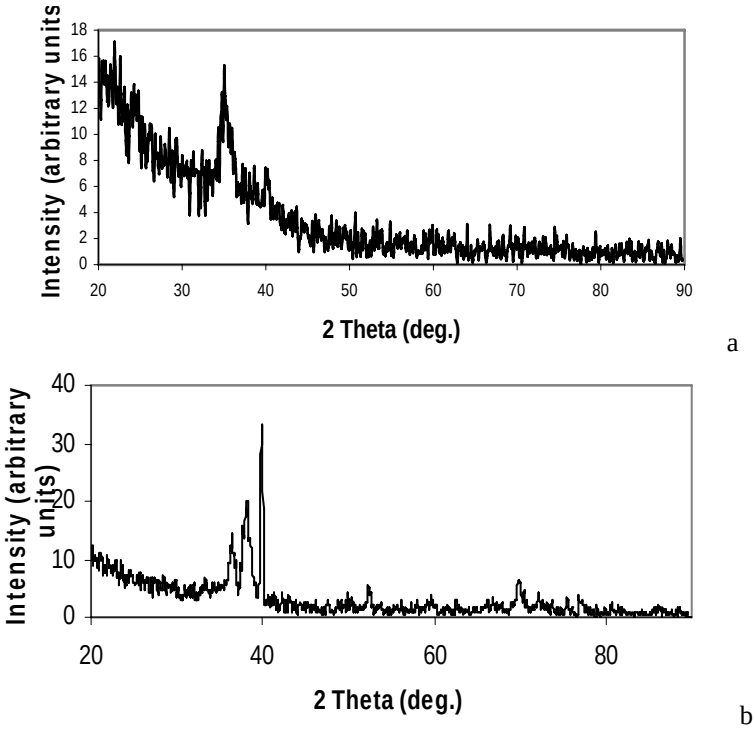


Fig.2. X-ray diffraction pattern of as-deposited (a) and heat-treated at 750°C (b) films.

Shown in Figure 1b is a SEM micrograph of the film after annealing. The film contains numerous cracks. These secondary cracks can be originated by carbon loss via diffusion of carbon atoms from the TaC film into the Ti substrate, resulting in the transformation of TaC into Ta_2C accompanying the shrinkage. The difference between the density of TaC ($14.4 \cdot 10^6$ g/m^3 [10]) and that of Ta_2C ($15.04 \cdot 10^6$ g/m^3 [10]) can result in tensile stress imposed onto the coating and, therefore, in the cracking of the coating due to more than 4% of the volume shrinkage.

Shown in Figure 3 is the composite hardness versus the inverse imprint diagonal plot. The plot was approximated well by a linear regression. A least-squares fit of the plot to the Equation (1) results in the slope $[B_s + 2ct(H_{f0} - H_{s0})]$, which is equal to $10.67 \cdot 10^{-6}$ GPa·m. Using the values of $B_s = 5.38 \cdot 10^{-6}$ GPa·m and $H_{s0} = 1.84 \pm 0.06$ GPa evaluated by the separate experiments with substrate only, the intrinsic hardness of the film, $H_{f0} = 12.4$ GPa, was calculated from the slope. The following data are known on the hardness of bulk tantalum carbides: 14.3 GPa for $TaC_{0.99}$ and 16.8 GPa for Ta_2C [10,14]. Estimated in this study hardness of the as-deposited film corresponds generally to that of the bulk TaC ceramics, being a little bit lower. However, it is difficult to compare those values, merely because the reported hardness value for the ceramics has been measured at an arbitrary load of 1 N and no indentation size effect has been taken into account [10]. It can result in overestimated data [12-14].

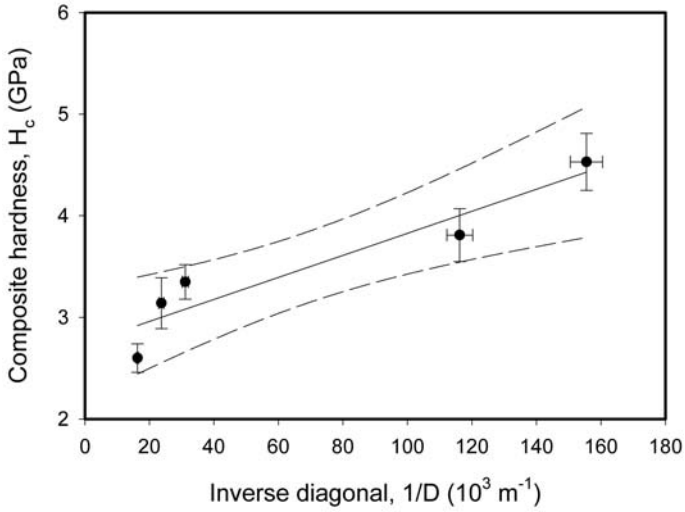


Fig.3. Composite hardness versus inverse imprint diagonal (dashed lines - 95% confidence interval).

A number of reasons for the lowering in the hardness of the refractory carbide films can be taken into account. One of the reasons is the deviation from the film stoichiometric composition due to carbon self-diffusion from the film into the substrate. For example, the microhardness of titanium carbide is known to reduce monotonously from approximately 38 GPa for $TiC_{0.99}$ to 15 for $TiC_{0.68}$ within the titanium carbide homogeneity region [10]. The effect of the reduced hardness has been previously observed also for the EB deposited titanium carbide film on pure titanium [9]. However, the degree of the reduction of hardness, if existing, is smaller for TaC compared with that for the EB deposited TiC film. Besides that, the reduced hardness of some coatings can be attributed to the features of the development of their phase composition, grain morphology, pores and cracks in its microstructure. High sensitivity of the hardness to the microstructure was demonstrated for TiN films on Ti, as an example [2]. The hardness was varied over a very wide range, from approximately 8 to 29 GPa, being dependent on the extent of the transformation of TiN into Ti_2N phase. For comparison, the reported typical values for the microhardness of Ti and TiN are 1.7 and 25 GPa, respectively [2]. Pores in the TaC coating (Fig.1a) can also reduce the hardness.

Because the wear resistance of materials is proportional to $H^{1/2}$ [15,16], the surface hardness of a TaC-coated system of approximately 12 GPa could ensure an enhanced wear resistance of the titanium implant. Obviously, a further study has to be performed to elucidate the features of the EB deposited TaC films on titanium to optimize processing parameters, properties and performance of the coated implants.

CONCLUSIONS

A thin film of tantalum carbide was electron beam deposited on the pre-heated pure titanium substrate using a hot-pressed TaC target. The deposited film consists of tantalum carbide, TaC. After the coated system was annealed at 750°C, the Ta_2C carbide appears as the main phase and the film becomes cracked. The hardness of the as-deposited film was about 12.4 GPa, being close to the reported data for TaC bulk ceramics.

Acknowledgements

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