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Hardness of electron beam deposited titanium carbide films on titanium substrate

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Increased use of titanium and titanium-base alloys in medicine is occurring due to their relatively low elasticity modulus and enhanced corrosion resistance as compared to more convenient alloys intended for implantation into the human body [1]. However, the properties of oxides present in the near-surface region of Ti-base materials deserve special attention. The titanium oxides from TiO to Ti_3O_5 can exist in a stable state at the harsh conditions of the body fluids surrounding the implant. Tribo-chemical reactions during use can modify the oxidized surface of the implant producing wear debris accumulation, which results in an adverse cellular response and implant loosening. To improve bone response and reliability of implanted device, the surface modification by coating of implants with various substances can be used. In particular, titanium carbide on titanium can provide protection against oxidation, excellent corrosion resistance, enhanced hardness, and superior wear resistance of the implant.

To cover a substrate with a thin carbide film, different methods are commonly used, e.g., chemical vapor phase deposition, pulsed laser ablation deposition (PLAD), magnetron sputtering [2–4]. The present study is aimed at the study of the hardness of electron beam deposited (EBD) titanium carbide films onto Ti substrates.

To prepare the targets for EBD, titanium carbide powder (Aldrich, 98% pure) was pressed into 18 mm diameter pellets. The pellets were placed into a crucible made of titanium diboride/boron nitride composite (Advanced Ceramics Corp. Europe, UK). The crucible was then inserted into a water-cooled electron beam gun (EVI-8, Ferrotec, Germany), which has been positioned into a stainless-steel chamber evacuated by a turbomolecular pump supported by a rotation pump. The electron beam gun was controlled by a joypad that permits a complete control of the accelerating voltage in the range between -3.05 and -10 kV, the shape, pattern and position of the beam. The maximum operation power was 5 kW. 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 substrates were heated under vacuum of 5.10^{-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 electron beam was circular and slow, to ensure uniform consumption of the evaporating material. The deposition was performed at the substrate pre-heating temperature 200 or 800 °C for several minutes. After the cooling and venting with N_2, the samples were of metallic luster and dark grey colored.

The thickness of film was evaluated by scanning electron microscopy observation of the cross-sections of the samples (a LEO 1530 SEM apparatus, Carl Zeiss, Germany). An absolute error of the thickness measurement was ±10 nm. The hardness was measured with the use of a Leica VMHT apparatus (Leica GmbH, Germany) equipped with a standard Vickers pyramidal indenter (square-based diamond pyramid of face angle 136 °). On each sample indentations were made with 5 to 7 loads ranging from 0.01 to 5 N. Both diagonals were measured to diminish the effects of asymmetry on the imprint. Standard deviation of the diagonal measurements was about 5 to 9% of the diagonal length. The measured hardness was that of the film-substrate composite system.

To separate the hardness of the film-substrate system on its constituents from the film and the substrate, a model based on an area "law-of-mixtures" approach was applied [5], where the composite hardness H_c of the film-substrate system is expressed as

$$H_c = (A_f/A)H_f + (A_s/A)H_s \qquad (1)$$

where A is total contact area; H is the hardness; subscripts f and s denote film and substrate, respectively; $A = A_f + A_s$ is the total contact area. From the geometric considerations Equation 1 was specified as follows

$$H_f = H_s + (H_c - H_s)/[2c(t/d) - c^2(t/d)^2] \qquad (2)$$

where $c = 2\sin^2 11^\circ \approx 0.07$ for hard brittle film on softer substrate; $d \approx (1/7)D$ is the indentation depth, and D is the imprint diagonal. The model is applicable at large indenter penetration depth where the surface displacement is more than thickness of the film.

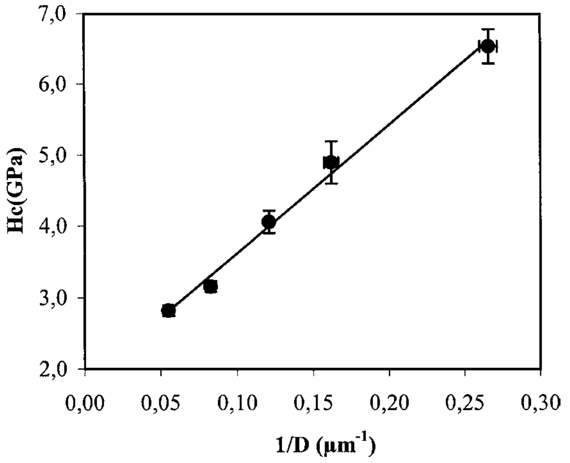

Figure 1 Composite system hardness versus inverse imprint diagonal for the EBD film of 700 nm thickness.

According to [6], this corresponds to the indentation loading region, where the fracture of film occurs, the film being bent to conform to the plastically deformed substrate. This is the region of the d/t ratio varying in the range from about 0.7 to 2 [6, 7]. As a consequence, special attention was paid to fit the experimental data with the above condition to calculate properly the film hardness. Further, the indentation size effect (ISE) was taken into account. The reasonable expression for the H_c based on an area law-of-mixtures approach and accounting for ISE is

$$H_c = H_{s0} + [B_s + 2c_1 t(H_{f0} - H_{s0})]/D \qquad (3)$$

where $c_1 = c(D/d) \approx 0.5$; H_{f0} and H_{s0} intrinsic hardness of the film and substrate; B_s is a coefficient [8].

The experimental plots H_c versus $1/D$ were approximated well by a linear regression. Fig. 1 shows the experimental data for one of the samples, as an example. A least-squares fit of the plots to the Equation 3 results in the slope $[B_s + 2c_1 t(H_{f0} - H_{s0})]$. Using the values of $B_s = 5.38 \pm 0.98$ GPa·m^{-6} and $H_{s0} = 1.84 \pm 0.06$ GPa evaluated by the separate experiments with substrate only, the intrinsic film hardness was calculated from the slope. Table I gives the parameters of the films and their intrinsic hardness values.

The thickness of the EB deposited TiC films increases with a rise of the substrate pre-heating temperature. The intrinsic hardness of the films is lower than that of the bulk TiC, which is equal to about 30 GPa [9, 10]. Even for thinnest films, of about 700 nm thickness, the hardness, 20 GPa, becomes lower than that of the PLAD deposited TiC on Si substrate film, about 32 GPa, at the same film thickness [11]. The hardness decreases down to 9–11 GPa with an increase in both the substrate pre-heating temperature up to 800 °C and the film thickness, being significantly less than the hardness of bulk near-stoichiometric titanium carbide (about 30 GPa). The reason is supposed to be the diffusion of carbon into the metallic titanium substrate during the deposition process, which is enhanced with the rise of the substrate pre-heating temperature.

TABLE I TiC on Ti films thickness and intrinsic hardness

Substrate pre-heating temperature (° C)	Film thickness (μm)	Intrinsic hardness (GPa)
200	0.7 ± 0.1	19 ± 5
	0.7 ± 0.1	20 ± 5
800	15.0 ± 1.0	11 ± 1
	17.0 ± 1.0	9 ± 1

The problem of the Ti/TiC thin films thermal stability is well known, especially in multilayer coatings [12]. Self-diffusion coefficient of non-metallic atom in the transient metal carbides is generally higher by two to three orders of value compared to that of metal atom, being increased significantly with an increase in temperature [9]. Taking into account a relatively wide homogeneity region of titanium carbide, from about 32.4 to 48.7 at% C at 1918 K [9], the formation of gradient carbon distribution in the near-surface layer can be supposed, especially at high deposition temperature, opposite to that for TiC coating on silicon. A decrease in carbon content in titanium carbide is known to lower the hardness, e.g., down to 11.76 GPa in the bulk sintered ceramics of $TiC_{0.58}$ composition [9]. This value is in agreement with the measured intrinsic hardness of the carbide film deposited at the substrate temperature 800 °C.

Thus, it can be concluded that high temperature of substrate pre-heating results in decreasing hardness of titanium carbide film onto titanium substrate, probably due to diffusion of carbon into substrate. Even at the substrate pre-heating temperature of about 200 °C, the hardness of EBD titanium carbide film is lower than that of bulk TiC ceramics. A barrier coating between Ti substrate and deposited film could be applied to increase further the hardness of film.

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