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Electrophoretic deposition and reaction-bond sintering of Al_2O_3/Ti composite coating: evaluation of microstructure, phase and wear resistance

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Abstract. **In this study, Al_2O_3/Ti composite coating was deposited on $TiAl_6V_4$ substrate in various compositions using the electrophoretic deposition method. After the deposition, samples were dried at room temperature then the coated samples were sintered at 1050°C for 4 h. Scanning electron microscope and X-ray diffraction analysis were used to analyse the microstructure and morphology of coatings. The friction coefficient, wear (missing volume) and hardness of coatings have been studied in comparison with uncoated sample. The results demonstrate that the density of Al_2O_3/Ti composite coating increased considerably after heat treatment process. Moreover, wearing resistance of $TiAl_6V_4$ alloy escalated considerably, increasing its potential for application in orthopedic implants and artificial joints.**

Keywords. **Electrophoretic deposition; alumina; $TiAl_6V_4$; wear; microhardness.**

1. Introduction

Several techniques have been used for the deposition of bioceramics, such as plasma spray, laser, magnetron sputtering, chemical vapour deposition and physical vapour deposition to promote mechanical behaviour of implants.[1–3] Electrophoretic deposition (EPD) techniques possess several advantages compared to other common methods of surface coating, including the low cost of equipments, simplicity of the process, control of coating thickness, low temperature of the process, capability of coating the complex substrates, uniform coating and short process time.[4–6] Thus, electrochemical methods have attracted much more attention in the recent years as a rapid way for deposition of bioceramics and organic materials on metallic surfaces. EPD process includes two steps; transition of the charged particles to solvent (electrophoresis); later on, movement of them to the electrode.[7] A major restriction of the EPD method is the weakness of particles bonding, which could be strengthened by subsequent heat treatment process.[8] However, there are some limitations in choosing high temperatures of heat treatment, considering the fact that the melting temperature of ceramic materials is generally much higher than or near to the melting point of the metallic substrates. In addition, low heating temperatures prohibit the activation of densification mechanisms, leading the poor densification and sintering, which is considered the main weakness of the EPD method.[9,10] Furthermore, the coating is susceptible to crack because of residual stresses produced by shrinkage during the sintering.[11] These weaknesses confine the industrialization of the EPD method, in comparison with other expensive and low quality methods, such as plasma spraying. However, many efforts have been done to overcome the weakness of EPD coatings, such as improving the density and strengthening particles bonding.[12] Ceramic–metal composite coating on metallic substrates was offered by Wang and his colleagues.[12,13] They overcame the problem of low adhesion of particles to each other in lower sintering temperatures by using reaction bond during sintering between metallic and ceramic particles. For zirconia coating on a metal substrate, Wang *et al*[12] compounded Al with zirconia which resulted in a dense coating with high hardness.

The aim of this study was to improve the reaction bond among particles in coatings fabricated by the EPD process during heat treatment in a controlled atmosphere to achieve a biological coating on $TiAl_6V_4$ substrate. The deposition of Al_2O_3–Ti composite coated on $TiAl_6V_4$ substrate via the EPD method was the main purpose of this paper, with high potential for biomedical applications. To do so, the Al_2O_3–Ti composite coating was produced using a combination of EPD and reaction bond techniques in a controlled atmosphere during heat treatment process. Morphology, phase analysis, wear behaviour and hardness of coatings were evaluated.

2. Materials and methods

Alumina powder (3 μm, Merck, Germany) and titanium powder (1 μm, Merck, Germany) were used as the raw materials.

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Surface preparation of $TiAl_6V_4$ samples were performed by grinding up to no. 1200 grit SiC waterproof paper, later the samples were cleaned by acetone, ethanol and water for 15 min in an ultrasonic bath.

In order to deposit composite coating, an electrophoretic cell was used including a 150 ml beaker, graphite electrode as the anode and $TiAl_6V_4$ sample as the cathode. The distance between electrodes was 1 cm. Suspensions were prepared by adding 6 g composite powder (three types of suspensions: Al_2O_3/Ti wt% = 3–7, 5–5, 7–3) to 100 ml mixed solvent containing butanol/ethanol (1–1). During the EPD process, a constant voltage of 50 V was applied by a power supply (Mastech, DC power supply HY30001E, 9225) for 90 s. In order to increase the adhesion and density, and reduce the porosity of coatings, samples were dried at room temperature for 24 h. Later on, samples were sintered in a tube furnace with the inert atmosphere (argon) at 1050°C for 4 h. The heating rate was 3°C min^{-1}. After sintering, the samples were cooled in the furnace under air atmosphere. The morphology of coatings was studied by scanning electron microscope (SEM) (Philips 515). X-ray diffraction (XRD) analysis (Philip Xpert-Pro) was used to determine the phases of the coatings. In order to determine the roughness of coating, a roughness measuring devices (Taylor & Hobson, Surtronic 25) was employed.

The friction and wear behaviour of Al_2O_3–Ti composite coatings were evaluated using pin on the plate method under the dry condition in air atmosphere. Wear test was carried out with a constant sliding velocity of 0.17 m/s under the applied load of 900 g. The hardness of coatings was measured using Vickers microhardness indenter (Struers, Duramin1) with an applied load of 200 g for 10 s.

3. Results and discussion

3.1 *Morphology*

The morphology of Al_2O_3–Ti composite coatings ((a) 30, (b) 50 and (c) 70 wt% Ti) after EPD process was analysed by SEM, which is shown in figure 1. As can be clearly seen, the amount of alumina particles (particle size of alumina is about 3 μm) in sample c is the lowest one. Figure 2 demonstrates the surfaces of Al_2O_3–Ti composite coatings after the heat treatment at 1050°C. Cooling in air atmosphere causes partial oxidation of titanium and promotion of its volume which compensates the coating shrinkage during sintering.

As a matter of fact, the aim of this paper was using the EPD technique to produce a biocompatible coating with high surface quality and without any micro-cracks and pores. The microstructure of coatings has a substantial effect on other characteristics of the coat layer such as mechanical and electrochemical behaviours.[5,6,14] As can be seen in figure 2, the density of composite coating elevated by increasing the amount of titanium (figure 2a and c), as the diffusion coefficient of titanium is higher than alumina during the heat treatment process. Increasing the amount of titanium strengthened the bonding between particles in coatings. The major problem that has been attributed to the EPD method is the temperature of sintering process. Choosing low sintering temperature for ceramic coatings produced by the EPD method, leads to the formation of a weak bond between particles and low-density coatings, whereas higher temperature can result in degradation of the metal substrate and decomposition of coating.[9]

Wang *et al*[12] took the advantage of combining EPD and ELD methods, in order to produce ceramic-metal coating. Liu *et al*[15] and Lu *et al*[16] used aluminium and zirconia to achieve a dense film using the EPD method for thermal barrier coatings. Moreover, they improved the quality of thermal barrier coatings on FeCr alloy using Al particles and heat treatment in oxygen atmosphere.[17] In this study, sintering of zirconia–aluminium composite coating in an oxygen atmosphere led to the formation of Al_2O_3 due to the oxidation of Al.[17] The increase in volume resulted by Al oxidation improved the coating density and compensated the shrinkage which previously has been induced during heat treatment process.[13,17] In the present work, high temperature of sintering process (1050°C in an inert atmosphere) caused diffusion of

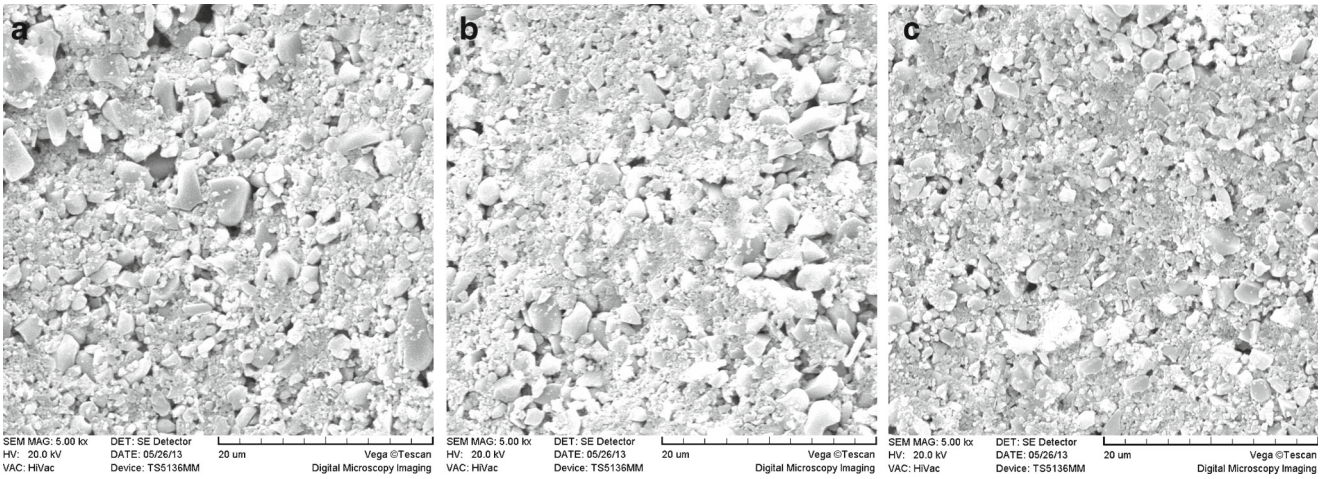

Figure 1. SEM of Al_2O_3–Ti composite coatings after the EPD process ((**a**) 30, (**b**) 50 and (**c**) 70 wt% Ti).

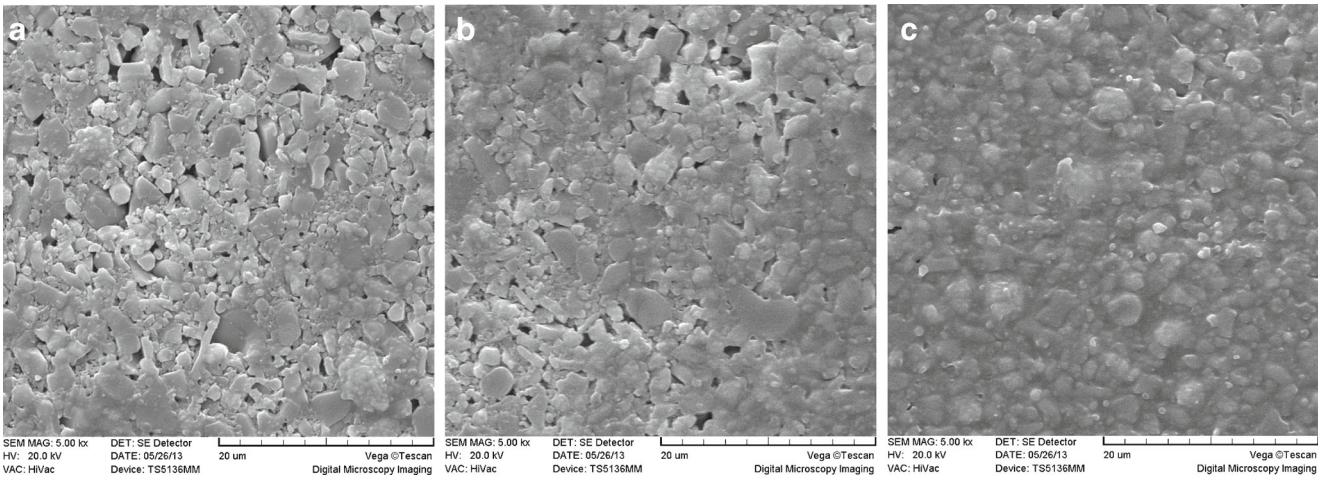

Figure 2. Influence of concentration of Ti particles on microstructure of Al_2O_3–Ti composite coating ((**a**) 30 wt%, (**b**) 50 wt% and (**c**) 70 wt% Ti) after sintering at 1050°C.

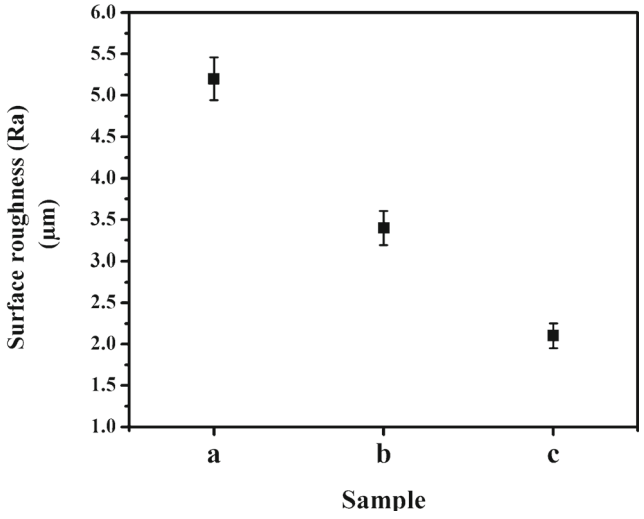

Figure 3. Roughness values of Al_2O_3–Ti composite coatings after sintering at 1050°C ((**a**) 30, (**b**) 50 and (**c**) 70 wt% Ti).

titanium in alumina particles and vice versa. The cooling in the presence of air atmosphere led to the oxidation of titanium, resulting in expansion of coated layer as well as omitting the porosity in order to reach a high-density coating during the heat treatment process.

Figure 3 demonstrates the R_a of Ti–Al_2O_3 composite coating (with wt% Ti, (a) 30%, (b) 50% and (c) 70%) after heat treatment. As can be seen, by increasing the amount of titanium in coating, the roughness decreases.

3.2 *Phase analysis of coating*

The XRD patterns of alumina–titanium coating (a: 30 wt%, b: 50 wt%, c: 70 wt%) on $TiAl_6V_4$ substrate after sintering at 1050°C are displayed in figure 4. According to this figure, $Al_3Ti_5O_2$, TiO_2, TiO and Al_2TiO_5 phases can be observed beside Al and Ti oxide phases, after the sintering of Al_2O_3–Ti composite coating at 1050°C.

It can be concluded that Ti particles interact with Al_2O_3 particles during the sintering, and aluminide–titanium oxide was produced. Besides, TiO_2 phase was observed due to the oxidation of titanium particles during the cooling process. Therefore, this transformation of Ti particles to TiO_2 led to the volume expansion of particles, compensating the shrinkage during heat treatment and decreased the porosity of the coating.[10]

3.3 *Mechanical behaviour of coating*

Figure 5 illustrates the wear rates of the composites with the different amount of Ti particles in the electrolyte (a: 30 wt%, b: 50 wt%, c: 70 wt%). Wear process is attributed to the interactions between surfaces and more specifically the removal and deformation of material on a surface as a result of mechanical action of the opposite surface.[18] Wear, unlike the elastic modulus and hardness, is not an inherent property of materials and it depends on some parameters such as the surface crystal structure, grain size, secondary phase distribution and surface morphology.[18,19]

As shown in figure 5, weight loss of the uncoated sample is the highest among all of the samples. This is due to the fact that the friction coefficient of ceramics is dramatically lower than metals.[20] Ti content of coating in sample b is virtually twice as much as that of sample a, causing the lower weight loss in b. It is mostly due to the lower surface roughness of sample b, as can be seen in figure 3. Increasing the surface roughness caused to increase the friction coefficient due to mechanical engagement in the surface.[21] With the increase in the amount of titanium (in sample c), the weight loss increases (regarding to sample b). It is not only due to the lower surface roughness (in sample c, figure 3) but also it might be due to lower alumina ceramic phase. Indeed, by decreasing the ceramic phase (alumina) and increasing the metal phase (titanium),

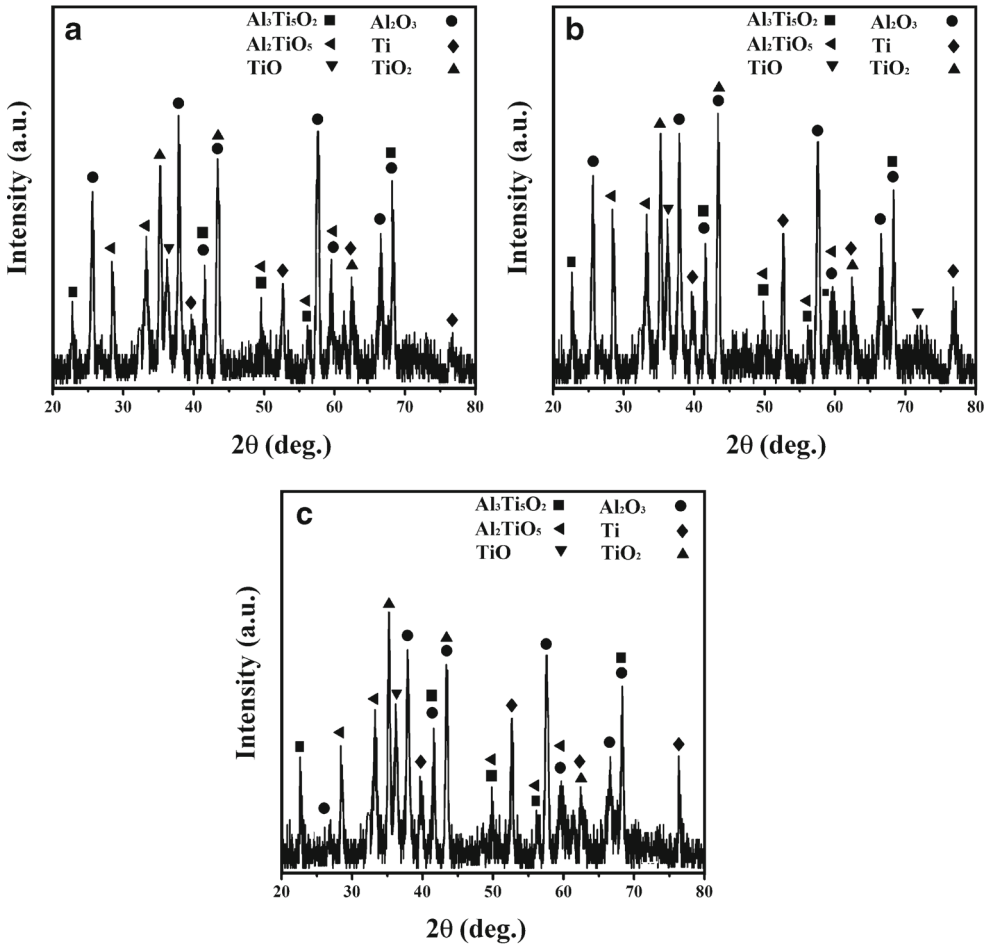

Figure 4. XRD pattern of Al_2O_3–Ti composite coating on $TiAl_6V_4$ substrate after sintering at 1050°C ((**a**) 30 wt%, (**b**) 50 wt% and (**c**) 70 wt% Ti).

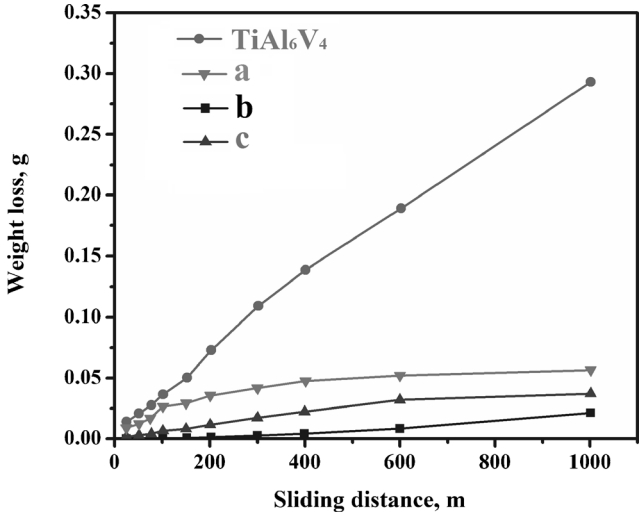

Figure 5. Variation of volume loss with sliding distance for $TiAl_6V_4$ composite coated prepared with different amounts of Ti ((**a**) 30 wt%, (**b**) 50 wt% and (**c**) 70 wt% Ti).

the friction coefficient is expected to reduce (figure 6). As can be clearly seen in figure 6, the uncoated sample experienced the highest friction coefficient among all samples. The friction coefficients of coatings are more stable and lower in comparison with uncoated sample. The friction coefficient of implant decreases by using bio-ceramic coating; moreover, it indicates that the $TiAl_6V_4$ *in vivo* application is supposed to increase.[15] It is well known that lower friction coefficient increases the wear resistance of implants (hip joints) and their safety in human's body.[22]

The microhardness testing of Al_2O_3–Ti composite coatings was performed using the Vickers microhardness instrument. Three measurements were conducted on each sample coated with different amounts of Ti particles. The Vickers microhardness of Al_2O_3–Ti composite coatings is plotted as a function of the amount of Ti particles in figure 7. It is apparent that the hardness of the coated samples is precisely higher than that of $TiAl_6V_4$ uncoated coatings. The hardness of coated sample increases with Ti up to 50 wt%, then it drops considerably. The hardness of coating depends on the materials (phases) and the surface morphology of the coating. The presence of titanium in ceramic coatings has been taken into account as a noticeable factor. The presence of metallic phase along with the ceramic phase caused the applied loads to be restrained in the composite coating by both the hard ceramic

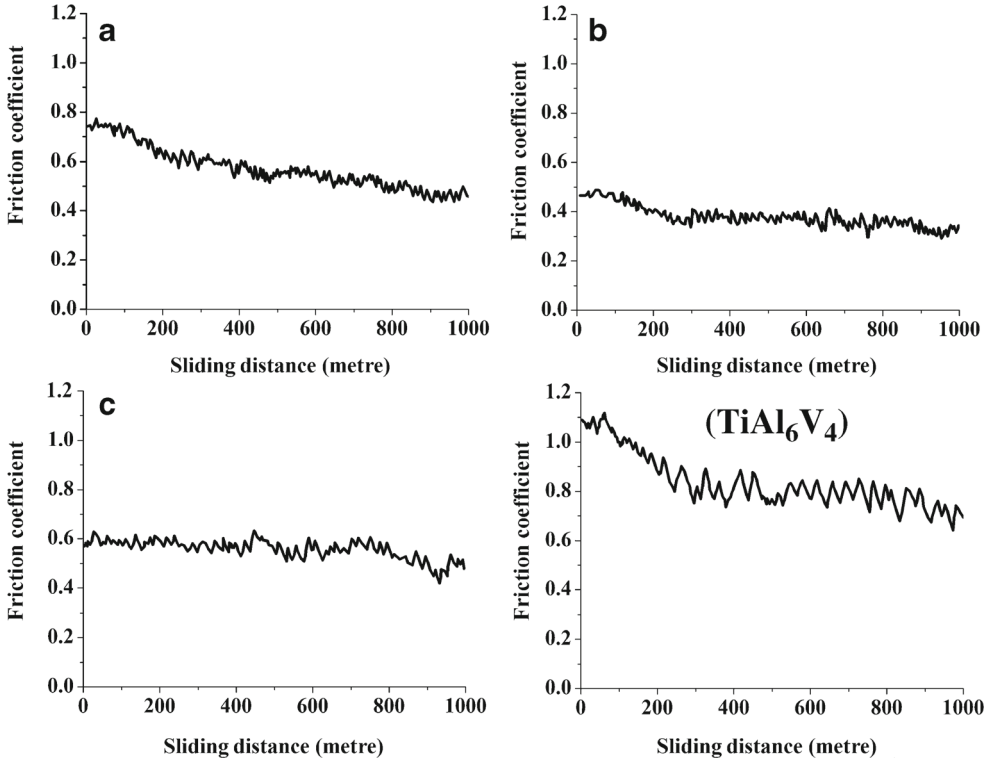

Figure 6. Friction coefficient as a function of sliding distance for uncoated and $TiAl_6V_4$ composite coating ((**a**) 30 wt%, (**b**) 50 wt% and (**c**) 70 wt% Ti).

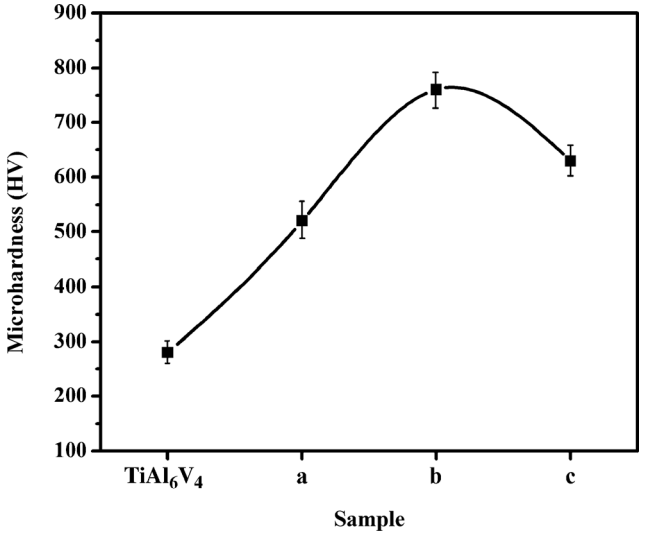

Figure 7. Vickers microhardness of uncoated and coated $TiAl_6V_4$ composite coatings with different amounts of Ti particles in coating ((**a**) 30 wt%, (**b**) 50 wt% and (**c**) 70 wt% Ti).

and the tough metallic phases; in other word it increases the energy absorbance of the surface.[18]

However the hardness of sample c is substantially less than sample B. It is due to the increase of titanium and decrease of hard alumina phase. The mechanical behaviour and hardness of coatings depends on the density and the amount of porosity, but the kind of the phase plays a significant role.[23]

In the same way, the hardness of sample a is lower than b. It is due to the lower density of surface while the hardness of sample c decreases as a result of lower hard alumina phase (figure 4).

4. Conclusion

In the present study, alumina–Ti composite coating with the different concentration of Ti particles in the electrolyte (30–50–70 wt%) deposited on $TiAl_6V_4$ substrate by the EPD method. Coatings sintered at 1050°C in Ar atmosphere, afterward cooling has been done in the air atmosphere. The morphology investigation of the coating after sintering reveals that the density of coating increases with rising of Ti content. The high sintering temperature (1050°C) facilitates the bond between particles due to the diffusion of ceramic particles, as the Al_2TiO_5, $Al_3Ti_5O_2$ phases in coating prove it. The high density of coating is the consequence of expansion which is induced by oxidation of Ti as it is shown in XRD pattern. Evaluation of mechanical properties of coating shows improving the wear behaviour of coated sample in comparison with $TiAl_6V_4$. The weight loss of uncoated $TiAl_6V_4$ sample is much higher than coated samples due to the lower friction coefficient. In addition, the weight loss declines with the increase in the Ti from 30 to 50 wt% because of the decrease in surface roughness of coating, while it increases from 50 to 70 wt% due to lower ceramic phase in coating. Likewise, the

microhardness of 50 wt% coated sample is 780 compared to uncoated sample 270.

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