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RESEARCH ARTICLE

Electrophoretic deposition of Al_2O_3/ZrO_2 layer with controllable thickness in ethanol medium

Chun-mei YANG, Xian-chun CHEN, Xiao-ming LIAO, Zhong-bing HUANG, Ya-dong YAO and Guang-fu YIN (✉)

ZrO_2 toughened Al_2O_3 (Al_2O_3/ZrO_2) ceramic layers with required thickness were prepared by electrophoretic deposition (EPD) method using ethanol suspensions with stabilizing agent of polyethyleneimine (PEI) under constant-voltage mode in this paper. The deposition of Al_2O_3/ZrO_2 ceramic powders occurred on the titanium alloy cathode. A stable suspension with 1wt% PEI in ethanol at pH 5 was prepared in terms of the zeta potential and sedimentation of the suspension. The effects of the suspension concentration, applied voltage, deposition time and processing method of titanium alloy cathode on the coating thickness and morphology were investigated. The deposition layers on titanium alloys with smooth surfaces and thickness of 0.35–1.2 mm could be obtained by adjusting the aforementioned parameters. In addition, after being sintered at 1500°C for 3 h in air atmosphere, ZrO_2 toughened Al_2O_3 ceramic layers became smooth and dense.

Keywords electrophoretic deposition, suspension, Al_2O_3, ZrO_2

1 Introduction

The phenomenon of electrophoretic deposition (EPD) has been known since 1808 [1]. The EPD technique is widely used in preparing advanced materials, including ceramic coatings, nanoscale assembly, solid oxide fuel cells, laminated and graded materials, etc. [1–5]. EPD was a process wherein ceramic bodies were shaped directly from a stable suspension by a DC electric field. Compared with conventional coating techniques such as dip-coating, spin-coating, sputter coating and plasma spray, EPD possessed the advantages of short formation time, little restriction in the shape of substrates, room temperature in deposition, high deposition rates, a good thickness control, a simple and cheap deposition apparatus [1,2,6]. Otherwise, EPD was a rapid and effective method to produce coatings with controllable thickness [3]. Thereby, more and more attention is increasingly paid to the application of EPD in preparation of coatings.

However, in aqueous-based EPD suspensions, this method presented several disadvantages, for example, corrosion of the electrodes and gas bubbles produced by electrolysis of water at the electrodes during the EPD, which would reduce the density of deposited layer [7–10]. To avoid the formation of gas bubbles, non-aqueous suspensions became a preferred choice. Among the non-aqueous media, ethanol was the common dispersing medium for EPD [6]. In this research, ethanol was used as a solvent for EPD because of its less toxicity, less harmfulness to the environment, and good volatility. In addition, the suspension must possess a high stability, thus charged polymers and surfactants were added to the suspension [1,11,12]. These additives, which were adsorbed onto the surfaces of ceramic particles, could generate steric and electrostatic stabilization and prevent particles agglomeration.

Thanks to the esthetical aspects and good biocompatibility, ceramics have been extensively applied in oral rehabilitation [7,11], and the application of ceramics in dental field could prevent allergic reactions and toxic tissue damages. The thickness of the all-ceramic crown substrate was required to be at least 0.5 mm [13], so the deposition layers should be thick enough due to the sintering shrinkage of ceramic. Besides, some studies reported that ZrO_2 toughened Al_2O_3 ceramics showed high compressive strength, good hardness, low mechanical abrasion, high toughness and small thermal conductivity [8]. Therefore, in this study, ZrO_2 toughened Al_2O_3 ceramic layers with appropriate thickness were prepared by EPD technique from ethanol suspensions. Furthermore, pure titanium and titanium alloys were widely used in metal-ceramic restorations and dental implantations owing to their superior mechanical properties and excellent biocompatibility [14]. Thus, in this paper, titanium alloys were used as substrates during EPD progress.

The quality of EPD coatings was influenced by the suspension properties and electrophoretic deposition conditions. In detail, the suspension properties included the dielectric constant of the suspension, the suspension viscosity, the zeta potential of the powder particles, suspension concentration and conductivity. And the electrophoretic deposition conditions contained the deposition time, applied voltage and conductivity of substrate. So the aim of this work

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College of Materials Science and Engineering, Sichuan University, Chengdu 610064, China
E-mail: nic0700@scu.edu.cn

was to investigate the effect of the interrelated parameters on the electrophoretic deposition of Al_2O_3/ZrO_2 onto a titanium alloy electrode from non-aqueous suspensions, and to obtain deposits with appropriate thickness by optimizing the suspension composition and electrical conditions.

2 Experimental

2.1 Materials

The following starting powders were used as raw material for deposition: (1) Al_2O_3, with a mean particle size of 0.2 μm and a specific surface area of 6–13 m^2/g, and (2) tetragonal zirconia polycrystals with 3% mol Y_2O_3, Y-TZP, with a mean particle size of 0.2 μm and a specific surface area of 8–20 m^2/g. Their SEM-pictures are shown in Fig. 1. The organic solvent of ethanol was used as the dispersion medium for preparing the suspensions of Al_2O_3 and ZrO_2 powders. Polyethyleneimine (PEI) was used as stabilizing and dispersing aid.

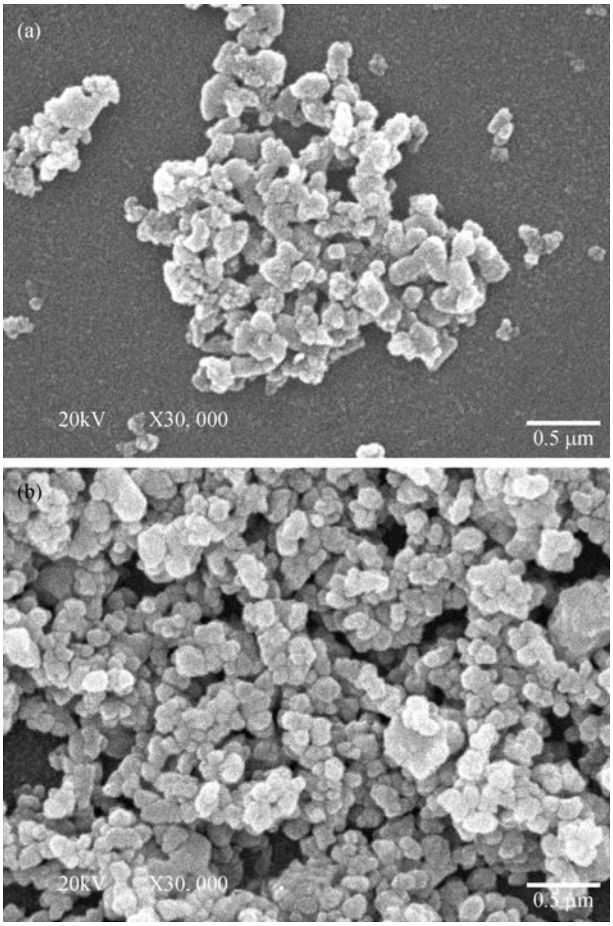

Figure 1 SEM images of the ceramic powders
(a) alumina; (b) zirconia

2.2 Preparation of suspension

The suspensions with different suspension concentrations (10–50 wt%) were prepared by adding the ceramic powders into liquid solvent followed by stirring for 1 h and ultrasonic treatment for 20 min. 0.1, 0.3, 0.5, 1, 1.5, 2 and 4 wt% of PEI were added into the liquid phase, respectively. The suspensions were sub-packed in 10 mL test tubes and placed for 24 h to investigate the stability. Suspension pH was adjusted using nitric acid (HNO_3) and sodium hydroxide solution (NaOH).

2.3 Electrophoretic deposition

The EPD experiments were performed using a power supplier (Electrophoresis Power Supply: JY600) which could work at both constant voltage and current density. In this research, all the experiments were carried out under constant voltage. The voltage was changed from 20 to 120 V during the experiment.

The electrolytic cell was a glass beaker containing the electrodes suspended in the beaker. The working electrode (cathode) was a square titanium alloy plate (10 mm × 10 mm × 1 mm) and the counter-electrode (anode) was a square platinum foil with a dimension of 10 mm × 10 mm × 0.3 mm. The distance between electrodes was 10 mm. After the deposition was finished, all the deposits were sintered at 1500°C for 3 h in air atmosphere in a high temperature box-type resistance furnace (SSX-8-16, China).

2.4 Evaluation of deposit properties

Zeta potential measurements were tested using a zeta potential analyzer (Zetasizer Nano ZS90, Malvern Instruments, UK). The current was measured by a multimeter. The surface morphology and the coating thickness were detected by scanning electron microscopy (TM1000, HITACHI, Japan) The crystal structure as examined with an X-ray diffractometer (DX-1000, China)

3 Results and discussion

3.1 Suspension stability

The stability of the suspension was a key factor for electrophoretic deposition process. Stable suspensions showed no tendency to flocculate, were settled slowly and would be helpful to form dense and strongly adhering deposits on substrates [1]. The direction and migration velocity of particles during EPD were determined by zeta potential. The high zeta potential was favorable for preventing particles flocculation and gaining deposit with high green density;

thereby the zeta potential of particles was an important evaluation indicator for the deposition suspension [1].

Figure 2 shows the relationship between the measured zeta potential and the PEI dispersant contents. It could be seen that the zeta potential without dispersant was positive in the ethanol and got the highest after the addition of 1 wt% dispersant, which was favorable to EPD procedure. The particles in unstable suspension would sink owing to the low zeta potential and flocculation of suspension. And the sinking would result in stratification of the suspensions sub-packed in 10 mL test tubes. Figure 3 displays sedimentation of the suspension with different PEI concentrations. When the amount of PEI additive was lower than 1 wt%, the flocculation was observed in the suspensions and the suspensions were unstable, and the same phenomenon was observed for bigger amount (>4 wt%) of PEI. According to Fig. 3, the suspensions with 1–2 wt% of PEI were more stable. Meanwhile, the absolute value of the zeta potential of suspension with 1 wt% PEI addition was the maximum in Fig. 2. Therefore, 1 wt% of PEI addition was most suitable for preparing the stable suspension, attributed to the high zeta potential and low sedimentation rate as shown in Fig. 2 and Fig. 3. The variation of the zeta potentials in the suspensions with 1 wt% PEI addition at different pH value is shown in Fig. 4. It was obvious that, when the pH value was 5, the absolute value of the zeta potential of suspension achieved the maximum. It could also be seen that the zeta potential increased with the decrease of the pH value until the pH value reached 5, wherein the zeta potential decreased when the pH went on increasing. Zhitomirsky indicated that PEI was a weak cationic polyelectrolyte. Its functional amine –NH groups needed to adsorb protons in the suspension to make the PEI charged positive, meanwhile, the degree of ionization was determined by the solution pH [6,15]. So the improvement of zeta potential by PEI should be under acid conditions. According to the above results, the pH of all the suspensions in this research was adjusted to 5.

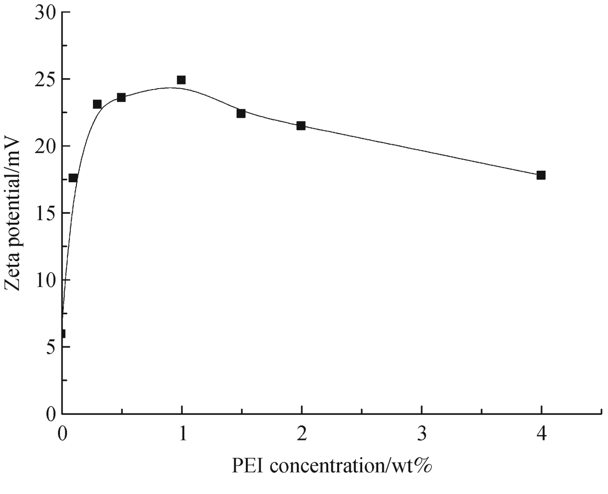

Figure 2 Zeta potentials of the suspensions with different PEI concentrations

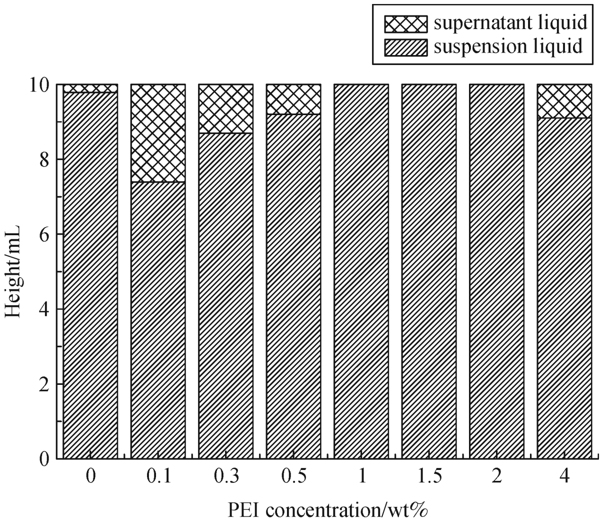

Figure 3 Sedimentation of the suspensions with different PEI concentrations

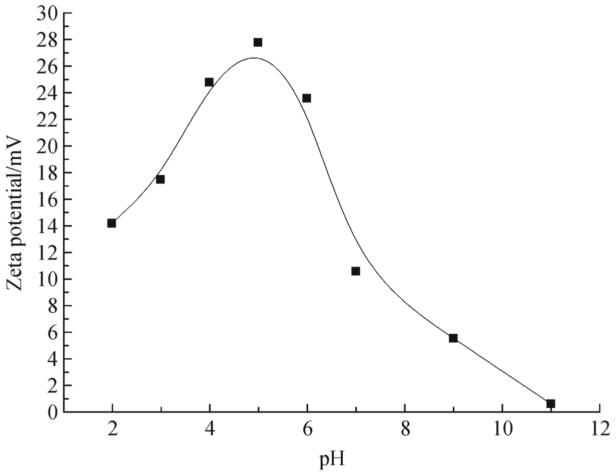

Figure 4 Zeta potentials of the suspension at different pH

Figure 5 displays the IR spectra of PEI, Al_2O_3/ZrO_2 powders and modified powders. It was also obvious that there were small differences between the IR spectra of the powders before and after modified, that is, in the spectrum of the modified powders, the characteristic peaks of $-CH_2-$ stretching vibration peaks of PEI at about 2833, 2863, 2917 and 2951 cm^{-1} were present. On the contrary, these $-CH_2-$ group characteristic peaks were not observed in the starting powders. The result indicated that the PEI was adsorbed onto the surface of powders, that is, the surface of modified powder was enwrapped by the positively charged PEI. As shown in Figs. 2 and 5, the results showed that the surface of $Al_2O_3/$

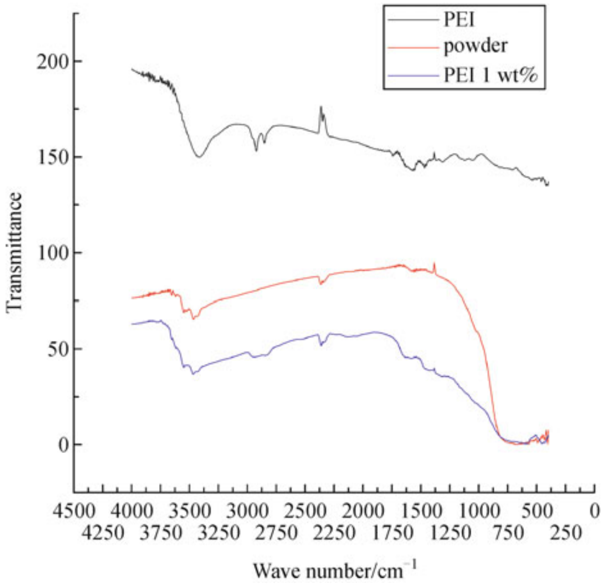

Figure 5 IR spectrums of PEI and Al_2O_3/ZrO_2 composite powders (a) PEI; (b) raw powders; (c) modified powders

ZrO_2 powders in the suspension could be modified by the PEI additive, and then the zeta potential was effectively improved.

3.2 Electrophoretic deposition

Electrophoretic deposition technique possessed two modes, namely, constant voltage and current mode [16]. The constant voltage mode was chosen in this research. Eq. (1) about the correlation of the weight of the deposited particles during EPD and different influencing factors was originally proposed by Hamaker [17] and Avgustinik et al. [18]:

$$w = \int_{t_1}^{t_2} \mu \cdot E \cdot A \cdot C \cdot \mathrm{d}t \tag{1}$$

where w, E, μ, A, C and t were the weight of the deposited particles, electric field strength, electrophoretic mobility, the surface area of the electrode, particle mass concentration in the suspension and deposition time, respectively.

As shown in the Equation, the weight of the deposited particles was directly proportional to time, electrophoretic mobility, surface area of the electrode and suspension concentration. Therefore, in this paper, the suspension concentration, voltage and time were adjusted to control the weight and thickness of the deposit films. In this research, the Al_2O_3/ZrO_2 powders suspension in ethanol were positively charged and moved toward the titanium alloy cathode under the applied electric field. Figure 6 exhibits the variation of the deposition weight per area versus different suspension concentrations at the same deposition time of 60 s under two different applied voltages. It was obvious that, in a constant voltage EPD, the deposition weight increased with the increase of the suspension concentration. In addition, the deposition weight grew linearly with the suspension concentration under the low voltage. A similar result was obtained in Meng Shan's study [6]. With the increase of the voltage, it deviated from the linear growth. The reason might be that, when the suspension concentration were kept constant, the particle migration rate increased with the increase of the voltage, which resulted in the increasing amount of powders deposited on the substrate in the same time period. The present experimental results demonstrated that the suspension concentration and applied voltages played an important role in obtaining layer with the required thickness. In this study, in order to gain thick enough layers, the suspension concentration should be within the range of 40–50 wt%.

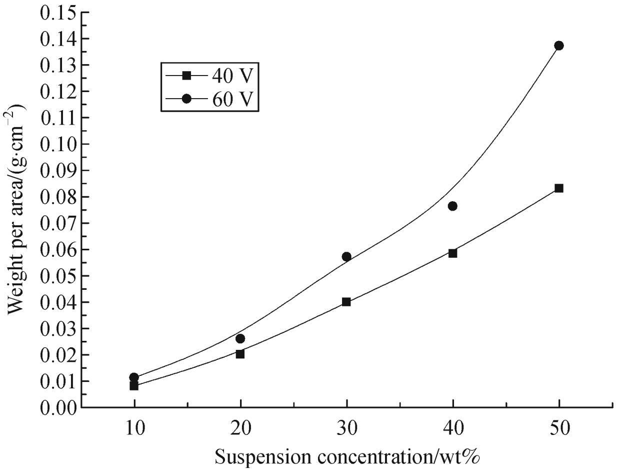

Figure 6 Variation of the deposition weight per area with suspension concentration under 40 V, 60 V applied voltage (deposition time: 60 s)

As shown in Fig. 7, the current density of ethanol solvent in an absence of powders increased and became unstable with

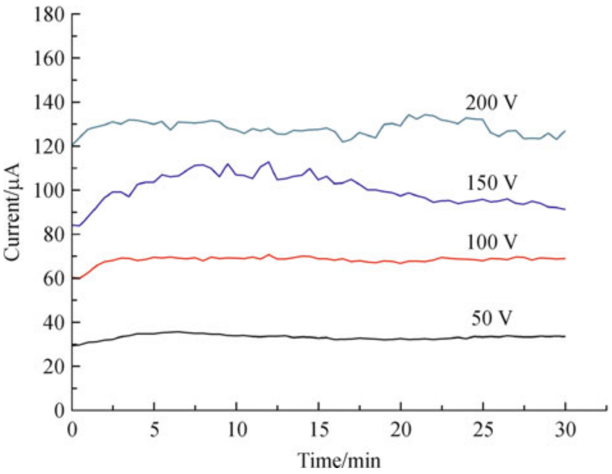

Figure 7 Stability of current density in ethanol under different applied voltages

increasing applied voltages. It was considered that the unstable current density would influence the quality of deposition morphology [19]. According to the current density profile in Fig. 7, to get the flat deposit surface morphologies, it was reasonable to conclude that the applied voltage should be less than 100 V. So the applied voltages below 100 V were chosen in this experiment. Figure 8 illustrates the variation curves of deposition weight under different applied voltages in 60 and 240 s. It could be seen that the deposition weight increased with the increase of time and the app1ied voltage, which was consistent with the Hamaker Equation. Moreover, the general trend of this plot might be adjusted to a linear evolution of the deposition weight with applied voltage, which might be used to presume the deposition weigh under a set applied voltage. Therefore, according to this law, the deposition weight and thickness could be controlled by changing the applied voltage.

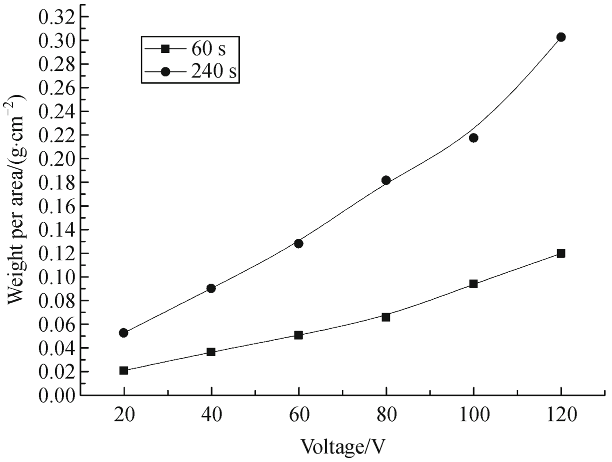

Figure 8 Variation of the deposition weight per area with applied voltages (suspension concentration: 40 wt%; deposition time: 60 s and 240 s)

As shown in Fig. 9, the weight per area under a fixed applied field of 20, 40, and 60 V increased with prolonged deposition time. It was observed that the deposition rates (slope of the curves) under the applied voltage of 20, 40, and 60 V decreased after a spell of deposition. Research by Sarkar et al. [16] on Kinetics of electrophoretic deposition indicated that, in constant voltage mode, both the concentration of suspension and particle velocity decreased with the increase of deposition time. Van der Biest and Vanderperre [1] thought that the total resistance of the EPD cell increased via depletion of charge carriers from the suspension. Consequently, as the deposit grew, the available electrical driving force or voltage per unit length of suspension decreased with the time, thereby the particle velocity decreased. Furthermore, the deposition weight and rates increased with the increasing app1ied voltage in the same time period, which was consistent with the abovementioned Hamaker Equation and Fig. 8.

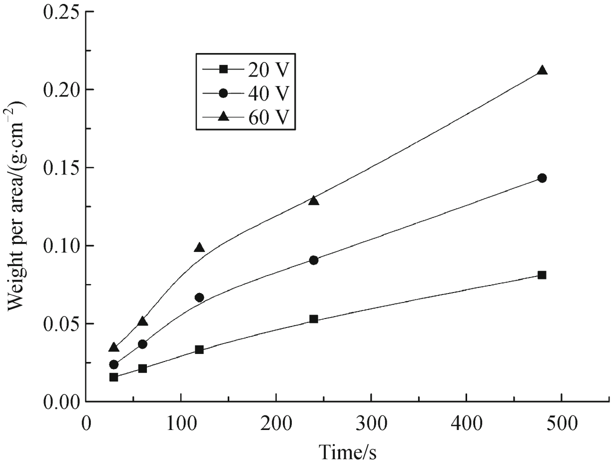

Figure 9 Variation of the deposition weight per area with deposition time (suspension concentration: 40 wt%; applied voltages: 20 V, 40 V, 60 V)

Finally, the methods of treating electrodes would also affect the deposition weight. In this paper, all of the titanium alloy electrodes were cleaned with acetone and ethanol in turn. A part of electrodes were polished using 120 to 1000 grit emery papers. Figure 10 shows the variation of the deposition weight per area in different deposition times under 20, 40, and 60 V applied voltage by different handling mode. It was obvious that the weight of particles deposited on the unpolished electrodes was much higher than the polished ones, suggesting that the surface morphology of the substrates also possessed an influence on the deposition weight.

3.3 Microstructure

The XRD patterns of the raw coating and the coating sintered at 1500°C are shown in Fig. 11. The main phases of the coating before and after heat treatment were composed of α-Al_2O_3, tetragonal zirconia polycrystal (t-ZrO_2) and monoclinic zirconia (m-ZrO_2). It was observed that, after the heat treatment, the intensity of tetragonal zirconia polycrystal peaks got higher. Therefore, it could toughen alumina ceramics by its phase transformation. In addition, the crystallinity of the coating was much higher than that of raw coatings.

The photographs of ZrO_2/Al_2O_3 layers on titanium alloy electrodes at (a) 40 V for 60 s and (b) 80 V for 240 s in the 40 wt% suspension are shown in Fig. 12. It was observed that the deposition layer surface was very smooth and dense, and the thickness of (b) was much bigger than (a), which was consistent with the result shown in Fig. 9. Figure 12(c) displays the cross section images of the layer deposited

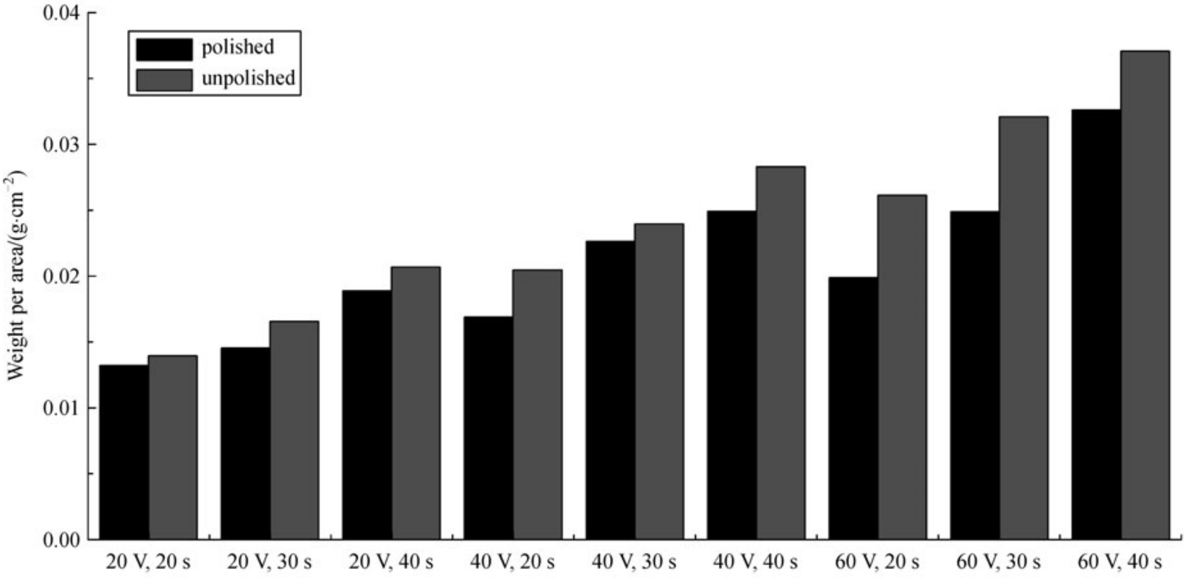

Figure 10 Variation of the deposition weight per area in different deposition times under 20 V, 40 V, and 60 V applied voltage by different handling mode

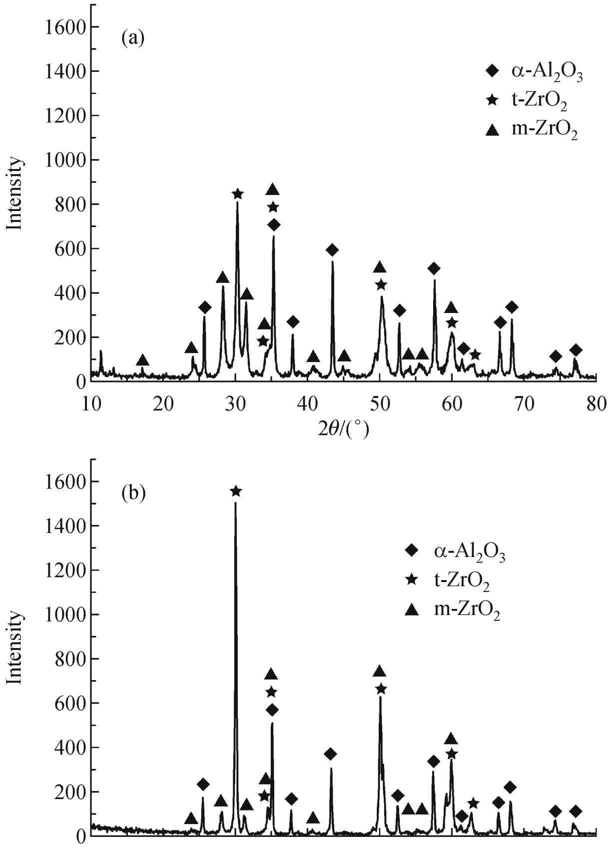

Figure 11 XRD patterns of the coating (a) before heat treatment and (b) after heat treatment

without heat-treatment under 40 V for 60 s in 40 wt% suspension. As shown in Fig. 12(c), the thickness of deposited layer was about 0.35 mm. The lower right corner of Fig. 12(c) shows the photographs of the microstructure of coating surface of EPD deposits. Fig. 12(d) shows the cross section images of the layer deposited under 80 V for 240 s in 40 wt% suspension and calcined at 1500°C for 3 h, and the lower right corner of Fig. 12(d) is the high magnification image of (d). As shown in Fig. 12(d), the layer with thickness about 1.2 mm was obtained. It could be seen that, after being sintered, the particles grew larger, the grain boundary could be observed cleanly, and the incompact coatings got denser. So the thickness of deposited layers could be controlled by the suspension concentration, applied voltage and deposition time. However, some holes were observed in the high magnification image of (d). So there might be much room for improvement on the EPD of Al_2O_3/ZrO_2 coatings on titanium alloy substrates.

4 Conclusions

Electrophoretic deposition of alumina and zirconia powders from ethanol suspension in the presence of polyethyleneimine (PEI) under constant voltage occurred on the titanium alloy cathode. PEI was used as a stabilizing and dispersing aid in order to obtain stable and suitable suspensions for the EPD process. And the results showed that the suspensions with 1 wt% PEI at pH 5 was most suitable for EPD. The deposition weight and thickness could be controlled by the suspension

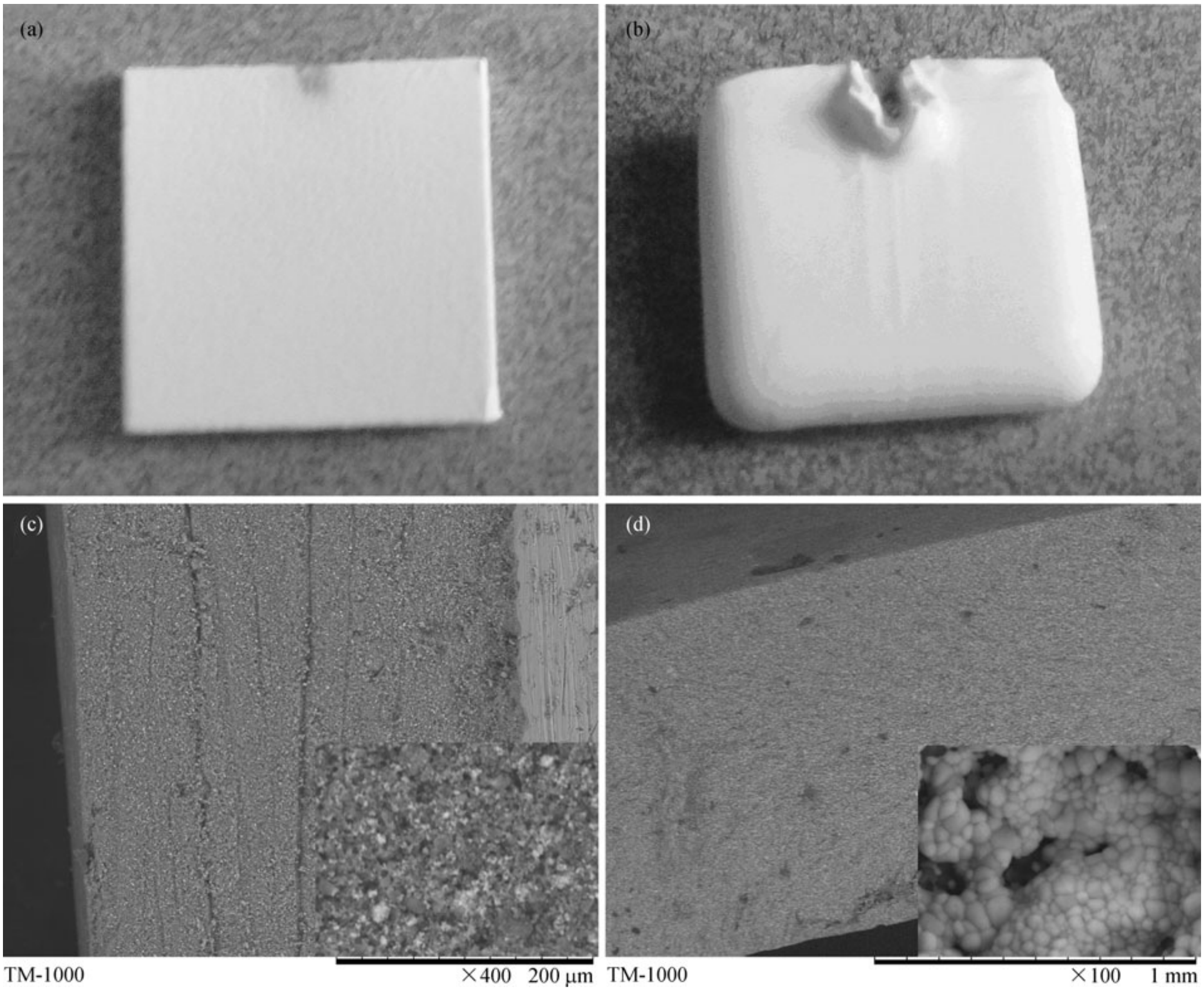

Figure 12 Photographs and SEM micrographs of ZrO_2/Al_2O_3 layers on titanium alloy electrodes in 40 wt% suspension
(a) 40 V for 60 s; (b) 80 V for 240 s; (c) SEM image of cross section of (a) without heat-treatment; (d) SEM image of cross section of (b) calcined at 1500°C. The high magnification images (×10,000) of (c) and (d) are shown in the lower right corner.

concentration, applied voltage, deposition time and processing method of titanium alloy cathode. After being sintered at 1500°C for 3 h in air atmosphere, homogeneous and dense zirconia toughened alumina ceramics coatings with thickness of 0.35–1.2 mm were obtained. The result showed that electrophoretic deposition was a promising and effective way to produce ZrO_2 toughened Al_2O_3 layers with controlled thickness. More researches were necessary to optimize the EPD conditions by investigating the influence of the related parameters on the Al_2O_3/ZrO_2 layer quality and mechanical properties in the future.

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