

Article

Low Current Density Cathode Plasma Electrolytic Deposition of Aluminum Alloy Based on a Bipolar Pulse Power Supply

Hang Li ^{1,*} , Guochen Zhao ^{1,*}, Huan Yu ¹, Kaiming Cheng ¹, Xuansheng Feng ¹, Yunteng Liu ¹, Jixue Zhou ^{1,*} , Minghua Bai ², Fengyao Ni ³, Jinkui Wu ³ and Zhizhuang Sun ³

¹ Shandong Provincial Key Laboratory of High Strength Lightweight Metallic Materials, Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250014, China

² College of Chemistry and Chemical Engineering, Shenyang Normal University, Shenyang 110034, China

³ Shandong Donghong Pipe Industry Co., Ltd., Jining 273100, China

* Correspondence: lih@sdas.org (H.L.); zhaogch@sdas.org (G.Z.); zhoujx@sdas.org (J.Z.)

Abstract: The present paper reported a novel bipolar-pulse cathodic plasma electrolytic deposition (BP-CPED) technique with a low current density. This newly developed CPED technique can break down the barriers of the existing CPED technique with higher current density. In this report, ceramic coatings were successfully prepared on aluminum alloy via the BP-CPED technique in an aqueous carbamide-based electrolyte. Data recording results in the reacting process show that there is the current density of the cathode below 0.15 A/cm² and that of the anode below 0.035 A/cm², which approximately reaches the level of conventional MAO technique. Interestingly, the addition of PEG into the electrolyte can further reduce the current density and effectively improve the coating quality. The kinetic of the BP-CPED process was discussed based on the evolution of current density/voltage-time curves and spark discharge phenomena. SEM observations illustrate that BP-CPED coatings possess a typical porous-surface feature. XRD analysis indicates that the coating was mainly composed of Al₂O₃ and Al₄C₃. Al₂O₃/Al₄C₃/ZrO₂ composite coatings fabricated after Zr-doping reflected the successful Zr-incorporation into the coating, which demonstrated that the BP-CPED technique can be used to design the coating composition by the doping modification. The direct pull-off and thermal shock tests confirmed that new BP-CPED coatings obtained under the cathodic plasma discharge have excellent bonding strength. It is possible that this novel BP-CPED technique can provide a promising choice in developing the large-area CPED surface treatment for the industrial application.

Keywords: cathodic plasma electrolytic deposition; low current density; bipolar pulse; aluminum alloy; doping modification



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1. Introduction

Lightweight aluminum has developed into a promising important alternative material to traditional steel [1]. However, insufficient environmental resistance and native surface passivation have seriously restricted extensive applications of aluminum alloys [2,3]. Ceramic materials are usually applied to coat aluminum alloys for improving the long-life service stability and the resistance from the external erosion/shock [4]. Therefore, surface treatment techniques of preparing ceramic protective coatings are used to enhance the performance and function of aluminum alloys, including anodizing, spraying, sputtering, PVD, and CVD [5–9]. Yet these technical procedures usually involve multi-step pre- or post-processes, long treating duration, specific reaction environments, and limitations on workpiece shapes and sizes. Plasma electrolytic deposition (PED) is an emerging technique combining traditional electrolysis with atmospheric plasma processing, and attracts much attention for the efficient processing, simple equipment operation, and an easier reaction environment [10,11]. The PED technique includes an anodic plasma processing (known

as micro-arc oxidation, MAO) and cathodic plasma processing, such as cathodic plasma electrolytic deposition (CPED).

Currently, scholars have employed the CPED technique to prepare various ceramic layers (carbides, nitrides, oxides, or their mixtures) [12,13]. However, in the case of DC mode, CPED confronts the challenge from a higher current density, which is about 2–3 orders of magnitude higher than that of the MAO technique ($0.05\text{--}0.2\text{ A/cm}^2$) [14]. For instance, H. Tavakoli et al. [15] employed a DC power supply to process cathode plasma electrolysis nitrocarburizing treatment of EN41B steel in the aqueous urea electrolyte, and the output cathode current-density showed that the peak values during the process reached up to about 3.0 A/cm^2 . Y. Zhang et al. [16] successfully prepared $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SiO}_2$ coatings with good oxidation resistance on cathodic carbon fiber/resin composites, and cathode-current peaks of DC power source recorded by a computer exhibited above the level of 5 A/cm^2 . The work of R. Ji et al. [17] applied DC-CPED technique to fabricate anticorrosion CeO_2 coatings on magnesium alloy, of which the investigation found that the glycerol addition into the electrolyte could significantly reduce the spark ignition current-density from about 10 A/cm^2 to 5 A/cm^2 . In order to improve the stabilization of Ti-45Al-8.5Nb alloys at high temperatures, Z. Jiang et al. [18] used a DC pulse power source to deposit $\gamma\text{-Al}_2\text{O}_3$ coatings, and the peak of the cathodic current-density reached up to 5 A/cm^2 in the DC-CPED process. Therefore, the CPED technique remains in the laboratory phase as it is difficult to achieve the industrial application as with the MAO technique.

Considering these technical bottleneck problems, few scholars have reduced current density in the CPED process by adding additives or pre-fabricating the insulative barrier coating. Y. He et al. [19] proposed a method of adding glass beads in the cathode region, and the current density of the super-alloy cathode was successfully decreased from about 6.0 A/cm^2 to 1.5 A/cm^2 in the DC-CPED process. Nonetheless, this method is difficult to apply to treat irregular workpieces. Y. He et al. [20] also found that adding polyethylene glycol (PEG) in the electrolyte can effectively reduce the cathodic current density during the DC-powered CPED reaction. Few studies have been conducted on the use of the CPED technique to deposit the ceramic coat on aluminum alloy. One relevant study saw P. Wang et al. [21] prepare the insulating barrier layer using the MAO method; they then used the DC-CPED technique to deposit Zr/Y-containing Al_2O_3 coatings on aluminum alloy. However, these tedious steps can greatly reduce the efficiency of the coating preparation. Above all, current research reports have failed to solve the high current density during the CPED process.

The bipolar pulse power source has been rarely employed in the CPED research, hence the efforts of this power type on the CPED reaction deserves exploration. Compared with DC mode, the bipolar pulse power supply can provide extra effective parameters involving the cathodic and anodic direction (the pulse number and duty cycle of the anode and cathode, the anode voltage). The purpose of this work is to confirm the feasibility of the pulsed bipolar power source employed to one-step deposit ceramic coatings on aluminum alloys via the CPED method. An exciting discovery was made, with the experimental data results of the cathodic current density in the reaction process showing a level similar to the MAO technique (below 0.15 A/cm^2). This technique can be referred to as a bipolar pulse cathodic plasma electrolytic deposition (BP-CPED). The kinetics of the BP-CPED process are necessarily investigated regarding the current density/voltage-time curves and spark phenomena. Moreover, the effects of PEG and on the current density are further studied, and the experiment of Zr-doping modification was used to verify the compositional designability of BP-CPED coatings. This work provides a novel feasible idea and approach for the use of the CPED technique for industrial application. It is expected that this BP-CPED technique will be further explored and extended to the surface modification of other conductor materials as well as the preparation of other coating types.

2. Materials and Methods

2.1. Preparation Procedure

The substrate material selected in this work was a commercial EN AW-6061 aluminum alloy for surface treating. Prior to BP-CPED treatment, alloy specimens were gradually polished with 800#, 1500#, and 2000# waterproof abrasive papers, then ultrasonically cleaned in ethanol for 10 min, and finally air dried for backup.

The BP-CPED process was performed using a conventional system comprising a 7-kW bipolar pulse power source and a high borosilicate glass container serving as the electrolytic cell. Details of the installation layout for the electrolytic cell used in this study are shown in Figure 1. The positive terminal of the power supply was connected to a graphite plate chosen as the anode and the negative terminal was connected to the aluminum workpiece as the cathode. The electrodes were immersed in a mixed organic-aqueous electrolyte consisting of 70 vol.% carbamide saturated solution, 30 vol.% water, and a little special regulator, as well as 100 g/L $(\text{NH}_4)_2\text{CO}_3$ used as an electrically conductive agent. The effect of adding 20 g/L polyethylene glycol 2000 (PEG) and 10 g/L $(\text{NH}_4)_2\text{ZrF}_6$ into the electrolyte was also investigated.

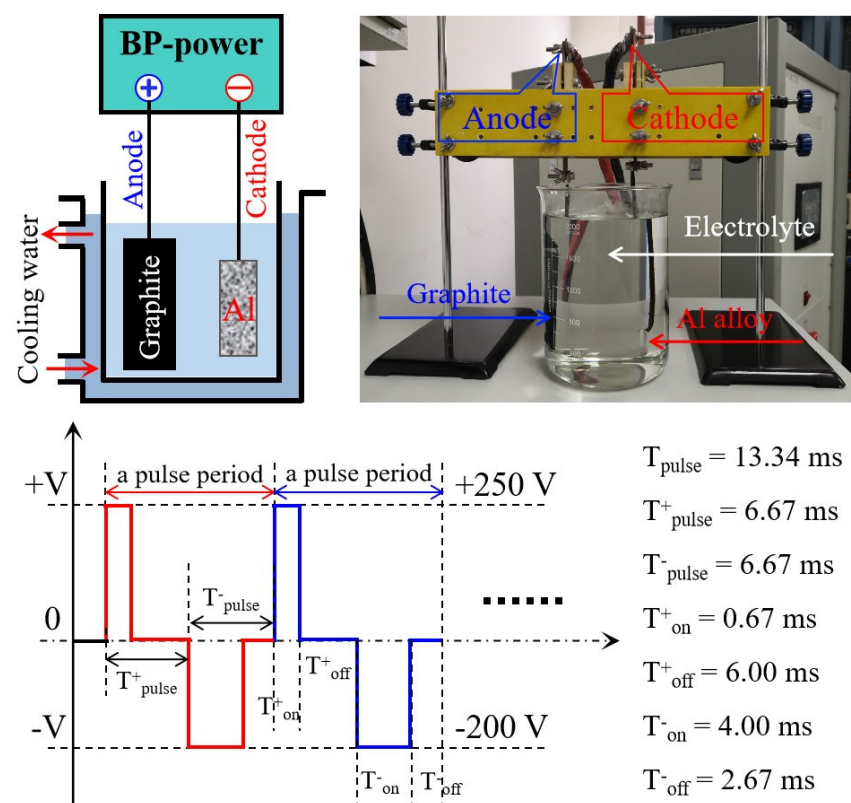


Figure 1. Installation layout of the BP-CPED electrolytic cell and the pulse waveform.

During the BP-CPED process, a circulating cooling system was employed to maintain the electrolyte at about 30 °C. The treatments were performed at a constant voltage model for 15 min, and voltage/current values and the cathodic spark phenomenon were recorded. The input voltage at the cathode terminal was set at 200 V and the anode voltage was kept at 250 V. The pulse number of the anode and cathode were all fixed at 1 in a pulse period. Frequency and duty cycles of the pulsed voltage were maintained at a constant 150 Hz, 60% cathodic direction, and 10% anodic direction. After the reaction, coated samples were thoroughly rinsed with distilled water and then air dried.

2.2. Characterization and Testing

Surface and cross-sectional micro-structures of the coating were observed by a scanning electron microscope (SEM; EVOMA10, Zeiss, Jena, Germany), and the element composition and distribution of coatings were investigated with energy dispersive spectroscopy (EDS) equipped on the SEM system. An X-ray diffraction (XRD; Bruker D8 advance, Bruker, Ettlingen, Germany) spectrometer with Cu-K α radiation was employed to examine the phase compositions of coatings.

The bonding strength evaluation between the coating and substrate was investigated using the direct pull-off tensile method and thermal shock tests. Figure 2 displays the schematic diagram and optical picture of pull-off tests based on ISO 14916-2017 [22]. For testing, a cylindrical sample (Φ 25 mm $\times$ 7 mm) with the coating on one end was sandwiched and bonded to two uncoated cylindrical fixtures (Φ 25 mm $\times$ 55 mm) using epoxy glue. Tensile load was applied to this splicing cylinder at a loading rate of 1 mm/min using an electronic universal testing machine and recorded until fracture occurred. Bonding strength values were calculated from the ratio of the instant fracture force and coating area. Thermal shock resistant experiments were carried out to qualitatively evaluate the adhesion of BP-CPED coatings using a cyclic heating-cooling method. Coated samples were placed into a Muffle furnace at 350 °C for 5 min and then rapidly immersed into room temperature water for 1 min. The procedure was repeated 100 times. A digital camera was employed to record changes of the coating surface before and after the thermal shock tests.



Figure 2. Illustration of the direct pull-off tensile test.

3. Results and Discussion

3.1. Investigation of BP-CPED Process

Our experimental results show that the CPED technique, based on a bipolar pulse power source, is able to deposit ceramic coatings on the surface of aluminum alloys. More importantly, the current density of the cathode in the BP-CPED process was found to be approximate to that of the anode in the conventional MAO process. Moreover, the BP-CPED reaction environment is an open atmosphere type, and there are no strict requirements for the anode size, the shape of cathode workpieces, the electrode spacing between anode and cathode, etc. This BP-CPED technique can provide a novel research approach to break through the technological bottleneck of the higher current needed for existing CPED methods.

A liquid electrode-plasma process during cathodic micro-arc discharge is a complex hybrid of conventional electrolysis, thermal diffusion, and electro-/plasma-chemistry, with a significant difference from Faraday's law of normal electrolysis. A significant difference between this method and the DC type is the presence and participation of effective parameters from the anodic direction in the BP power type. So far, the kinetic investigation of the PED process has usually been described and explained by the regulation evolution of the current density and voltage over a given time scale. Figures 3 and 4 display

the curves of the current density-time ($I_{cathode}/I_{anode}-t$) and voltage-time ($V_{cathode}/V_{anode}-t$) measured during the BP-CPED process in the electrolyte without/with PEG. We made exciting discoveries from observing $I-t$ curves; the numeric values of the cathodic current density on the working electrode were lower than 0.15 A/cm^2 and presented values similar to the current density of the anodic direction in the MAO process. Furthermore, the anodic current density was found to be in the range of 10^{-2} A/cm^2 , an order of magnitude below that of the cathode in BP-CPED reaction. This interesting discovery can indirectly explain why the area ratio of two electrodes was not strictly required in the BP-CPED technique. Therefore, the BP-CPED technique shown herein can be used to treat an area 10 to 100 times larger than the current CPED method under the same electrical parameters.

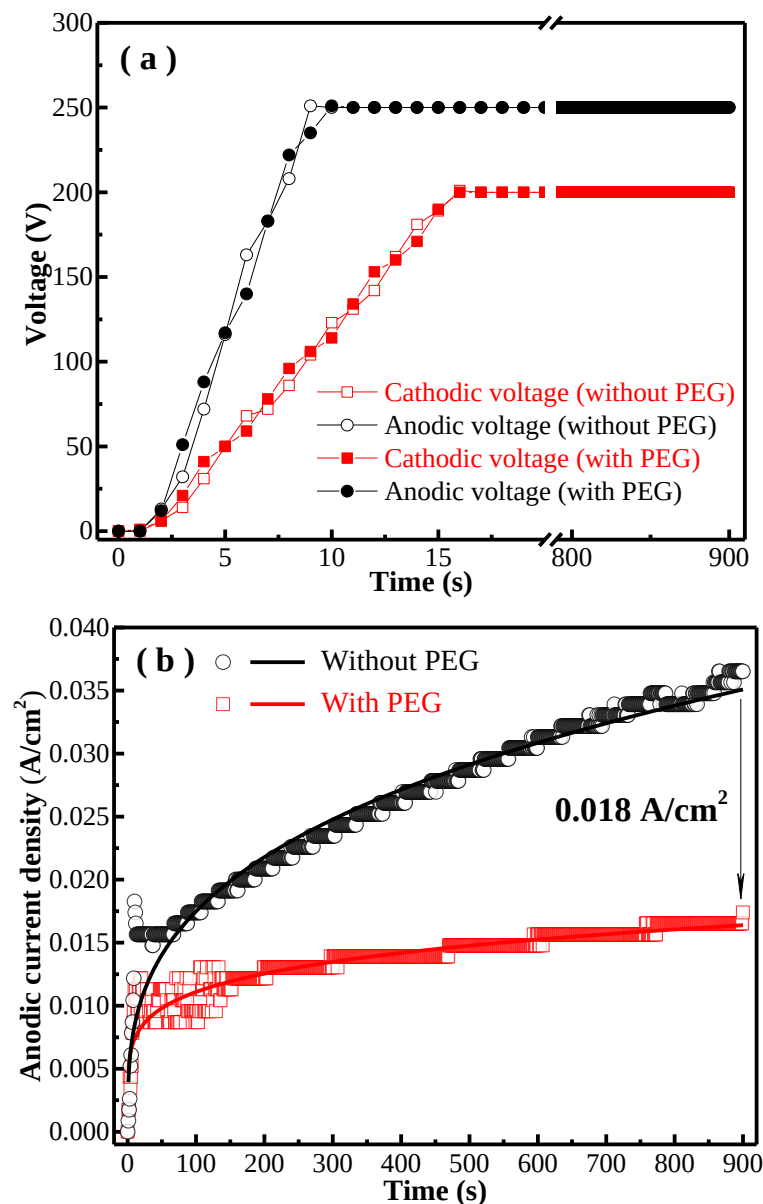


Figure 3. Voltage (a) and anodic current density (b) curves of the BP-CPED process in the electrolyte without and with PEG.

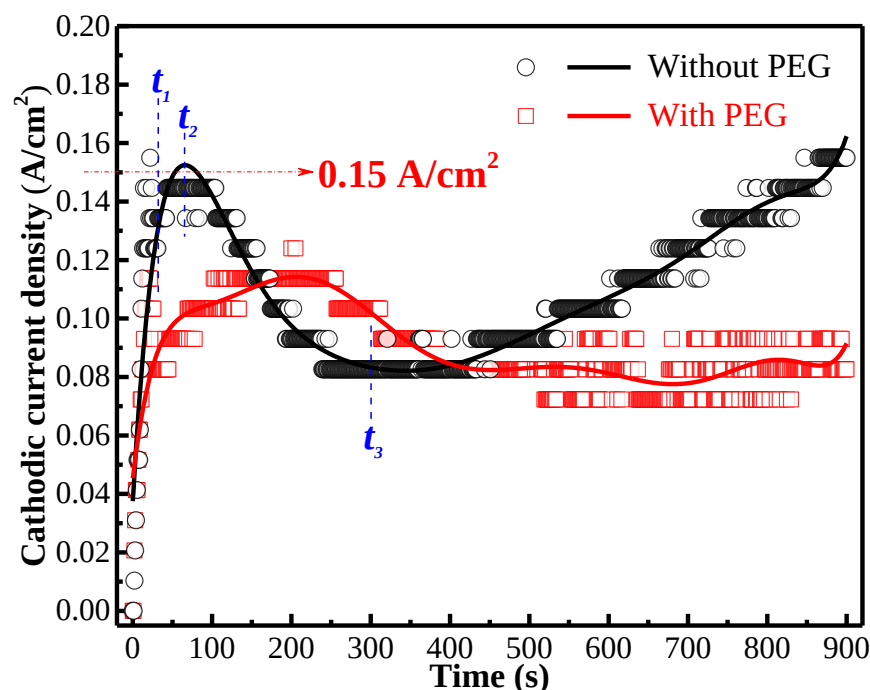


Figure 4. Cathodic current density variation with time in the electrolyte without and with PEG.

Compared with the I/V - t curves recorded in the electrolyte with and without PEG, there is almost no difference in the tendency and data variation of V - t curves. Despite this, the current density in the cathode and anode direction are all significantly reduced after adding PEG2000. As a result, the cathodic current density was further reduced to around 0.10 A/cm^2 with the addition of PEG, and the anodic current density was reduced from around 0.035 A/cm^2 to 0.015 A/cm^2 . By adopting a constant-voltage operation in this work, the change tendency in $V_{\text{cathode}}/V_{\text{anode}}-t$ curves could include two things: a voltage-raising process and a voltage-stabilizing period, as shown in Figure 3a. In addition, it can be seen that raising the rate of the anodic/cathodic voltage has not caused obvious changes alongside the addition of PEG.

A bipolar pulse power source has rarely been used in CPED studies. The difference of this BP-type from the conventional DC-type is that the kinetics description of the BP-CPED process under the characteristic voltage involved the variation tendency and features in effective current densities of the anode and cathode directions versus time. It can be observed from Figure 3b that changes to the anodic current density over the entire process first showed a linear increase and then flattened out, and that the presence of PEG can greatly inhibit the anode current rising rate, making it possible to stay within a stable and lower numerical value during the second period.

Previous studies about the DC-powered CPED technique showed that $I_{\text{cathode}}-t$ curves can quantitatively describe the kinetics of the reaction process under a constant voltage [23–26]. Based on the variation of $I_{\text{cathode}}-t$ curves in Figure 4, the BP-CPED process can be divided into three stages. In the initial stage ($0-t_1$), the cathodic current density increases linearly with time, which accords with the Ohm and Faraday laws. In the initial stage, lots of H_2 bubbles can be observed in the electrolyte generating on the cathodic Al surface. Meanwhile, O_2 bubbles are produced on the anodic graphite surface. With the increasing voltage, the increase of the current density can cause more H_2 bubbles to form electro-chemically on the cathode. As such, a great amount of Joule heating, generated by the enhanced electric energy, could arouse the local evaporation and boiling of the electrolyte around the cathode to produce vapor bubbles. Hence, bubbles formed on the cathode are a coalescence of vapors and gases. Eventually, enough bubbles gradually cover the entire cathode surface to form a stable and continuous vapor-gaseous envelope between the cathode and electrolyte, leading to an increase in the resistance of the cathode surface.

Once this envelope reaches a certain thickness, the applied voltage continues up to a satisfactory level, which could result in the formation of a high electrical field within the envelope; this field would induce gas ionization and an electronic avalanche to incur, causing an electric breakdown of gases and an initial plasma discharge in the bubbles. Simultaneously, active products from the decomposition of organics and OH^- surrounding the cathode migrate and deposit on the cathodic surface under the electric field, which can combine with Al^{3+} from the substrate to generate Al-matrix ceramics. In comparison with the single vapor-gaseous envelope in the initial stage, an insulation barrier with a gas/solid double-layer (an outer vapor-gaseous envelope and an inner coating) was generated on the cathodic surface at this time [10], as shown in Figure 5. This deposition process was mainly co-influenced by the over-potential issuing from the vapor-gaseous envelope and coating.

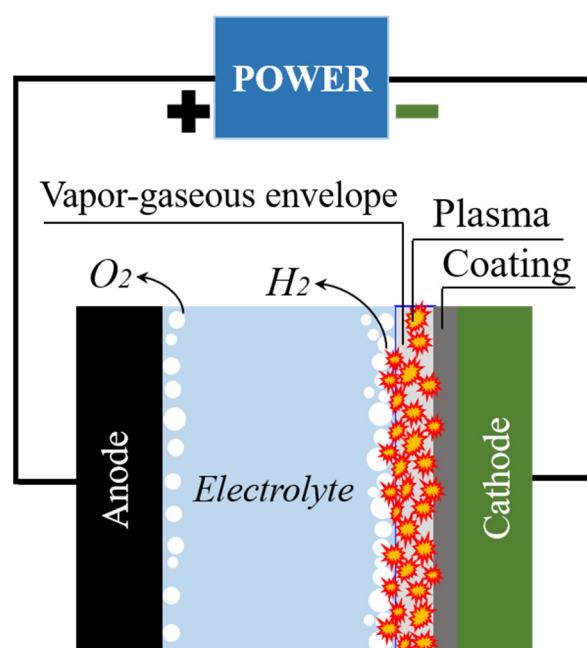


Figure 5. Schematic depiction of the plasma discharging during the BP-CPED process.

Based on the Maxwell–Wagner model [27–29], previous studies deduced that the electric field strength of the vapor-gaseous envelope is higher than that of the ceramic layer in the CPED process. It was known that the critical breakdown electric field strength of the gas layer (about 3 MV/m) is substantially lower than that of the ceramic layer (9.9–15.8 MV/m), and thus the vapor-gaseous envelope is broken down first. Subsequently, the over-potential is primarily concentrated on the internal coating. This is to say that the electric field strength acting on the depositing coating would be enhanced as a result of substantial joule heat produced from the plasma discharge of the vapor-gaseous envelope. These two factors can synergistically induce the electric breakdown of the ceramic coating, whereas the higher critical breakdown strength of the coating, in the case of a given voltage, would require a continued higher output current. Hence, as shown during stage-II in Figure 4 (the t_1 – t_2 time segment), the coating was electrically punctured, and the cathodic current density would rise to the maximum. After the envelope/coating double-layer discharge, in the region t_2 – t_3 , the cathodic current density sharply dropped on account of the hydrodynamic stabilization of the vapor-gaseous envelope [10]. Beyond the t_3 point in time, the convection and discharge heating on the cathodic surface promoted the migrating and transferring efficiency, while the reaction process moved into stage-IV of the coating deposition. Greater production of joule heat could give rise to a high escaping rate of bubbles and then cause instability of the vapor-gaseous envelope. It can be observed that the stable/intensive discharge on the cathode transformed into violent arcing accompanied by a typical acoustic emission.

3.2. Effect of Adding PEG on the BP-CPED Process

To further investigate the effect of water-soluble polymer PEG on the BP-CPED process, Figure 6 displays images of the vapor-gaseous envelope and the coating structure before and after adding PEG. It can be observed that a stable bubble envelope on the cathode is generated by using the BP type power. With the addition of PEG into the electrolyte, the bubble size was reduced and the uniformity/compactness was increased to further improve the obstructing capability of the envelope. Compared with their state before adding PEG, the porosity and pores size of the coatings were decreased and the thickness of the coating increased from 11.6 μm to 15.8 μm . The deposition time of the BP-CPED process was 15 min, so the deposition rate of coatings before and after adding PEG were 0.77 $\mu\text{m}/\text{min}$ and 1.05 $\mu\text{m}/\text{min}$, respectively. High molecular polymer PEG could increase the electrolyte viscosity to limit the escape rate of bubbles from the cathode, meaning that the bubbles accumulated and extruded to prompt the vapor-gaseous envelope become more uniform and compact [30,31]. Thus, the distance between the cathode and electrolyte was greater than that before adding PEG. As a result, the shielding effect of the envelope would be enhanced in order to cause further decreasing of the cathodic current density, as shown in Figure 4. Moreover, in this case, the occurrence probability of destructive arcs can also be decreased to improve the coating quality.

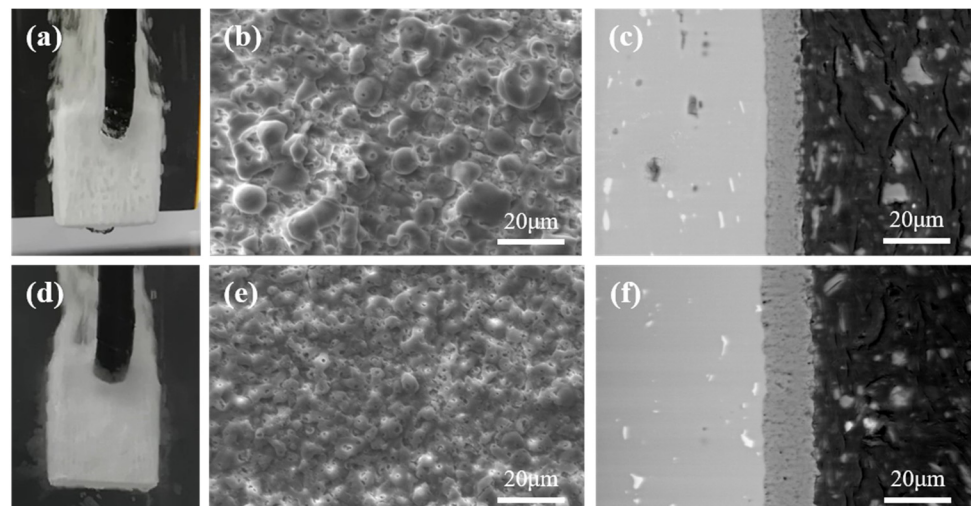


Figure 6. Bubble envelope on the cathode and the coating structure in the electrolyte without (a–c) and with (d–f) PEG.

Figure 7 shows images of the evolution of spark-discharging on the cathode in the electrolyte with PEG2000. Real-time images recorded at different times illustrated that the size and illumination intensity of discharging sparks obviously increased as time went on. Like the anodic MAO process, the BP-CPED process includes three stages: gas generation (0 s–16 s), visible sparks (17 s–720 s), and violent discharging (720 s–900 s). When the essential conditions of forming a continuous gas envelope and reaching the breakdown electric field strength are all satisfied, plasma discharging would appear on the cathodic surface. As seen from Figure 7, orange discharging sparks appeared within the vapor-gaseous envelope at 17 s, and this phenomenon was consistent with the previous kinetic analysis. Corresponding current densities at this 17 s arcing point could be obtained from I-t curves; the current density at the cathode was 0.04 A/cm² and the anode reached 0.001 A/cm². As the reaction continues, the sparks became more and more violent, and lots of micro-bubbles can be observed dispersing in the electrolyte.

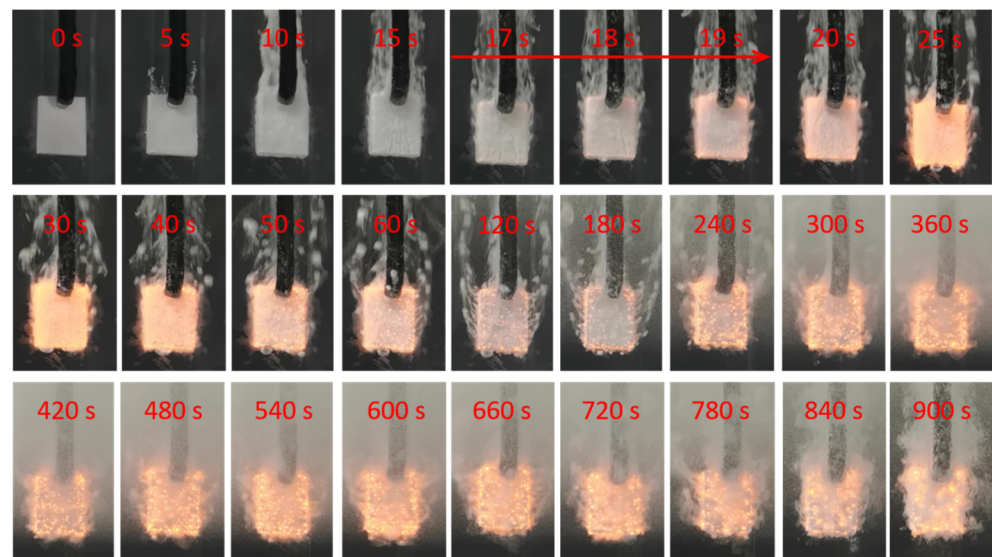


Figure 7. Evolution pictures of the cathodic spark-discharging in the electrolyte with PEG.

Figure 8 displays XRD patterns of coatings obtained using the BP-CPED technique in the electrolyte both with and without the addition of PEG. The analysis results show that both coatings are composed of Al_4C_3 and Al_2O_3 . Diffraction angles are detected at 38.5° , 44.7° , 65.2° , 78.3° , and 82.4° in the diffraction pattern, which are associated with Al in the substrate (PDF—#65-2869). Two diffraction angles, found at 37.8° and 77.2° , are characterized as $\alpha\text{-Al}_2\text{O}_3$ (PDF—#46-1212), and those at 19.5° , 39.5° , 45.6° , 64.2° , 67.3° , and 85.0° are matched with correlative characteristic diffraction angles of the $\gamma\text{-Al}_2\text{O}_3$ phase (PDF—#04-0877). Interestingly, obvious diffraction angles detected at 32.2° , 40.2° , 43.4° , and 61.0° are identified as Al_4C_3 (PDF—#65-9731). This means that activated carbon species (ions or atoms), decomposed from the carbamide through the plasma discharge, reacted with active aluminum ions on the cathode to form aluminum carbides. Diffractograms showed that the BP-CPED technique can be used to prepare the composite coating composed of oxide/non-oxide ceramics on aluminum alloys in the carbamide-based electrolyte.

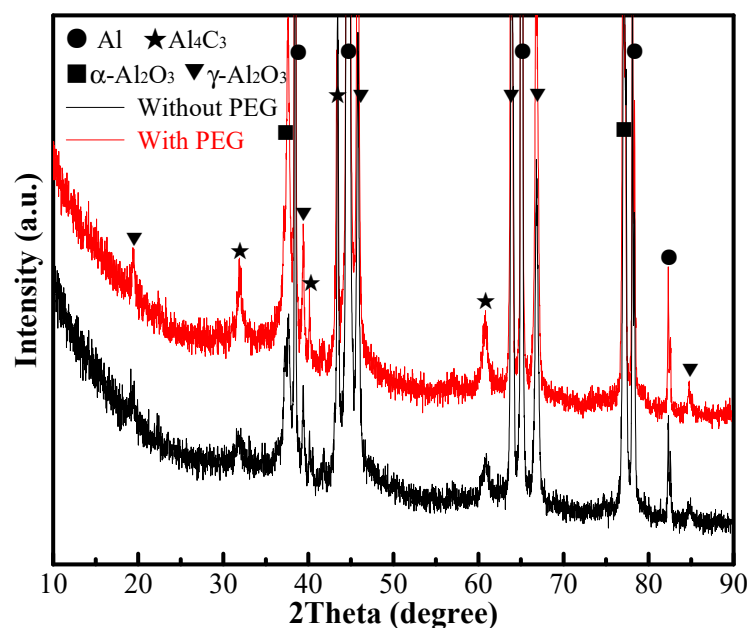


Figure 8. XRD patterns of BP-CPED coatings obtained in the electrolyte with and without PEG.

The addition of PEG into the electrolyte did not change the chemical composition of the coating, and yet the peak intensity of ceramic phases was enhanced to some extent. One possible factor for this phenomenon was that the increasing viscosity of the electrolyte after adding PEG caused more bubbles to be constrained around the cathode, meaning that more ionized and active products were enriched on the cathode. Analytical results of the corresponding elemental distribution of the coating section are shown in Figure 9. As can be seen from the line-scanning, Al, O, and C elements were present in the coating. Clearly, the Al element in the substrate was incorporated into the coating, and others were mainly incorporated from the electrolyte. It is interesting to note that the C element is almost completely distributed on the coating surface and has no presence in the internal coating. This unique profile of the elemental distribution is one of the obvious characteristics of the BP-CPED technique used in this work. This result will be studied in-depth to explore and ascertain the immanent cause in a future study.

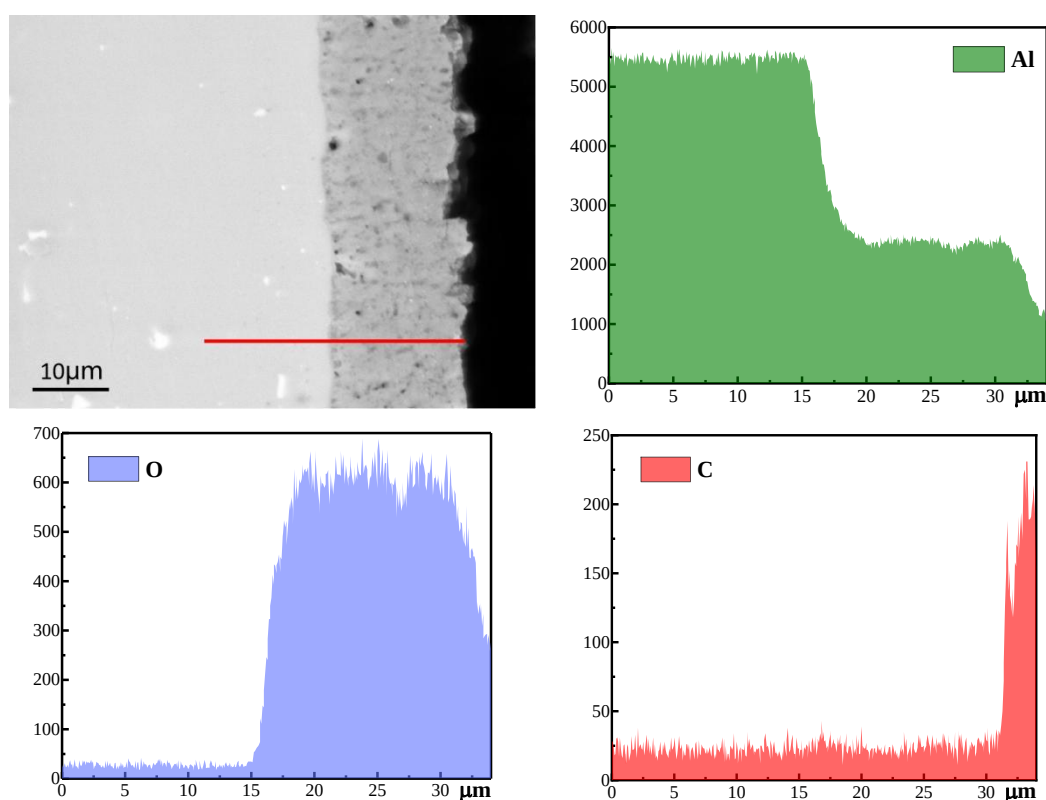


Figure 9. EDS line scanning of BP-CPED coatings obtained in the electrolyte with PEG.

3.3. Doping Modification

Concerning surface treating performed in a liquid environment, there is no doubt that doping modification via the incorporation of ions or particles to optimize the coating structure and composition is a better choice to acquire more efficient protection and performance. It has been well-evidenced that the MAO technique can be used to modulate doping additives and to improve the coating quality on valve-metal alloys [32–34]. Indeed, several studies on the DC-CPED technique found that the cathodic surface can be created as a result of the plasma discharging in an electrolyte doped with ions or particles, and that the performance of the obtained coatings is significantly improved [35–37]. Thus, in this work, we investigated the feasibility of the BP-CPED reaction in an electrolyte doped with Zr^{4+} ions. We are happy to report that it has been shown that the BP-CPED technique can successfully implement doping modifications in a way similar to the MAO and DC-CPED methods. This successful exploratory experiment provides a feasible and promising channel for a controllable design and further extends the application of BP-CPED

coatings. Figure 10 shows the changing curves in the current-density/voltage versus time after doping Zr^{4+} ions.

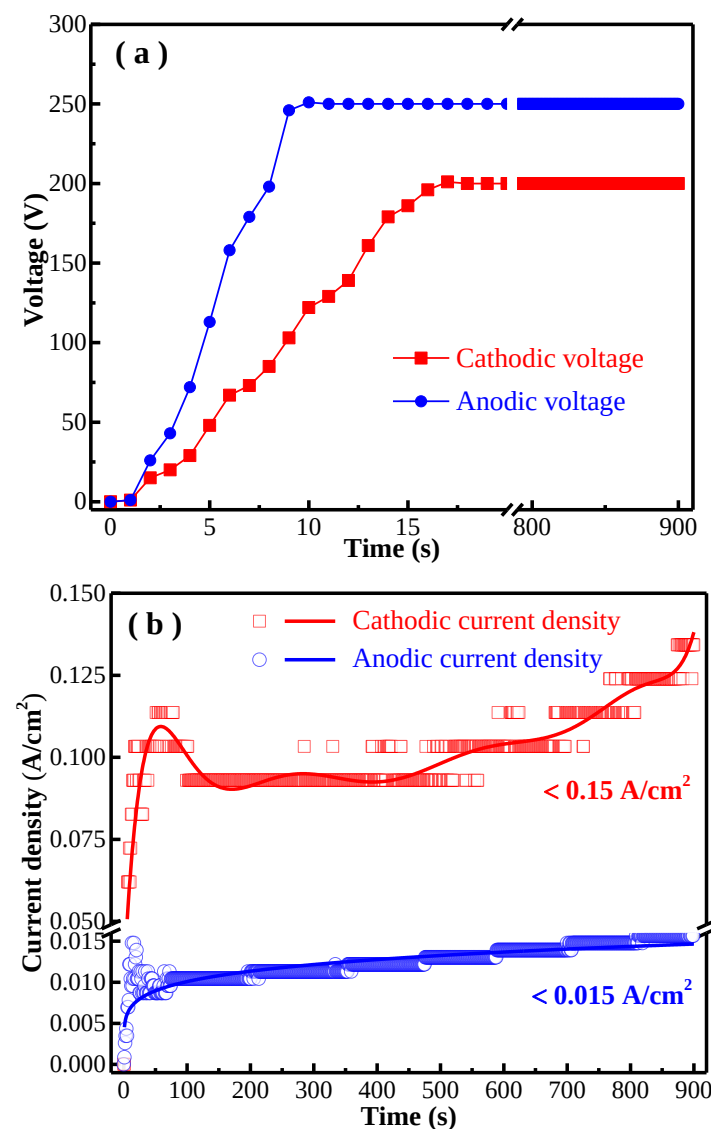


Figure 10. Voltage (a) and current density (b) variation with time after doping Zr^{4+} ions.

Rising rates of applied voltages in the anodic/cathodic direction showed no changes following doping with 10 g/L of $(\text{NH}_4)_2\text{ZrF}_6$ additives. Meanwhile, the main characteristic of the variation tendency in the current density versus time did not lead to major changes, particularly in the average current density. On the other hand, a minor difference from the status before doping could be observed; an obvious peak in the $I_{\text{cathode}}-t$ curve after doping appeared between stage II and stage III, as shown in Figure 10b. This appearance resembled the $I_{\text{cathode}}-t$ curve changing in the electrolyte without PEG (seen from Figure 4).

This result can possibly be ascribed to the fact that doping $(\text{NH}_4)_2\text{ZrF}_6$ could decrease the electrolyte viscosity, thereby resulting in the distance between the cathode and electrolyte being reduced. Therefore, it can be proved that by adding ionic additives into the base electrolyte, the BP-CPED process still possesses the characteristic of the lower-current-density. To thoroughly ascertain the composition evolution of obtained coatings before and after doping Zr^{4+} ions, XRD detection equipment was used to evaluate the chemical component of the BP-CPED coatings. The detecting results, as shown in Figure 11, revealed that all coatings contained Al_4C_3 and Al_2O_3 . For the sample deposited in the Zr-containing electrolyte, two obvious diffraction angles (30.3° and 50.4°) are matched with

the characteristic diffraction angle of t-ZrO₂ (PDF—#50-1089). This result reflected that Zr ions were involved in the reaction, being incorporated into the ceramic coat, with the t-ZrO₂ phase being formed under the plasma micro-discharging. The existence of t-ZrO₂ proves that the plasma temperature of the cathode surface exceeded 1170 °C during the BP-CPED process [38,39].

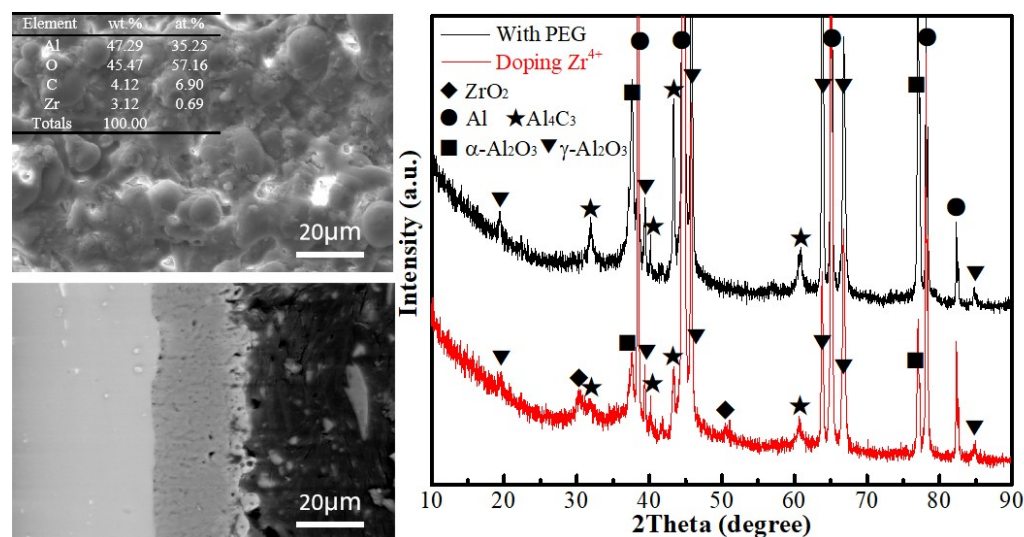


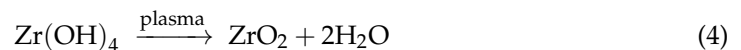
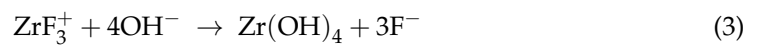
Figure 11. Structure and composition of the BP-CPED coating after doping Zr⁴⁺ ions.

Figure 11 shows SEM images and the elemental analysis of obtained composite coatings in the Zr-containing electrolyte. It can be seen that the morphology of the composite coatings retained the features of a typical porous structure. In comparison to coatings obtained before doping, the size and number of micro-pores on the coating surface reduced and the coating thickness and roughness increased after doping. The thickness and deposition rate of obtained composite coatings after Zr-doping were 28.3 μm and 1.89 μm/min, respectively. The formation of ZrO₂ needs to consume some of the oxygen atoms around the cathode; this causes an increase in the concentration of activated atoms and cations of oxygen. It can be seen from the $I_{cathode}-t$ curves before and after Zr-doping that the cathodic current density after doping showed an upward trend. This result indicated that more electrical energy was inputted to increase the concentration of activated oxygen atoms. A high concentration of active oxygen atoms resulted in a relatively high rate of reaction, which can form more molten products and thereby increase the coating thickness. The continuous accumulation of molten products led to an increase in the roughness and a decrease in the micro-pore size/number on the coating surface.

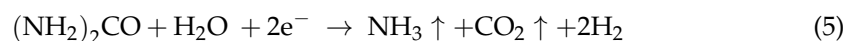
The cross-section picture shows that the coating can be divided into a compact inner layer and a loose outer layer. This result indicated that doping Zr⁴⁺ ions increased the deposition rate of the BP-CPED coatings. Moreover, EDS results confirm that the presence of the Zr element further reflected the successful participation of Zr ions into the reaction of the cathodic surface. It can be seen from the above that the vapor-gaseous envelope surrounding the cathode can be broken down to generate the plasma discharge with the advanced high temperature during the BP-CPED process. An extremely high electrical field was applied to the envelope; as a result, vapor and gaseous products can be ionized and polarized to eventually form the plasma state. As a consequence of the plasmonization, lots of active atomic/ionic/molecular species and electrons are generated on the cathodic surface [40–42]. Furthermore, it should be noted that the aqueous electrolyte is based primarily on water, and the pulsed discharge plasma on the cathode can prompt the water vapor to produce several chemically active H and OH radicals [43–45].

Thus, a possible reaction mechanism could be concluded. According to the research of V.P. Tolstoy [46], when (NH₄)₂ZrF₆ was dissolved in an aqueous solution, ZrF_x^{m+} complexes

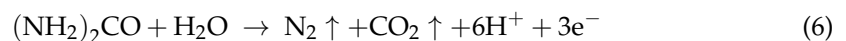
were possibly present in the form of ZrF_3^+ . In accordance with the basic electrolysis principle, ZrF_3^+ ions migrated from the electrolyte towards the cathodic interface and attracted OH^- anions to form $\text{Zr}(\text{OH})_4$. Thereafter, $\text{Zr}(\text{OH})_4$ could decompose on the cathode surface into ZrO_2 under the plasma discharge. The possible reactions on the cathode are listed as follows:



According to the disruptive discharge principle [47], the plasma discharge on the cathode is affected by both the voltage and thickness of the gas envelope. The larger molecule of carbamide, when compared with H_2O , are large enough to bind to the gas at the interface of the metal/electrolyte. The cathodic process of hydrogen formation is accompanied by a reduction of ammonia in the carbamide solution [48]:



Thus, the reduction of ammonia on the cathode increased the thickness of the gas envelope. The corresponding reaction on the anode can be expressed as:



In the plasma-discharging region, organic molecules could be decomposed into the product of C/O-containing active ions/atoms. These active species could react with Al on the cathodic surface, as shown in Formulas (7) and (8). In addition, Al actions formed under the action of the electrical field can attract OH^- anions to produce $\text{Al}(\text{OH})_3$. $\text{Al}(\text{OH})_3$ was pyrolyzed to generate Al_2O_3 under the plasma discharge.



3.4. Bonding Strength

Before proving valuable and useful as a surface engineering technique for industrial manufacturing, BP-CPED coatings must possess a good bonding strength to the substrates and high resistance to the spallation induced thermal shock. Normally, the rupture types are divided into three categories [49]: (a) rupture occurs inside the resin; (b) rupture occurs inside the coating, or at part coating and part resin; (c) adhesive failure occurs at the interface between the substrate and coating. The adhesive strength of the used resin is above 30 MPa, so rupture type (a) means that the real bonding strength of tested coatings is higher than the adhesive strength of the resin. If the fracture surface shows up as rupture type (b), it can be determined that the bonding strength between the coating and substrate is higher than the rupture strength. A rupture state belonging to type (c) indicates that the bonding strength of the coating is just the rupture strength.

The results of pull-off tests of BP-CPED coatings prepared in the carbamide-based electrolyte (Base-I), the electrolyte with PEG2000 (PEG-II), and the Zr-containing electrolyte (Zr-III), including the optical images of the ruptured surfaces, are shown in Figure 12. It

can be seen that all ruptures of the samples belonged to type (b), which means that the bonding strength between BP-CPED coatings and the substrates are higher than that of the adhesive strength inside the coatings (cohesion strength). To evaluate the degree of damage to the coating, the damage proportion of the Base-I sample was maximum and that of the PEG-II was minimum. The bonding strength values of three samples are displayed in Figure 12. Data results revealed that the bonding strength decreased as the extent of the coating damage increased. The bonding strength of the PEG-II sample reached about 18.2 MPa and that of Zr-III sample reached about 17.4 MPa. The failure locations at the interfacial debonding inside the coating also reflected the structural characteristic of the inner/outer layer in the BP-CPED coating. The lower cohesion of the Base-I coating can possibly be attributed to more micro-cracks on the surface. During the pull-off tests, these defects could be regarded as nucleation points of new cracks forming, and the tensile force would result in newly generated cracks propagating and then converging until the rupture took place [50]. Therefore, this developed BP-CPED technique for aluminum alloys can fulfill the requirements of industrial application.

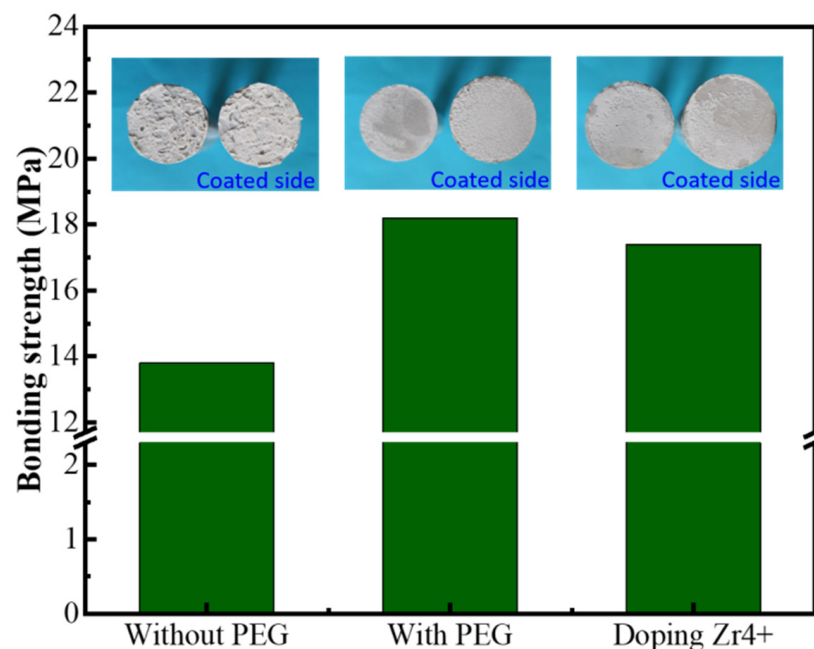


Figure 12. Bonding strength of the BP-CPED coatings and ruptured surfaces after pull-off tests.

To evaluate the coating adhesion under the thermal-cold cycling, Figure 13 displays optical images of Base-I, PEG-II, and Zr-III samples during thermal shock testing. For all samples, no interfacial delamination and spallation on the coating were found after 100-cycles testing, which indicated that BP-CPED coatings possess an outstanding thermal shock resistance. It can be seen from micro-images taken after testing that the typical porous-structure was retained and that no obvious crack-defects were found at the interface between the coating and substrate. These results also support the observation results that the obvious phenomenon of the coating damage was not found after the thermal shock testing.

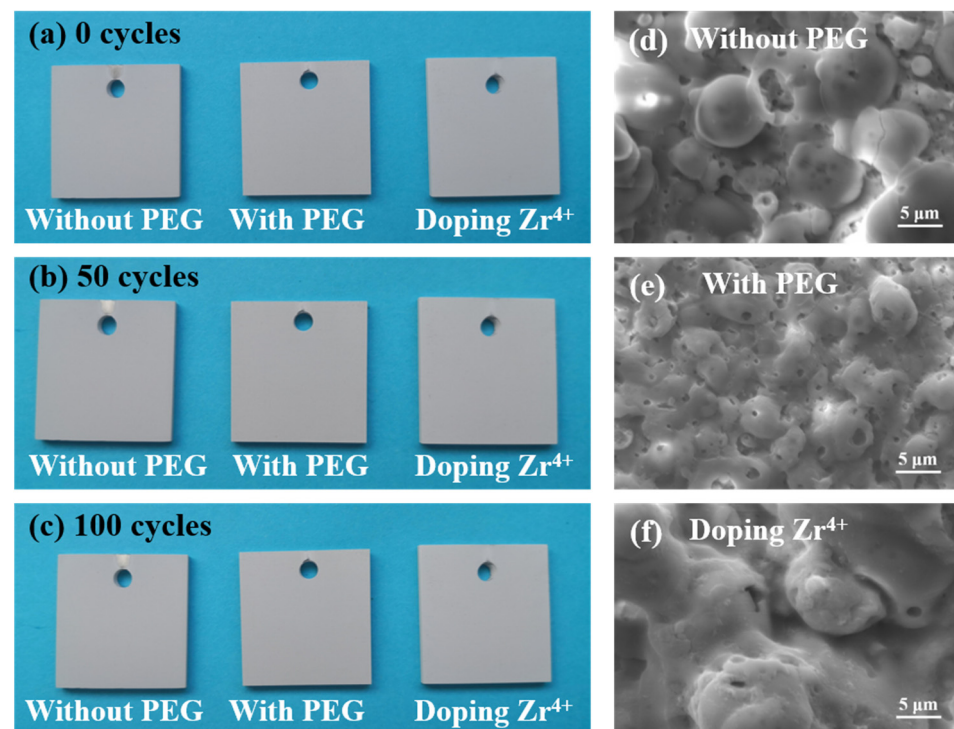


Figure 13. Optical photos (a–c) of BP-CPED coatings after different cycles and SEM surface morphologies (d–f) after 100 cycles of the thermal shock test.

4. Conclusions

In this work, an original BP-CPED technique was developed to successfully deposit the ceramic coating on aluminum alloy in the aqueous carbamide-based electrolyte. Under an open atmospheric reaction-system, we applied the relatively appropriate cathode-voltage (200 V) and anode-voltage (250 V); the output cathodic current-density of the depositing process was lower than 0.15 A/cm², which approximates the required anodic current-density of the ordinary MAO technique. The anodic current-density was one order of magnitude lower than that of the cathode. *I/V-t* curves were used to investigate in detail the kinetics of the BP-CPED process. The deposited coating mainly consisted of Al₂O₃ and Al₄C₃ and presented a typical porous structure. The addition of PEG into the electrolyte was beneficial for further reducing the current-density and improving the coating quality but did not change the composition. EDS analysis results showed the existence of Al, O, and C, of which C elements were mostly distributed in the surface layer. Additionally, when the BP-CPED process was performed when the electrolyte was doped with Zr⁴⁺ ions, the current-density did not change much; it can be concluded that a new phase, t-ZrO₂, was incorporated into the coating, and the depositing rate and roughness of the coating was increased; the size and number of micro-pores on the coating surface decreased after Zr-doping. Testing results indicated that the bonding strength of the interface between the BP-CPED coating and substrate is excellent, and no interfacial delamination was observed after 100 cycles of thermal shock testing. Future research works will focus on applying the BP-powered CPED technique to surface treat other materials and produce other types of coatings. We believe that this BP-CPED technique will solve the problems of large-area manufacturing when using the existing CPED technique.

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