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Synthesis of Y_2O_3-ZrO_2-SiO_2 composite coatings on carbon fiber reinforced resin matrix composite by an electro-plasma process

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ABSTRACT

In the present paper the Y_2O_3-ZrO_2-SiO_2 composite coating was successfully synthesized on carbon fiber reinforced resin matrix composite by an electro-plasma process. The deposition process, microstructures and oxidation resistance of the coatings with different SiO_2 concentrations were systematically investigated. A relatively dense microstructure was observed for the Y_2O_3-ZrO_2-SiO_2 composite coating with the SiO_2 concentration above 5 g/L. The coating exhibited very good oxidation resistance at 1273 K with the mass loss rate as low as ~30 wt.%, compared to 100 wt.% of the substrate. The formation of the ceramic composites was discussed in detail based on the electrochemical mechanism and the deposition dynamics in order to explain the effect of the plasma discharge. We believe that the electro-plasma process will find wide applications in preparing ceramics and coatings in industries.

1. Introduction

The carbon fiber reinforced resin matrix composite is one of the most advanced composite materials due to its low density, high fatigue resistance, low coefficient of thermal expansion and high strength-to-weight ratio. Therefore, the composite is considered as a leading candidate for high temperature applications in aeronautical and aerospace fields [1–3]. However, the carbon fiber reinforced resin matrix composite has a poor oxidation resistance, significantly limiting the application in oxidation environments.

At present, coating is considered as the most effective method to solve the problem. Among all kinds of coatings, the ceramic coating is believed to be optimal in order to significantly improve the oxidation resistance of the carbon fiber reinforced resin matrix composite. Meanwhile, the ceramic coating is required to behave a good adhesion with the composite substrate. The resin matrix is relatively soft and have large thermal expansion coefficient, compared to the hard surface and small thermal expansion coefficient of the ceramic coating. Obviously the resin matrix and the ceramic coating have fully different physical properties, therefore it is relatively difficult to achieve a good adhesion between them. The traditional methods, including thermal spray and PVD [4–7], are unable to directly synthesize the ceramic coating with good adhesion on the carbon fiber reinforced resin matrix composite. Therefore, it is necessary to apply for a new technique to synthesize good-adhesive ceramic coatings on the composite.

The electro-plasma process is a hybrid of conventional electrolysis and atmospheric plasma process [8]. The process utilizes basic principles of electrolytic plasma, where DC potential is applied between two electrodes in an aqueous media. At a certain value of voltage between two electrodes in an aqueous electrolyte, a deviation exists from Faraday's electrolytic regime. A stable plasma field is formed on the surface of working pieces, where the thermal and physical/chemical effects exist. Based on the effects during the electro-plasma process, ceramic coatings are easily synthesized on a conductive substrate, including ZrO_2-Y_2O_3 coating, Al_2O_3 coating. The presence of plasma micro-discharges over the work piece may also lead to melting of localized micro-zones on the surface, significantly improving the bonding strength between the coating and the substrate [9,10]. Based on the above characteristics of the electro-plasma process, it is well expected that a ceramic coating is able to be successfully synthesized on the carbon fiber reinforced resin matrix composite with good properties.

According to the Y_2O_3-ZrO_2 phase diagram [11], a single-phase zone exists as the volume percentage of ZrO_2 ranges from 15% to 30%. Moreover, the zone is able to stably exist up to ~2500 °C, providing very good oxidation resistance and mechanical properties at high temperatures. In order to release the thermal stress formed at high temperatures, SiO_2 phase is often incorporated into a ceramic. Correspondingly the spallation resistance of the ceramic coating is significantly improved. SiO_2 itself also has excellent oxidation resistance. Therefore, the Y_2O_3-ZrO_2-SiO_2 composite system may

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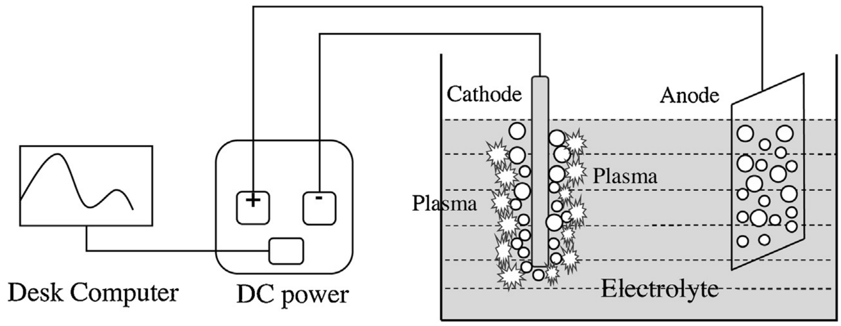

Fig. 1. The schematic diagram of the experimental apparatus.

behave good oxidation resistance as well as the spallation resistance at high temperatures.

Based on the above analysis, the electro-plasma process was successfully applied in the present manuscript in order to synthesize the Y_2O_3-ZrO_2-SiO_2 composite coating on the carbon fiber reinforced resin matrix composite. The microstructure of the ceramic coating was systematically investigated. The oxidation resistance was also measured. Finally we discussed the formation of the ceramic composites based on the electrochemical mechanism and the deposition dynamics in order to explain the effect of the plasma discharge. We believe that the electro-plasma process will find wide applications in preparing ceramics and coatings in industries.

2. Experimental

2.1. The electro-plasma process

The commercialized carbon fiber reinforced resin matrix composite was used as the substrate with the size of 12 mm × 5 mm × 2.5 mm. The substrate was ultrasonically cleaned in acetone in order to remove the oil on the surface, and then dried. The electro-plasma process was conducted in the 0.1 mol/L $Y(NO_3)_3$ and $Zr(NO_3)_4$ mixed electrolyte with the mole percentage of $Zr(NO_3)_4$ at 30%. The SiO_2 nano-particles (average size of 80 nm) were also added into the electrolyte with the concentration of 1, 5 and 10 g/L, respectively. The electrolyte was continuously magnetically stirred at a rate of 100 rpm.

The schematic diagram of the electro-plasma process was shown in Fig. 1. An electric field was applied between the graphite counter electrode (anode) and the substrate (cathode). During the electro-plasma process, a constant voltage of 170 V was applied between both electrodes at room temperature with the deposition time of 60 s. The cathodic current density was automatically recorded by the desk computer in order to characterize the current density-time relation.

2.2. Characterization of coatings

The morphologies and compositions of the coatings were analyzed using a scanning electron microscope (SEM) with an energy dispersive spectroscope (EDS) attached. The SiO_2 content in the coating was calculated based on the weight percentage of Si measured by EDS, that is, the content of Si in the coating was firstly measured by EDS, and then the content of SiO_2 was obtained with the Si content divided by the relative content of Si in SiO_2. The phase structure of the coatings was determined using X-ray diffraction (XRD) with Cu Kα radiation. Diffraction patterns were recorded with the diffraction angle (2θ) ranging from 10 to 90° at a scanning rate of 0.02° s^{-1}.

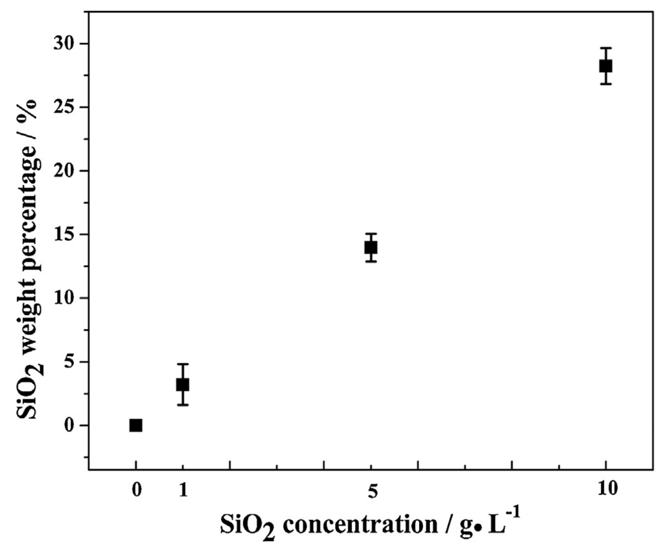

Fig. 2. Dependence of SiO_2 weight percentage in ceramic coating on SiO_2 concentration.

2.3. Oxidation resistance measurement

In order to investigate the oxidation resistance of the coatings, the isothermal oxidation test was carried out at 1273 K for 15 min in air. The weight loss rate was calculated by the equation below:

$$\rho = (m_0 - m_i)/m_0 \times 100\% \tag{1}$$

where ρ is the rate of weight loss, m_0 is the weight of sample before the oxidation test, and m_i is the weight of sample after the oxidation test.

3. Results

3.1. SiO_2 content in the coating

Fig. 2 shows the dependence of the SiO_2 content (wt.%) on the SiO_2 concentration. It can be clearly indicated that the SiO_2 content was almost linearly increased from ~3.2 wt.% to ~28.2 wt.% when SiO_2 nano-particles was added into the electrolyte with the concentration increased from 1 g/L to 10 g/L.

The increase of SiO_2 content in the coating may be qualitatively explained based on the Whithers' theory [12] and the two-step adsorption model of Guglielmi [13]. According to the Whithers' theory, the SiO_2 nano-particles could immediately adsorb the hydrate metal ions in the electrolyte, followed by a powerful transportation to the cathode surface under the effect of the electrical field. On the electrode surface, the ion-adsorbed SiO_2 nano-particles were mainly controlled by two-step adsorption processes. In the first