Structural characterization of YSZ/Al$_2$O$_3$ nanostructured composite coating fabricated by electrophoretic deposition and reaction bonding

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**A R T I C L E   I N F O**

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**A B S T R A C T**

Suspension of YSZ and Al particles in acetone in presence of 1.2 g/l iodine as dispersant was used for electrophoretic deposition of green form YSZ/Al coating. Results revealed that applied voltage of 6 V and deposition time of 3 min were appropriate for deposition of green composite form coating. After deposition, a nanostructured dense YSZ/Al$_2$O$_3$ composite coating was fabricated by oxidation of Al particles at 600 °C for 2 h and subsequently sintering heat treatment at 1000 °C for 2 h. Melting and oxidation of Al particles in the green form composite coating not only caused reaction bonding between the particles but also lowered the sintering temperature of the ceramic coating about 200 °C. The EDS maps confirmed that the composition of fabricated coating was uniform and Al$_2$O$_3$ particles were dispersed homogeneously in YSZ matrix.

1. Introduction

Iron-nickel based superalloys are of primary importance in high temperature applications such as gas turbine engines due to maintenance of structural properties and low thermal expansion coefficient at high temperatures. The main uses of these superalloys in jet engines are in production of blades, discs and castings. To increase the operating temperature of jet engine and subsequently increase the efficiency, hot parts of jet engines are coated with a thin ceramic coating called a thermal barrier coating [1–3]. Yttria-stabilized zirconia has many merits such as high melting temperature, low thermal conductivity and high thermal expansion coefficient among ceramic materials which make it applicable suggestion for thermal barrier coatings [4–6]. Electrophoretic deposition (EPD) is a colloidal process for manufacturing dense coatings in different thicknesses [7,8]. In 1940 Hamaker studied electrophoresis phenomenon for different ceramic materials and this research was the starting point for using EPD in manufacturing ceramic coatings and in 1978 EPD has been used for manufacturing industrial particles [9]. In EPD, charged particles dispersed in a liquid medium are migrated and then deposited on a conductive substrate by applying an electric field [10]. In comparison with other coating methods, EPD has some benefits such as versatility for a specific application, simplicity and low cost equipment, easy control of thickness and morphology of deposited coating, low geometrical restrictions of substrate and short time of deposition, which made it applicable for production of wide variety of ceramic coatings [9,11]. Suspension properties play an important role in quality of the coatings deposited by EPD method. Physical properties of the solvent such as viscosity [12], relative dielectric constant [13] and conductivity [14] must be considered in selection of solvent for EPD process. Among different organic solvents ethanol [15], acetone [16,17] and acetylacetone [18] are used mainly in EPD of YSZ particles. Development of electrical charge on surface of the particles dispersed in the suspension is necessary for EPD process. It is reported that addition of iodine to organic solvents as a dispersant cause formation of protons in the suspension and adsorption of these protons on surface of YSZ particles causes enhancement of electrical charge of the particles [19]. Applied voltage and deposition time are other important parameters should be optimized in EPD process [20]. After applying the green deposition, post-deposition sintering treatments are required to produce a dense and adherent coating [11,21]. Generally, ceramic coatings applied by EPD are deposited on metal substrates that cannot endure the high temperature necessary to sinter ceramic coatings. Lowering the sintering temperature can reduce damages of the metal substrate. Reaction
bonding (RB) is one of the methods to reduce the sintering temperature of ceramic coatings [22–25]. This method consists of adding some elements or compounds to green coating which produce ceramic materials during heat treatment in an oxidant or reducing atmosphere [11]. Oxidation of Al particles in the electrophoretically deposited PSZ/Al composite coating not only leads to formation of crack-free coating by compensating the volume shrinkage of the coating during sintering by the volume expansion arising from oxidation of Al particles to Al₂O₃ particles, but also causes sintering of the ceramic coating at a low temperature that metal substrate can resist [22,23].

The purpose of this research was to fabricate YSZ/Al₂O₃ nanostructured composite coating on an iron-nickel based superalloy using EPD and RB processes and investigate its microstructure. Electrophoretic deposition process was carried out at different applied voltages and deposition times. Optical microscopy and scanning electron microscopy were used for investigating the quality of green form

Fig. 1. Optical microscope images of the green form coatings deposited at constant deposition time of 1 min and different applied voltages of (a) 3 V, (b) 6 V, (c) 9 V, (d) 12 V and (e) 15 V.
coatings. Thermogravimetric analysis (TGA) was used for determination of the oxidation temperature of Al particles. Microstructural characterization of heat treated composite coating was done using X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and atomic force microscopy (AFM).

2. Materials and methods

Commercially available Yttria-stabilized Zirconia nano-powder (3 mol% Y₂O₃, Sigma-Aldrich, Germany) with spherical morphology, an average particle size of 50 nm and specific surface area > 17 m²/g and aluminum powder (with purity of 99.5%, Sigma-Aldrich, Germany)
with flake morphology and an average particle size of < 5 µm were used as raw materials. The suspension medium was acetone (with purity of 99 vol%) and iodine (with purity of 99.8%, Carlo Erba, France) was used as dispersant.

As reported in previous study [17], a well-stabilized suspension of YSZ nanoparticles in acetone medium is obtainable in presence of 1.2 g/l iodine. Accordingly, 1.2 g/l iodine was used for electrophoretic deposition of YSZ/Al green coating. In order to homogenize the mixing of powders, a combination of YSZ and Al powders in ratio of 5:1 by weight (as reported in [22]) subjected to zirconia ball milling in a polyethylene container with a velocity of 100 rpm for 2 h. In order to prepare the suspension, iodine was added to the solvent and magnetically stirred for 0.5 h and then the mixture of YSZ and Al powders was added to the solution in concentration of 10 g/l and mixed for 1 h by magnetic stirrer (Alfa Co., Iran). Then the suspension was subjected to ultrasonic bath (Sonic 6MX, James Products Europe Ltd., England) for 45 min. Zeta potential value for YSZ and Al particles in this suspension was measured by zeta potential analyzer (Microtrac, NanoSpray Wave, Germany).

Specimens (10 × 10 × 3 mm) were cut from Incoloy 825 superalloy as substrates and specimens (20 × 30 × 1 mm) were cut from stainless steel as counter electrodes. The substrate was placed between two stainless steel electrodes parallel with distance of 1 cm from them. Electrophoretic deposition was carried out by applying a D.C. electric field (D.C. power supply PS 405 Adak Co., Iran) between electrodes using applied voltages in the range of 3–15 V. After determination of optimized voltage, EPD process was done at a constant voltage and deposition times of 1–5 min. Quality of the coatings deposited at different voltages were studied by optical microscopy (Lissview, China).

The specimens coated with the composite green coating were dried in the laboratory environment for 24 h. Thermogravimetric analysis (LINSEIS STA PT-1000) has been carried out to determine oxidation temperature of Al particles. After determination of oxidation temperature, the specimens placed in a tube furnace in air atmosphere for oxidation and sintering treatment.

In order to investigate the phases present in the green form and sintered coatings, X-ray diffraction (XRD) analysis (Cu lamp, λ = 1.54 Å, 40 kV, 30 mA, Siemens D5000) was used. Also, to investigate the microstructure of the coatings scanning electron microscopy (FE-SEM, Mira3 Tescan, Czech Republic) was used. Distribution of the elements in the surface of the coating was examined using energy dispersive spectroscopy (EDS) maps and surface topography studies of green form and heat treated samples have been carried out using atomic force microscopy (Nanosurf Mobile S, Switzerland).

3. Results and discussion

Suspension of mixed YSZ and Al powders with YSZ to Al ratio of 5:1 by weight and solid concentration of 10 g/l in acetone in presence of 1.2 g/l iodine was prepared for electrophoretic deposition of green form composite coating. Zeta potential value in this suspension was measured about + 50 mV and + 16 mV for YSZ and Al particles, respectively. As a result, both YSZ and Al particles had positive surface charge in this suspension and therefore both powders could be deposited on cathodic electrode with negative charge in presence of electric field. Applied voltage is one of the important parameters in quality of deposited green form. In order to determine the optimum value of applied voltage, EPD process was carried out at applied voltages of 3, 6, 9, 12 and 15 V. Fig. 1 shows the optical microscope images of the coatings deposited at different voltages. It is observable that the substrate was not completely covered at applied voltage of 3 V and the deposition was not uniform all over the surface of the substrate (Fig. 1a). In fact in this voltage the particles had not adequate motivation force to move toward the substrate. Generally, the amount of deposited particles increases with increasing of applied voltage. As it is obvious, the coating deposited at applied voltage of 6 V covered the substrate completely and a uniform and crack-free deposition was obtained in this voltage (Fig. 1b). Although increasing of applied voltage leads to enhancement of deposited particles, it can damage the quality of the deposition. Extra high applied voltage can cause turbulence in the suspension, which may cause disruption in the deposition microstructure. Furthermore, with applying high voltage, particles move toward the substrate with high velocities and have not enough time to deposit in best positions to form an arranged and close-packed microstructure. Increasing of applied voltage to values more than 6 V, resulted in formation of cracks in the
microstructure of deposition (Fig. 1c, d and e). It can be concluded that uniform and crack-free green composite deposition was formed at moderate applied voltage of 6 V.

Deposition time is another important parameter affecting the quality of green deposition. Fig. 2 shows the macroscopic images of the depositions at constant applied voltage of 6 V and different deposition times. It can be observed that depositions formed during 1–3 min were crack-free, but further increasing of deposition time to more than 3 min caused formation of some cracks in the surface of the depositions. The reason of this fact is related to enhancement of insulator layer thickness on the conducting substrate. In fact, with increasing of insulator layer thickness, electrical field between the electrodes causing electrophoresis movement of the particles decreases and consequently adhesion of particles on the surface of earlier deposited particles decreases and they can easily be detached from the surface (Fig. 2d and e).

These results clearly showed the significance of the applied voltage and deposition time. Accordingly, a uniform and crack-free green deposition was formed at applied voltage of 6 V and deposition time of 3 min (Fig. 2c). Fig. 3 demonstrates SEM images of microstructure and cross-sectional view of this sample. It can be seen that the size of YSZ and Al particles in the green form was approximately as same as the original raw powders. The green form was not densely packed and sintering treatment was necessary to reach a well-packed and adequately strength coating. As it is demonstrated in Fig. 3b the thickness of the composite green form was measured about 19 µm.

As mentioned before, the main problem associated with sintering treatment of EPD coatings is high sintering temperature of ceramic coatings which is not endurable for metal substrates. In order to decrease the sintering temperature and overcome this problem, reaction bonding process was used. Fig. 4 illustrates the TGA curve for Al particles used in this research. According to this curve, oxidation temperature of Al particles determined as 600 °C. Therefore, the oxidation treatment was carried out at 600 °C for 2 h.

Fig. 5 portrays the XRD spectra of green form and heat treated coatings at 600°C for 2 h. The XRD spectrum of specimen with green form coating showed pronounced peaks of aluminum and a little Al2O3 phase. Presence of Al2O3 phase in green form coating was due to the high tendency of pure aluminum to react with oxygen of the atmosphere which causes surface oxidation of aluminum particles. After oxidation treatment at 600 °C for 2 h, there was little aluminum phase remained in the coating. It shows that oxidation of Al particles was occurred and approximately all of Al particles in the green coating were converted to Al2O3 during oxidation treatment.

After oxidation treatment at 600 °C for 2 h, sintering treatment was
done at 1000 °C for 2 h. Fig. 6 portrays SEM image of microstructure of this sample in comparison with pure YSZ coating heat treated at 1000 °C for 2 h. As it is obvious from Fig. 6a, melting and oxidation of Al particles was occurred, the pores between the particles were eliminated and the density of the coating was increased. Deformation of the particles from initial morphology, neck formation between the particles and elimination of pores between the particles confirmed the success of the sintering process at this temperature. It can be concluded that melting and oxidation of Al particles caused reaction bonding between the particles and reduction of sintering temperature of the coating about 200 °C in comparison with that of reported in researches about 1200 °C. As it is shown in Fig. 6b, in the case of pure YSZ coating, temperature of 1000 °C was not adequate for sintering treatment of this sample and pores between the particles remained after heat treating at this temperature for 2 h. Cross-sectional view of the sintered composite coating is illustrated in Fig. 7. As it is shown, the thickness of the coating was measured about 10 µm which showed a reduction of about

Fig. 8. EDS maps showing distribution of elements (a) Zr, (b) Y, (c) Al and (d) O.

Fig. 9. EDS spectrum of the elements in the final coating.
9 µm in comparison with green form coating. Reduction of the coating thickness confirmed the success of sintering treatment in enhancement of density.

Homogeneous distribution of the particles is one of the important factors in multi-component coatings. Fig. 8 shows elemental distribution maps obtained from EDS system for Zr, Y, Al and O elements. As it is clear, Al₂O₃ particles were dispersed in YSZ matrix and distribution of all four elements was homogeneous. Furthermore, EDS spectrum of the elements in the coating is illustrated (Fig. 9) and quantitative analysis of this spectrum is given in Table 1. Accordingly, the ratio of YSZ to Al in the final coating was approximately 16:1 by weight, while this ratio was 5:1 by weight in the initial suspension. Low amount of aluminum in the final coating in comparison with initial suspension had two reasons: (1) coarse size of the Al particles used as raw material caused more settlement of these particles in the suspension and (2) in multi-component EPD, the particles can deposit at rates proportional to their zeta potential and mobility in the electric field. Higher zeta potential value of YSZ particles (about +50 mV) in comparison with Al particles (about +16 mV) caused higher rate of deposition for YSZ particles.

Topography image and roughness curve of the surface for the composite coating before and after heat treatment are illustrated in Fig. 10. Surface roughness (Ra) was measured in three different points for each sample. According to results, Ra for the samples before and after heat treatment was measured about 139 nm and 90 nm, respectively. So, it can be concluded that heat treatment caused reduction in roughness of the coating surface.

4. Conclusions

Fabrication of nanostructured YSZ/Al₂O₃ composite coating on

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Table 1
Quantitative results of EDS spectrum.
incoloy 825 superalloy using electrophoretic deposition and reaction bonding was investigated. Microstructure studies indicated that YSZ/Al green coating deposited at applied voltage of 6 V and deposition time of 3 min was homogenous and crack-free. Phase analysis of the green form and sintered coatings revealed that Al particles were converted to Al2O3 during oxidation treatment at 600 °C for 2 h. Melting and oxidation of Al particles in the green form coating caused formation of reaction bonded Al2O3 phase and sintering of the ceramic composite coating at relatively low temperature of 1000 °C. EDS maps showed that the Al2O3 particles were dispersed homogenously in YSZ matrix and the fabricated composite coating was uniform.

References