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Suspension chemistry and electrophoretic deposition of YSZ-NiO nano-composite films on an iron-nickel based superalloy

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ABSTRACT
Suspensions of mixed YSZ (3 mol%) and Ni particles in acetylacetone medium were prepared using iodine as a dispersant. The effect of iodine concentration on suspension stability, particle size distribution and zeta potential of suspensions were studied to optimize the suspension chemistry. Electrophoretic deposition (EPD) method was applied for the preparation of green form YSZ/Ni nano-composite coating with suspension of YSZ and Ni particles in acetylacetone in presence of 0.2 g/l iodine. Based on the derived results, both applied voltage of 7 V and deposition time of 4 min are suitable for deposition of green composite coating. After deposition, green form coatings were heat treated at 500 °C for 1 h for oxidation of nickel particles and further sintered at 1100 °C for 4 h in the air. For the first time, the reaction bonding process along with the sintering heat treatment were studied and developed to fabricate uniform, crack-free and dense YSZ/NiO coatings. The volume shrinkage of the coating was compensated by the volume expansion, caused by oxidation of nickel in the green coatings. Also, addition of Ni particles to YSZ lowered the sintering temperature of the coating about 300 °C, since sintering temperature of the pure YSZ is 1400 °C but after addition of nickel the coating was sintered at 1100 °C. The coating adhesion to substrate was evaluated using ASTM D3359 and Rockwell C indentation (VDI 3398) methods. The result of adhesion tests showed that the coatings have good adhesion strength (5B according to ASTM D3359B).

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Introduction

For steam turbines, boilers, gas turbines and many other high temperature applications, using thermal resistant coatings is very important. Thermal barrier coatings (TBCs) are mainly made of ceramic materials that are coated on metal substrates. The main role of TBCs is to reduce the working temperature of the metal substrate. Iron-nickel base superalloys due to their low expansion coefficient at high temperatures and suitable structural properties are used in gas turbine engines. These superalloys usually include 15–60% iron and 25–45% nickel, and are mainly used in turbine blades, disks, and jet assemblies that require low thermal expansion. The other advantage of iron-nickel superalloys is their lower price compared to nickel and cobalt base superalloys.[1,2] Compared to other ceramics, yttria-stabilized zirconia (YSZ) has been mostly used in the production of thermal barrier coatings because of its low thermal conductivity, high thermal expansion coefficient and high phase stability.[3,4] Several methods have been used to apply TBCs, such as chemical vapor deposition (CVD)[5] and the plasma spray.[6] Electrophoretic deposition (EPD) has been recommended in recent years due to its simplicity and low cost for applying uniform coatings.[7,8] In EPD method the green coatings ought to be sintered at relatively high temperatures to obtain the desired compaction and good adhesion. To avoid damaging effects of sintering on the metal substrate, heat treatments must be done at temperatures below 1250 °C.[9,10] Addition of sintering additives,[11] using nano-sized particles[12] and reaction bonding (RB) process[13–15] are three methods to reduce the sintering temperature and improve densification.

Most of the studies about YSZ/Ni mixture have concentrated on nickels application in fabrication of anodes for solid oxide fuel cells.[16,20] Due to the excessive amount of Ni concentrations in most of these studies (up to 50 mol%), Ni could not be considered as a dopant anymore.[20] It has been reported that addition of Ni to YSZ increased the theoretical density of YSZ after sintering at 1200 °C from 60% up to 90%, stabilized the cubic phase in YSZ and promoted the grain growth.[11]

A reaction bonding (RB) technique has been developed to produce near net shape ceramics which overcomes the shrinkage of ceramics during sintering.[21,22] Not only the volume expansion related to the oxidation of Ni particles compensates the sintering shrinkage of the coating but also oxidation of Ni particles causes the ceramic coatings sintering to be completed at lower temperatures that metal substrate could resist.[2,13]

The purpose of this study was to stabilize the suspension containing YSZ and Ni nano-particles in acetylacetone and fabricate YSZ/NiO nano-composite coating on an iron-nickel base superalloy using EPD and RB processes.

Experimental procedure

Materials

Commercially available yttria stabilized zirconia nanopowder (3 mol% Y₂O₃, Sigma-Aldrich, Germany) with an average particle size of 50 nm, spherical morphology and specific surface area more than 17 m²/g and Ni nanopowder (Vday co., China) with an average particle size of 50 nm, purity of 99.9%, spherical morphology, and specific surface area more than 12 m²/g were used in this investigation. Acetylacetone (Merck, Germany) with purity of 99% was used as solvent. Iodine (Carlo Erba, France) with purity of 99.8% was used as dispersant.

Suspension preparation

Suspensions of 10 g/l YSZ and 0, 0.2, 0.4, 0.6, 0.8 and 1 g/l iodine in acetylacetone was prepared. Then suspensions were mixed for 1 h by magnetic stirrer (Alfa Co., Iran). In order to deflocculate the particles, the suspensions were sonicated in ultrasonic bath (Sonic 6MX, James Products Europe Ltd., England) for 1 h. 10 ml of each suspension were poured into a test tube. Sedimentation behavior of suspensions were studied in different time durations. The effect of iodine concentration on average particle size and zeta potential of suspensions were studied.

In order to prepare the suspension used for Electrophoretic deposition, 3 suspensions each containing 10 g/l YSZ and optimum amount of iodine in acetylacetone were prepared separately. The suspensions were exposed to ultrasonic bath for 1 h. 10 ml of each suspension were poured into a test tube. Sedimentation behavior of suspensions were studied in different time durations. The effect of iodine concentration on average particle size and zeta potential of suspensions were studied.

In order to prepare the suspension used for Electrophoretic deposition, 3 suspensions each containing 10 g/l YSZ and optimum amount of iodine in acetylacetone were mixed for 1 h by magnetic stirrer. Then the Ni with concentration of 1, 2 and 3 g/l were added to suspensions. Finally, the suspensions were exposed to ultrasonic bath for 1 h.

Electrophoretic deposition

Electrophoretic deposition was carried out by applying a D.C. electric field (D.C. power supply PS 405 Adak Co., Iran) between 316 stainless steel electrode (20 × 30 × 1 mm-anode) and Incoloy 825 superalloy specimens (12 × 12 × 3 mm-cathode).
The specimens were degreased with mixture of acetone and ethanol and then dried in the air at room temperature prior to deposition. Distance between electrodes was 1 cm as demonstrated schematically in Figure 1. Deposition carried out at room temperature using applied voltages of 5, 7, 9, 11 and 13 V with current density of 0.03 to 0.2 mA/cm² and deposition times of 1 to 5 min. Coated specimens were weighed before and after deposition process by a digital scale (with accuracy of 0.0001 g, RADWAG:AS310/C/2, Poland) in order to obtain deposited coatings mass on the substrates.

The deposited green coatings were dried in the laboratory environment for 24 h in the air. In order to investigate the surface quality of the coatings deposited at different voltages and times optical microscopy (Lissview, China) was used. Green form coatings were placed in the tube furnace (TF5/40-1250 Azartube, Iran) and heat treated at 500°C for 4 h for oxidation of nickel particles and further sintered at 1000°C, 1100°C and 1200°C for 4 h in air with heating rate of 5°C/min. Coatings were cooled in the furnace in order to reduce cracking.

**Characterizations**

Particles size in the prepared suspensions was measured by dynamic light scattering (DLS, Microtrac, Nanotrac Wave, Germany). Zeta potential analyzer (Microtrac, Nanotrac Wave, Germany) was used to measure zeta potential values of YSZ and Ni particles. In order to investigate the chemical effect of iodine on stability of suspensions, FT-IR analysis (Bruker- TENSOR27, Germany) was used. The microstructure and thickness of composite coatings were studied using scanning electron microscopy (FE-SEM, Mira3 Tescan, Czech Republic). The phase and chemical composition were identified by X-Ray diffraction (XRD, PW1730, Philips, Netherlands) using Cu lamp (λ = 1.5406 Å) at 40 kV and 40 mA, in the 2θ range of 10°C–120°C with the step size of 0.02°. Energy dispersive spectroscopy (EDS, Mira3 Tescan, Czech Republic) was used to evaluate the distribution of elements and atomic force microscopy, (AFM, Nanosurf Mobile S, Switzerland) was used to optimize the surface topography of the coatings. Adhesion of coatings to substrate tests were performed in accordance with ASTM D3359 B and VDI 3198 standards.

With regards to ASTM D3359 B test method, a pattern was created over the coating by a sharp cutting tool. As the amount of iodine is not sufficiently high to produce enough positive charges that are on the surface of particles. Protons are generated, as a result, the surface charge of the YSZ particles also increases. If the amount of these protons, increases too much, due to the compression of electrical double layer, the zeta potential and the stability of the suspension decreases. In the case of low iodine concentrations, the reason for not stabilizing the suspension is that amount of iodine is not sufficiently high to produce enough positive charge and cover the surface of all particles. With increasing of iodine content up to 0.4 g/l, the zeta potential value was increased up to 53.5 mV and for the amounts greater than 0.4 g/l it was decreased. This phenomenon is due to the charges that are on the surface of particles. Protons are generated by iodine addition to acetylacetone via the reaction as given in Eq. (1).

\[
\begin{align*}
\text{CH}_3\text{CO CH}_2\text{CO CH}_3 & + 2\text{I}_2 \rightarrow \text{ICH}_3\text{CO CH}_2\text{CO CH}_3\text{I} + 2\text{I}^- + 2\text{H}^+ \\
\end{align*}
\]

Typically, YSZ particles contain some hydroxyl groups on their surface that are absorbed from air moisture. Protons generated in suspension were adsorbed by these hydroxyl groups, which caused a positive charge on the YSZ particles surface. As the amount of iodine content increases, more protons are generated, as a result, the surface charge of the YSZ particles also increases. If the amount of these protons, increases too much, due to the compression of electrical double layer, the zeta potential and the stability of the suspension decreases. In the case of low iodine concentrations, the reason for not stabilizing the suspension is that amount of iodine is not sufficiently high to produce enough positive charge and cover the surface of all particles.

Size distribution of the particles has major role in the stability of the suspension. Particles having large particle size desire to settle down due to gravity. Average particle size results matches with the zeta potential results. With an increase in iodine content up to 0.4 g/l, the average particle size has decreased from 1503 nm to 113.5 nm and in the values higher than 0.4 g/l, it has increased up to 627.6 nm.

**Results and discussion**

**Suspension characterization**

Deposition of YSZ and nickel powders simultaneously requires a suspension where both particles stay stable in the acetylacetone solvent and do not precipitate.

Macroscopic imaging of the prepared suspensions containing YSZ showed that suspension which did not contain iodine was completely settled down after 24 h but rest of the suspensions were completely stable in this time. After one week, the rest of the suspensions partially precipitated and particles were coagulated but the coagulated part was smaller for the suspensions which contained 0.2, 0.4 and 0.6 g/l iodine that means the mentioned suspensions were more stable. It was observed that after 3 weeks all suspensions had precipitated. To evaluate more precisely and determine the most stable suspension, measuring the zeta potential and particle size is required. Smaller particle size and higher zeta potential are two important factors for the stabilization of suspensions in the EPD process. Following data has been extracted from an article. With increasing of iodine content up to 0.4 g/l, the zeta potential value was increased up to 53.5 mV and for the amounts greater than 0.4 g/l it was decreased.

![Image](image-url)
FT-IR analysis was used to investigate the effect of iodine on the chemical structure of suspension containing YSZ particles. In an FT-IR spectrum peaks are unique and different chemical bonds have specific peaks in this spectrum. Figure 2 shows FT-IR spectrum of pure YSZ nanoparticles, YSZ suspension in acetylacetone and YSZ suspension in acetylacetone with 0.2 g/l iodine. According to Basu et al., the peak located within the range of $3200 - 3600 \text{ cm}^{-1}$ in the FT-IR pattern corresponds to the O-H bonds group. As shown in Figure 2, for pure YSZ particles, peak I at $3378 \text{ cm}^{-1}$ and for suspension of YSZ particles in acetylacetone, peak II at $3304 \text{ cm}^{-1}$ in the spectra corresponds to the presence of Hydroxyl groups which was absorbed from air moisture by YSZ particles. However, after adding iodine the related peak in the spectrum becomes sharper (peak III

Figure 2. FT-IR spectra of (a) pure YSZ nanoparticles, (b) YSZ suspension in acetylacetone and (c) YSZ suspension in acetylacetone in presence of 0.2 g/l iodine.
in 3445 cm$^{-1}$). This is associated with the effect of adding iodine on the increment of protons, and therefore this pattern corresponds to the Eq. (1). Thus, the reason for increasing the zeta potential, reducing the size of the particles in the suspension and improving the stability of the suspension after addition of iodine, is related to the adsorption of generated protons in the suspension and increase of the charge on the surface of YSZ particles.

Macroscopic observations of Ni containing suspensions with different amounts of iodine after different periods of time showed that after 30 min (except for the suspension without iodine and for the suspension, contained 0.2 g/l iodine), the higher the amount of added iodine to the suspension, the faster Ni particles settled down. After 1 h suspensions containing 0.4, 0.6, 0.8 and 1 g/l iodine were completely settled down. After 3 days the suspension without iodine and the suspension which contained 0.2 g/l of iodine retained their stability. It can be concluded that adding more than 0.2 g/l iodine didn’t have any beneficial effect on the stability of nickel particles in acetylacetone. Zeta potential value for the most stable Ni suspension which contained 0.2 g/l iodine was measured about +46.7 mV. Figure 3 shows FT-IR spectra of Ni particles in acetylacetone and Ni suspension in acetylacetone with 0.2 g/l iodine. As mentioned before the peak located within the range of 3200–3600 cm$^{-1}$ in the FT-IR pattern corresponds to the O-H bonds group. As shown in Figure 3, for suspension of Ni particles in acetylacetone, peak I at 3404 cm$^{-1}$ in the spectra is related to the partial surface oxidation of the metallic particles caused by being in the air atmosphere. So, it is possible to associate the presence of the OH group peak with the absorption of air moisture by oxygen atoms.

Stability of Ni suspension which did not contain iodine can also be related to the same reason. However, after adding iodine the related peak in the spectrum becomes sharper (peak II in 3446 cm$^{-1}$). After addition of iodine, H$^+$ ions were adsorbed by the oxygen on the surface of the particles, which increased the OH group peak intensity. Addition of a small amount of iodine to a suspension containing nickel particles had a significant effect on sharpening the peak of OH groups. So, it can be concluded that the increased sedimentation of nickel particles in suspension containing more than 0.2 g/l

![Figure 3. FT-IR spectra of (a) Ni suspension in acetylacetone and (b) Ni suspension in acetylacetone in presence of 0.2 g/l iodine.](image-url)
iodine is due to excessive increase of $H^+$ ions which results in the compression of the electrical double layer.

Although the Zeta potential for the suspensions containing YSZ particles and 0.2 g/l iodine (31.7 mV) is not maximum measured value, but it is high enough to stabilize the YSZ particles in the suspension. Therefore, since both YSZ and Ni particles are stable in suspensions containing 0.2 g/l iodine, 0.2 g/l iodine was chosen for simultaneous deposition of these two powders.

**Electrophoretic deposition**

In order to control the deposition rate and achieve the desired microstructure, it is essential to know about the kinetic aspects of the electrophoretic deposition process. Achieving an appropriate thickness of the coating requires optimization of some parameters like applied voltage and deposition time. In general, by applying a larger voltage, the particles deposit more quickly, but in such a situation quality of the coating can be reduced. Uniform coatings are created when the applied voltage is moderate. Suspension of YSZ and Ni with solid concentration of 10 and 1 g/l, respectively, in presence of 0.2 g/l iodine was prepared for deposition of green form coating. Electrophoretic deposition process was performed at applied voltages of 5, 7, 9, 11 and 13 V and deposition time of 1, 2, 3, 4 and 5 min. Zeta potential values of this suspension was measured about +46.7 mV for YSZ and +31.7 mV for Ni particles. Therefore, both YSZ and Ni particles surface were positively charged. Accordingly, YSZ and Ni particles were deposited on an electrode which had negative charge. Figure 4 shows the changes in deposited coatings mass with applied voltage for different deposition times. As it can be seen the mass of the coating increased with increase in

Figure 4. Variation of deposition mass with applied voltage for different deposition times.

Figure 5. Variation of current density with deposition time for deposition of YSZ/Ni particles at different applied voltages.
applied voltages. But at higher applied voltages the mass of the coating started to decrease. The reason is related to the fast movement of the particles in the suspension at higher applied voltages that would degrade the coating during deposition. In addition, the particles move much faster than having enough time to deposit into the desired positions.

Also, as it is illustrated, in Figure 4 the deposition mass during the initial time of deposition increases constantly. But the passage of time, leads to reduction of the deposition rate. The reason for this behavior is that with the lapse of time and deposition of particles on the substrate, the concentration of suspension was reduced. Therefore the mass of the deposited coating did not increase with the former rate. Cause of this behavior is also explained by Figure 5 that shows the changes of current density with deposition time at different applied voltages. As it is shown, by increasing the deposition time, the current density for all of the applied voltages is first reduced and then, at longer periods of time becomes constant. This behavior was caused by formation of an insulating layer of ceramic particles on the conducting substrate electrode surface. So, the electrical conductivity of the substrate was decreased by increasing the deposition time and with thickening the deposited ceramic layer, less charged particles were deposited on the substrate.

Figure 6 shows macroscopic and optical microscope images of green coatings. As can be seen in the Figure 6a, for the deposition time of 1 min, the deposited coating was thin, and the surface of the substrate was not completely and uniformly covered, and only the lower parts of substrate was covered. As the deposition time increased, although the load of deposited coating on the substrate increased, but still some parts of the substrate remained uncovered (Figure 6b). This could be, due to the fact that in applied voltage of 5 V the motivation force of the particles to move toward the substrate was not adequate. In general, it can be concluded that the quality of the coatings, created at applied voltage of 5 V were not good and this voltage was not suitable to create uniform coatings.
Figure 9. AFM roughness curves and topography images for composite coatings deposited at: (a) 5, (b) 7, (c) 9, (d) 11 and (e) 13 V and deposition time of 4 min.
For coatings deposited at applied voltage of 7 V, and deposition time of 1, 2 and 3 min, the particles didn’t have enough time to deposit on the substrate and the upper part of the substrate was not full covered with the deposit. For the deposition times of 4 and 5 min, the coatings were uniform and crack-free (Figure 6c). The applied voltage of 7 V as a moderate voltage was suitable for obtaining a uniform deposition.

Increasing the applied voltage to amounts of applied voltages such as 9, 11 and 13 V at all deposition times of 1 to 5 min led to formation of cracks in the microstructure of deposition. Figure 7 shows the optical microscope images of the coatings deposited at the applied voltages of 9, 11 and 13 V with deposition time of 3 min. As it can be seen, the coatings deposited at these voltages had a non-uniform surface and some cracks at the sides of substrate. Excessive increase of the applied voltage results in irregular deposition of the particles on substrate and, consequently, creates a non-uniform coating. Accordingly, a uniform and crack-free green deposition was formed at applied voltage of 7 V and deposition time of 4 and 5 min (Figure 6c and d).

<table>
<thead>
<tr>
<th>Applied voltage (V)</th>
<th>R_a (nm)</th>
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<tbody>
<tr>
<td>5</td>
<td>67.7</td>
</tr>
<tr>
<td>7</td>
<td>62.3</td>
</tr>
<tr>
<td>9</td>
<td>72.6</td>
</tr>
<tr>
<td>11</td>
<td>79.2</td>
</tr>
<tr>
<td>13</td>
<td>97.5</td>
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Figure 10. SEM images of microstructure and cross-sectional view of green form composite coating deposited at applied voltage of 7 V and deposition time of 4 min.

Figure 11. EDS spectrum of elements in the green coating.
Electrophoretic deposition carried on for suspensions containing 10 g/l YSZ and 0.2 g/l iodine with nickel concentrations of 2 and 3 g/l at different applied voltages and times. Coatings at higher concentrations of nickel at all applied voltages were non-uniform and cracked. Figure 8 shows the macroscopic and microscopic images of green form coatings which were deposited from the suspensions containing 2 and 3 g/l nickel at applied voltage of 7 V and deposition time of 4 min. As shown in the Figure 8, structure of this coatings is non-uniform and full of macro cracks. Generally, increasing solid concentration leads in increment of the mass of deposited particles. But excessive presence of particles can harden the movement of particles in the suspension, which can negatively affect quality of the final deposited coating and the particles deposit heterogeneously on the substrate. Therefore, an optimum concentration of the suspension needs to be determined for the suspension. As a result, the nickel concentration of 1 g/l was selected as the optimum nickel concentration.

The average surface roughness values ($R_a$) for the green form coatings deposited at the applied voltages of 5, 7, 9, 11 and 13 V and the deposition time of 4 min are presented in Table 1. Figure 9 shows surface roughness curves and three-dimensional topographic images for the green coatings created at the various applied voltages.

As shown in Table 1, the lowest average surface roughness is related to the applied voltage of 7 V and its value is 62.3 nm. Afterwards, the average surface roughness increased with the increase of applied voltage. The reason could be related to the fast movement of particles in higher potentials in the suspension which did not allow the particles to deposit at appropriate positions, so the coating surface is non-uniform and rougher. As shown in Figure 5, the suspension density tends to be unstable with increasing applied voltages. In this diagram, the variations of current density with time for applied voltages of 9, 11 and 13 V is unstable, and it is stable for applied voltages of 5 and 7 V. It is said that the unstable current density affects the quality of coatings morphology. The unstable current density influences the microstructure of the coating and causes irregular arrangement of particles. Therefore, the higher voltages are

Table 2. Quantitative results of EDS spectrum.

<table>
<thead>
<tr>
<th>Elt</th>
<th>Line</th>
<th>Int</th>
<th>Error</th>
<th>K</th>
<th>Kr</th>
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<th>A%</th>
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<tr>
<td>Ni</td>
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<td>Zr</td>
<td>La</td>
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<td>0.7881</td>
<td>84.57</td>
<td>77.91</td>
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</tbody>
</table>

Table 2.

Figure 12. XRD spectra of: (a) green form and (b) heat treated coatings at 500 °C for 1 h and then sintered at 1100 °C for 4 h.
not suitable for deposition. In the case of applied voltage of 5 V the value of current density and subsequently the motivation force of the particles to move towards the substrate is not adequate. Thus, coatings created at this voltage were not uniform. Because of the stability of the current density at the applied voltage of 7 V and with regard to uniform and flat coatings created at this voltage (Figure 6), also considering the results obtained from the AFM analysis (Table 1 and Figure 5), it can be said that applied voltage of 7 V was suitable for deposition and was chosen as the optimum applied voltage for electrophoretic deposition process.

Figure 10 shows SEM images of microstructure and cross-sectional view of green coating. The green form coating was relatively dense, but the sintering treatment was required to reach a dense and compact coating. As it can be seen in (Figure 10b) the thickness of the green form deposited coating was measured about 32.04 μm.

Figure 11 shows EDS spectrum of the elements in the composite coatings and Table 2 provides quantitative analysis of EDS spectrum. According to Table 2, the ratio of Ni to YSZ in the green coating was approximately 1:10 by weight, while in the initial suspension this ratio was 1.5:8.5 by weight. The reason for this difference can be related to the different mobility of nickel and YSZ particles in Figures 13.

Figure 14. SEM images of the surface of the composite coatings: (a) heat-treated of oxidation at 500 °C for 1 h and sintering heat treatment at (a) 1000, (b) 1100 and (c) 1200 °C for 4 h.

Figure 15. SEM image of cross-sectional view of the final sintered composite coating.
suspension. The Zeta potential value for suspensions containing YSZ particles was measured about 31.7 mV, and for the suspension containing Ni particles was measured about 46.4 mV. Therefore, due to the higher zeta potential of suspension containing nickel particles, the mobility of the nickel particles in the suspension was higher than YSZ particles. As a result, the ratio of nickel to YSZ in coating is greater than its ratio in suspension.

High temperature of sintering heat treatment in EPD is a major problem of this process, because the metal substrate cannot endure high temperatures. In order to decrease the sintering temperature and overcome this problem, reaction bonding process was used. Ni particles oxidize into NiO between 400 and 600 °C. Therefore, the oxidation treatment was performed at 500 °C for 1 h. Figure 12 shows the XRD spectra of green form and heat-treated composite coatings at 500 °C for 1 h and subsequently heat treated at 1100 °C for 4 h. XRD pattern of green coating specimen contain the peaks that are related to the existence of nickel in the coating. XRD spectrum shows that after heat treatment of oxidation and sintering, Ni particles were oxidized and almost all Ni particles in the green coating were converted to NiO.

After Oxidation of Ni at 500 °C for 1 h, sintering treatment was done at 1000 °C, 1100 °C and 1200 °C for 4 h. Figure 13 shows the microstructural images of sintered composite coatings. As shown in Figure 13a, particles were attached together, but the sintering operation has not been done completely in 1000 °C and the particles have sustained their initial shape. There are also empty spaces between particle aggregations and porosity in the structure. Therefore, this temperature is not high enough to create adequate compaction and adherent coating. Therefore, reaching higher density requires higher temperature.

For the coating sintered at 1100 °C (Figure 13b), the particles have grown and become larger, also the interface between the particles is quite apparent. From the observations it can be claimed that the density of the coating has been increased and the porosities have been eliminated.
Therefore, it can be said that at 1100 °C, the sintering operation of the coating was relatively done.

For the coating heat treated at 1200 °C the structure of the coating was not dense and it had larger porosities (Figure 13c). With increase in the temperature, particles have grown enormously and caused the coating to be degraded. Also, at 1200 °C, the metal substrate has also been slightly damaged. For this reason, this temperature was not appropriate for the sintering treatment of coatings. Therefore, the temperature of 1100 °C was selected as the optimum temperature for the sintering heat treatment.

Figure 14 compares the SEM images of the surface of the sintered composite coatings that were oxidized at 500 °C and then sintered at 1100 °C for 4 h in air with a non-oxidized coating sintered at 1100 °C in argon atmosphere without oxidation. As it is shown, the coating that was also exposed to oxidation heat treatment was very uniform, smooth and without cracks and cavities. But the surface of the coating, which was only subjected to Ar atmosphere, had cracks and non-uniformity. The reason for this, is the reaction bonding process (RB). Reaction bonding process along with the sintering heat treatment fabricated uniform, crack-free ceramic coatings. The volume expansion caused by the nickel particles oxidation, compensated the volume shrinkage of the coating.

Figure 15 exhibits the cross-sectional SEM image of the sintered coating. The thickness of the coating was measured about 29.05 μm. The thickness of the sintered coating reduced about 3 μm compared to unsintered coating. Reduction of the pores and porosities during the sintering process resulted in improvement of the coating density and reduction of coating thickness.

AFM studies on the composite coating showed that average surface roughness (R_a) for the samples before and after heat treatment was about 62.3 nm and 57.3 nm, respectively. So, it can be concluded that sintering has caused reduction in roughness of the coating surface due to reduction in porosity of the surface.

To evaluate adhesion strength of the coatings, ASTM D3359 was performed. According to this standard and due to the fact regarding that the coating thickness was less than 50 μm, the surface of the coatings was scratched with a sharp tool to eleven horizontal lines and eleven vertical lines. The patterns appearance after scratching is shown in Figure 16a. A tape was applied on the created pattern, then the tape was quickly peeled off. This test was repeated on for two samples. Figure 16b illustrates the surface of coatings after peeling off the tape. By comparing the quality of coating surface shown in Figure 16b with the standard D3359 classification of adhesion test results, the quality of the coating is standardized in the 5B category, since none of the patterns has been detached. So, it can be deducted that the coatings had good adhesion strength.

Also, VDI 3198 standard was used to verify the adhesion results. Figure 17 shows SEM images of the surface of the heat-treated coatings at two temperatures of 1000 °C and 1100 °C, respectively, after the Rockwell C indentation test. Applying a load of 150 kgf results in a radial plastic deformation on the coating that creates circumferential cracking around the indentation area. These cracks are related to the strength and adhesion of the coating to the substrate. As illustrated in Figure 17a, which is related to the coating sintered at 1000 °C, radial cracks and a wide area of delamination and flaking is observable around the indentation. The reason for this, is that the sintering heat treatment process is not completely done at the temperature of 1000 °C, which results to insufficient adhesion strength of the coating. As shown in Figure 17b, there are few radial micro-cracks around the indentation area, and some cracks on the right-side image can be observed. By comparing the images with the principle of the VDI 3198 indentation test it can be concluded that the coating that heat treated at 1100 °C had good adhesion strength.

Conclusion

In this study, fabrication of YSZ/NiO nano-composite coating on Incoloy 825 superalloy using EPD and reaction bonding was investigated. For better stability of both YSZ and Ni particles in acetylacetone, 0.2 g/l iodine was added to the suspension as a dispersant. Microstructural studies indicated that YSZ/Ni green coating deposited at applied voltage of 7 V and deposition time of 4 min was crack-free and uniform. Phase analysis of the green and sintered coatings showed that Ni particles were converted to NiO during heat treatment of oxidation at 500 °C for 1 hr. Oxidation of Ni particles in the green composite coating caused formation of reaction bonded NiO. Sintering heat treatment of the ceramic composite coating was carried out at relatively low temperature of 1100 °C. Adhesion of coating to substrate was evaluated as good adhesion strength according to ASTM D3359 and VDI 3198 standards.

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