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Fabrication of ceramic composite coatings using electrophoretic deposition, reaction bonding and low temperature sintering

Zhoucheng Wang, Jane Shemilt, Ping Xiao*

Department of Materials Engineering, Brunel University, Uxbridge UB8 3PH, UK

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Abstract

We have developed a novel combination of electrophoretic deposition (EPD), reaction bonding and low temperature sintering techniques for the fabrication of yttria stablised zirconia (YSZ)/alumina composite coatings on Fecralloys. A mixture of ethanol and acetylacetone solvent was found to be an effective medium for YSZ and aluminium particle suspension. With the particle size of YSZ and aluminium being significantly reduced during ball milling. By using the EPD process, uniform green form coatings containing YSZ and aluminium particles were produced on Fecralloys. After oxidation of aluminium at 500°C and sintering at 1200°C, a dense and adherent YSZ/Al_2O_3 coating was produced. The presence of aluminium in the green form coatings not only contribute to the bonding between the coating and the metal substrate, but also compensate for the volume shrinkage of the coatings during sintering by the volume expansion arising from oxidation of aluminium to alumina.

Keywords: Al_2O_3; Electrophoretic deposition; Sintering; Suspensions; ZrO_2

1. Introduction

Ceramic coatings are currently of much interest for applications in high-temperature and highly corrosive environments. Formation of ceramic coatings by electrochemical processing is a relatively new technique.[1,2] It presents several advantages over alternative coating techniques; the thickness and morphology of the deposit can be controlled by the electrochemical parameters, relatively uniform deposits are obtainable on complex shapes, the deposition rate is higher than that using most other methods, and the equipment required is of low cost.[3,4] Recently we developed a novel fabrication technique for the production of ceramic/ceramic and metal/ceramic composite coatings by electrochemical processing.[5] The technique combined two electrochemical deposition methods, electrophoretic deposition (EPD) and electrolytic deposition, which can produce uniform composite layers of closely controlled thickness on both metallic and ceramic substrates at ambient temperature with inexpensive equipment. The results obtained have significant potential for the economic mass production of a wide variety of composites, including high temperature intermetallic/ceramic and wear resistant coatings and components for solid oxide fuel cells. However, the main problem associated with this process is the difficulty in sintering of the coatings. Firstly, high temperature is required for sintering of the coatings. Secondly, the volume shrinkage of the coatings during sintering leads to the formation of cracks in coatings bonded to metal substrates.

A reaction forming technique, reaction-bonding of Al_2O_3 (RBAO), has been developed to produce near net-shape ceramics, which overcomes problems caused by the shrinkage of ceramics during sintering.[6,7] In this technique, RBAO precursor powders were prepared by attrition milling Al/Al_2O_3 mixtures. During heat treatment in an oxidising atmosphere (usually air), the metal phase in RBAO powder compacts was fully converted to nanometer-sized oxide crystals which were sintered and bonded the primary Al_2O_3 particles. The volume expansion associated with the $Al \rightarrow Al_2O_3$ reaction partially compensated for the sintering shrinkage, hence low-shrinkage Al_2O_3 ceramics were fabricated. We have developed the reaction bonding process, combined with EPD process, to fabricate crack-free and relatively dense

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* Corresponding author. Fax: +44-1895-256392.
*E-mail addresses:*ping.xiao@brunel.ac.uk (P. Xiao).

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ceramic coatings.[8] However, to fabricate relatively dense coatings using EPD and reaction bonding process, sintering temperature should be in the range 1350–1500°C, which is too high for metal substrates to withstand.

Previous studies have demonstrated that well-dispersed particles are necessary to produce densely packed deposits.[11,14] On the contrary, aggregates form loosely bound structures, with low green densities and poor sintering behaviour. Recently, many studies have experimentally found that dense ceramic parts can be achieved at a sintering temperature lower by several hundred degrees celsius for nano-sized and submicron-sized powders than for coarse powders.[9,10] Therefore, it is highly desirable to produce stable ceramic suspensions containing fine ceramic particles. There have been several studies published on the effect of milling conditions on the particle-size distribution of various powders.[14–16] Experiments have been conducted to examine the effect of different milling liquids on milling rate, the results are usually interpreted in terms of difference in viscosity. However, very few studies have addressed specifically the relation between composition of solvents, stability of suspension and microstructure of green form. Moreover, there have been no significant effect found on the reduction of the ceramic particle size. In this work, we have found that a mixture of acetyleacetone and ethanol can be used as the milling liquid to reduce the particle size and produce a stable ceramic suspension containing both yttria partially stablised zirconia and Al powder. EPD was used to deposit PSZ/Al composite coatings. Both sintering and the reaction bonding process occured at low temperature upto 1200°C, which minimises any effects on the metal substrate. Also, the volume shrinkage due to sintering was compensated by the volume expansion due to the oxidation of aluminium in the green form coatings eliminating cracking of the coating.

2. Experimental techniques

In this study, fine yttria PSZ powder HSY-3 (3 mol% Y_2O_3) with an average particle size of 0.47 μm (Mandoval Ltd, UK) and fine aluminium (Al) powder with an average particle size of 1.0 μm (Riedel-deHaen, Germany) were used to produce suspensions. The suspension medium was an organic solvent. Solvents used were ethanol (Aldrich Chemical Co., UK), acetyleacetone (Aldrich Chemical Co., UK), a mixture of ethanol and distilled water in a ratio of 1:1 by volume, or a mixture of ethanol and acetylacetone in a ratio of 1:1 by volume. The powder concentrations used were 50 g l^{-1} for PSZ and 10 g l^{-1} for Al. All suspensions were subjected to zirconia ball milling for 48 h before use. A small amount of zirconia particles might come off from the zirconia balls during milling. However, the presence of the zirconia particles did not affect the composition of zirconialalumina composite coatings.

EPD was carried out by applying a d.c. electric field between a platinum counter electrode (anode) and a substrate (cathode), distance between electrodes 15 mm, in a suspension at room temperature using applied voltages in the range 20–100 V with current density of 0.l–5 mA/cm^2 and deposition times of 0.5–5 min. The substrate was a commercial Fecralloy foil (Fe–Cr–Al; Goodfellow Cambridge Ltd, UK).

The specimens coated with the composite green forms were dried at room temperature for 24 h and then placed in a tube furnace in air for oxidation and sintering. It has been observed that the oxidation of Al exhibits a maximum reaction rate at ~520°C.[7] Therefore, the heat treatment was carried out at a rate of 2°C/min to 520°C and held at this temperature for 2 h to allow oxidation of Al to occur. The temperature was then increased at 2°C/min to 1200°C and held for 4 h for sintering.

The phases present in the mixed powders, green form and sintered coatings were determined using X-ray powder diffraction (XRD; Philips PW1 050 X-ray Diffractometer, CuK_α radiation). The microstructures of coatings were examined using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) (Jeol JXA840 Microprobe).

3. Results and discussion

3.1. Deposition of green form coatings

The quality of the green forms prepared using the EPD method depended strongly on the stability of the suspension used. Since composite green forms are fabricated by the accumulation of ceramic powders from a suspension on a substrate by a d.c. field, the choice of a solvent is important in the EPD method in order

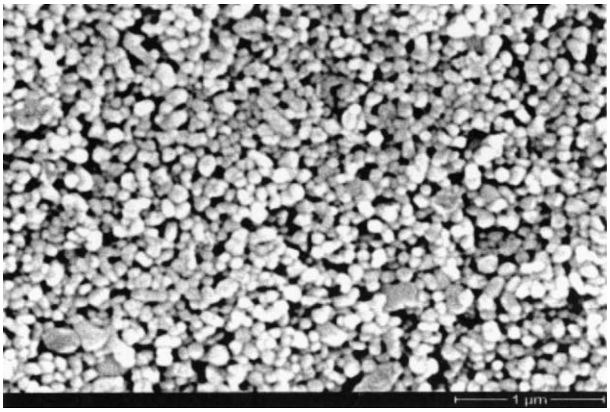


Fig. 1. Scanning electron microscopy image of the surface morphology of PSZ/Al composite green form electrophoretically deposited on a Fecralloy substrate from a suspension using mixed ethanol and acetylacetone solvent, applied voltage 40 V for 1 min.

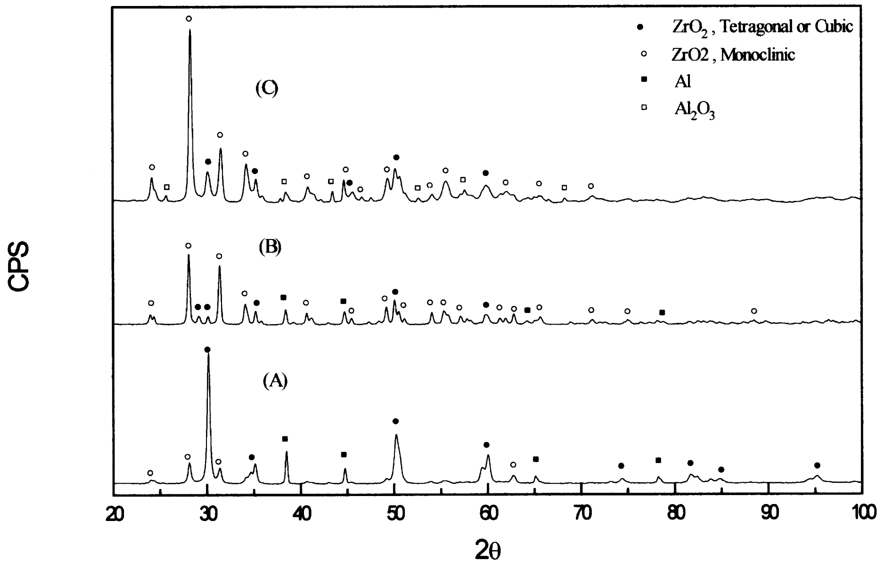


Fig. 2. X-ray powder diffraction spectra of: (A) the PSZ/Al mixed powder; (B) the green form deposited from a suspension using mixed ethanol and acetylacetone solvent; (C) the coating after oxidation at 520°C for 2 h and sintering at 1200°C for 4 h.

effectively to disperse ceramic powders and to produce a colloidally stable suspension. Ethanol and/or water are generally used as the solvent.[11,12] The use of water has the advantage of a high dielectric constant and is beneficial in preparing stable suspensions of oxide powders, but the electrolysis of water that accompanies EPD interferes with the quality of deposited films at high applied voltage. Besides, suspensions containing Al powder will become unstable and may become unusable due to the reaction between Al and water. On the other hand, oxide powders cannot be readily deposited electrophoretically from a pure organic solvent, as small amounts of free ions exist in a pure organic solvent. This means that the electric charge on the particles in the organic solvent is extremely low so that a stable suspension cannot be achieved. In an effort to overcome this disadvantage, we have discovered that a mixed organic solution is an effective suspension medium for yttria stabilised zirconia (YSZ) and Al powders.

The suspension prepared using a mixture of ethanol and acetylacetone with a ratio of 1:1 by volume as solvent was colloidally stable for a long period of time. This suspension enabled a PSZ/Al composite green form to be easily and directly electrophoretically deposited. Fig. 1 shows a SEM image of the surface morphology of PSZ/Al composite green form electrophoretically deposited on a Fecralloy substrate from this suspension using an applied voltage of 40 V for 1 min. It can be seen that the green form was densely packed. It is worth notice that the particle size (about 0.1 μm) in the green form is much finer than the original PSZ (average particle size of 0.47 μm) and Al (average particle size of 1.0 μm) particles. This indicates that this mixed solvent was effective in breaking up the agglomerates present in the as received ceramic and metal powders to produce a colloidally stable suspension. Ball milling of this dispersed suspension resulted in a significant reduction in the average particle size. Fig. 2 shows the XRD spectra obtained from the PSZ/Al mixed powder (before ball milling) and the green form deposited from this suspension (after ball milling). We can see that there was a phase transformation of tetragonal to monoclinic (t→m) in the PSZ particles during ball milling. This martensitic phase transformation from the metastable tetragonal to the monoclinic form of zirconia was probably induced by the fracture of PSZ particles.[13] The low content of yttria stabiliser also contribute the phase transformation.

The suspension prepared using a mixture of ethanol and distilled water with a ratio of 1:1 by volume as solvent was not as colloidally stable as for that of using the ethanol and acetylacetone mixture, with serious sedimentation occurring after standing for a prolonged period. A PSZ/Al composite green form could not be directly electrophoretically deposited from this suspension. Using

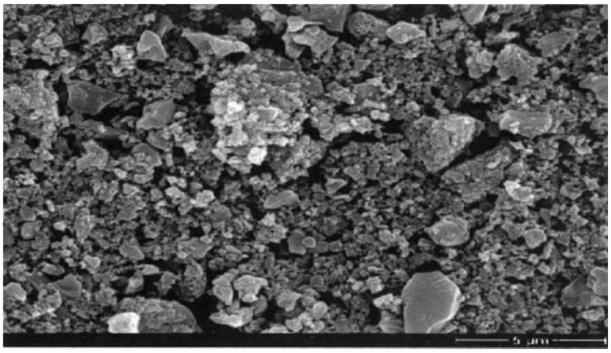


Fig. 3. Scanning electron microscopy image of the surface morphology of PSZ/Al composite green form electrophoretically deposited on a Fecralloy from a suspension using mixed ethanol and distilled water solvent, applied voltage 50 V for 1 min.

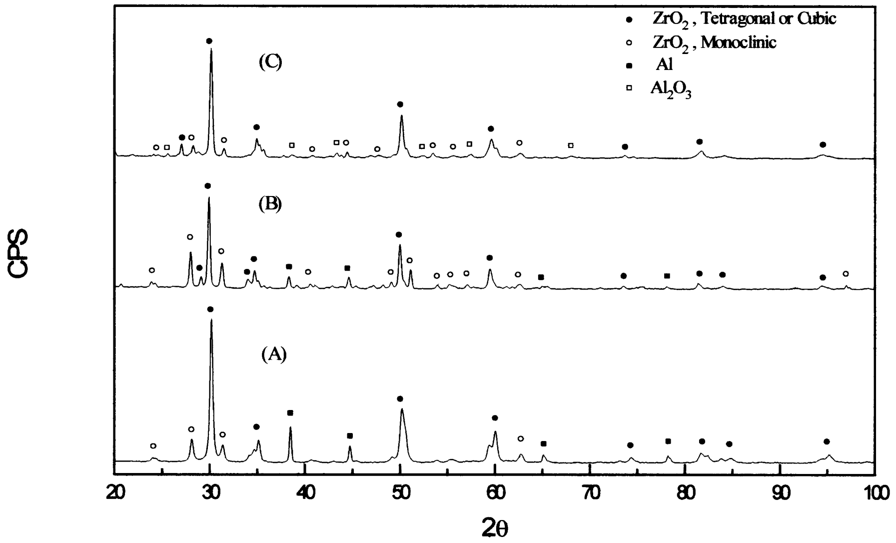


Fig. 4. X-ray powder diffraction spectra of: (A) the PSZJ/Al mixed powder; (B) the green form deposited from a suspension using mixed ethanol and distilled water solvent; (C) the coating after oxidation at 520°C for 2 h and sintering at 1200°C for 4 h.

ethanoic acid to control the suspension pH at approximately 3.5, the green form was deposited. Fig. 3 shows a SEM image of the surface morphology of a PSZ/Al composite green form deposited from this suspension using an applied voltage of 50 V for 1 min. It can be seen that the green form was not densely packed and the particle size in the green form was approximately the same size as the original PSZ and Al powders. Fig. 4 shows the XRD spectra of the PSZ/Al mixed powder (before ball milling) and the green form deposited from this suspension (after ball milling). We can see that there was little phase transformation (t→m) in the PSZ particles during ball milling. This indicates that the agglomerates were not dispersed in this suspension and that ball milling was ineffective in reducing the average particle size by particle fracture.

The suspensions using either pure ethanol or pure acetone as solvent were not colloidally stable, and the green form was difficult to deposit from these suspensions. Using ethanoic acid to control the suspension pH at approximately 3.5 and with magnetic stirring, a poorly packed green form was deposited from the suspension using ethanol as solvent at an applied voltage of 100 V for 2 min (Fig. 5). The particle size in the green form was approximately the same size as the original PSZ and Al particles. Fig. 6 shows the XRD spectra of the PSZ/Al mixed powder (before ball milling) and the green form deposited from this suspension (after ball milling). We can see that there was very little or no phase transformation (t→m) in the PSZ particles during ball milling. This indicates that the agglomerates were not dispersed in this suspension and that ball milling was ineffective in reducing the average particle size by particle fracture, similar to the specimens prepared using the ethanol and distilled water mixed solvent.

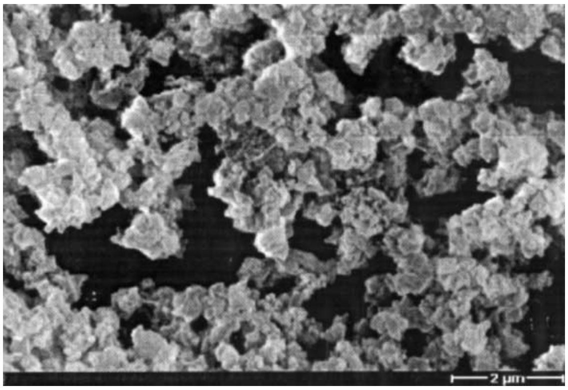


Fig. 5. Scanning electron microscopy image of the surface morphology of PSZ/Al composite green form electrophoretically deposited on a Fecralloy substrate from a suspension using ethanol solvent, applied voltage 100 V for 2 min.

These results clearly demonstrate the vital importance of the choice of a suitable suspension medium for the ceramic and metal particles when using EPD to deposit composite coatings. A colloidally stable suspension containing well-dispersed particles is necessary to produce a densely packed green form. The effectiveness of the mixed solution of ethanol and acetylacetone for the deposition of PSZ/Al composite green forms can be attributed to the presence of protons in the form of $CH_3CH_2OHH(+)$, arising from the reaction between the two solvents. Acetylacetone CH_2–C(O)–CH_2–C(O)–CH_3 has an acidic proton due to the two C(O) functional groups. Therefore, in the presence of base, it will be ionised to form CH_3–C(O)–CH(negative charge)–C(O)–CH_3. Ethanol is a weak base, and it will help shift the equilibrium by stablising H(+) in the form of $CH_3CH_2OHH(+)$. The $CH_3CH_2OHH(+)$ in organic solvents will prefer to be absorbed at the surface of

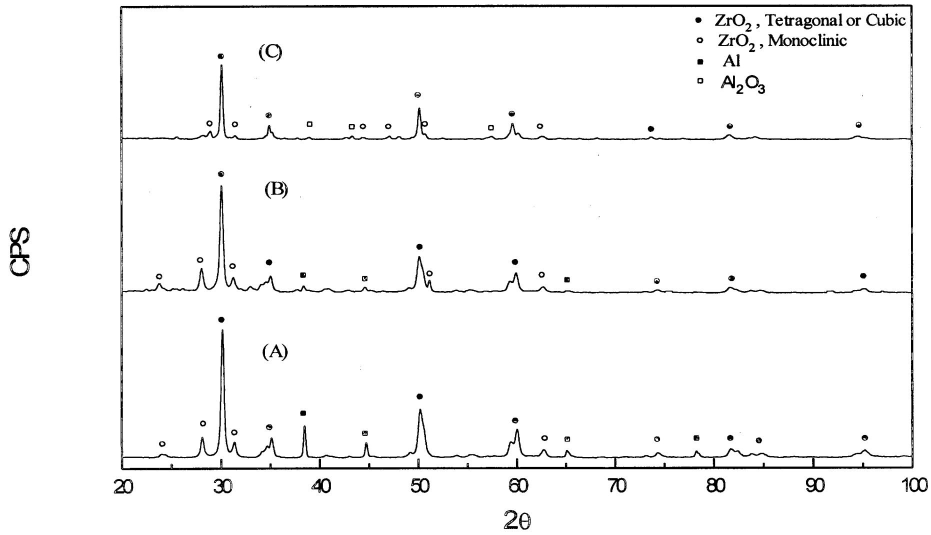


Fig. 6. X-ray powder diffraction spectra of: (A) the PSZ/Al mixed powder; (B) the green form deposited from a suspension using ethanol solvent; (C) the coating after oxidation at 520°C for 2 h and sintering at 1200°C for 4 h.

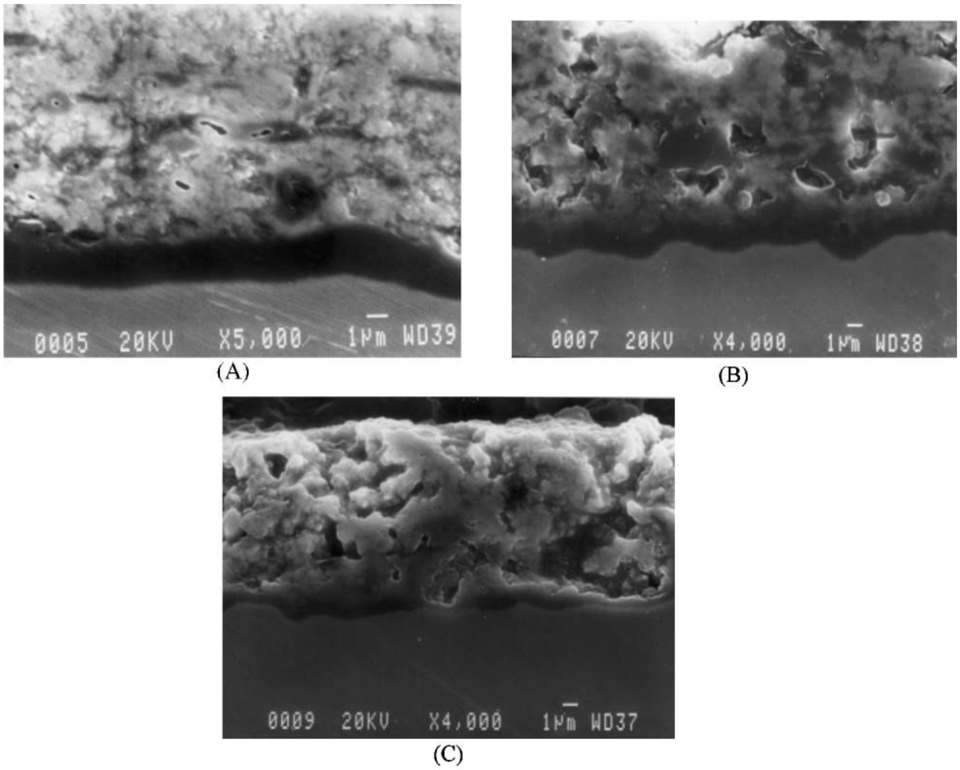


Fig. 7. Scanning electron microscopy images of the cross section of coatings deposited from suspensions using; (A) a mixed ethanol and acetylacetone solvent; (B) a mixed ethanol and distilled water solvent; (C) pure ethanol solvent. All coatings sectioned after oxidation at 520°C for 2 h and sintering at 1200°C for 4 h in air.

particles in suspension and help the break-up of particle agglomerates during ball milling. Then the EPD of fine particles in suspension will produce the green coatings of high density.

3.2. Sintered coatings

The presence of Al in the green form coating is essential for producing dense and adherent coatings on

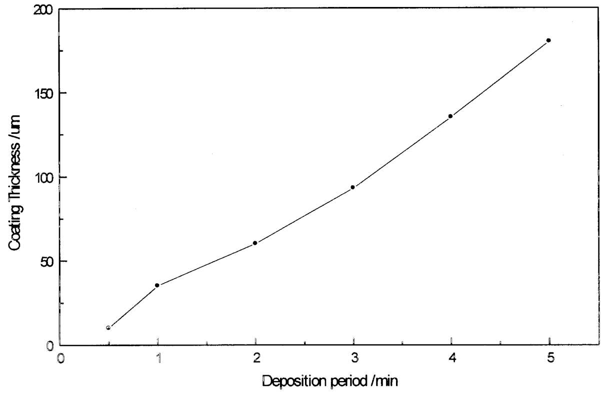
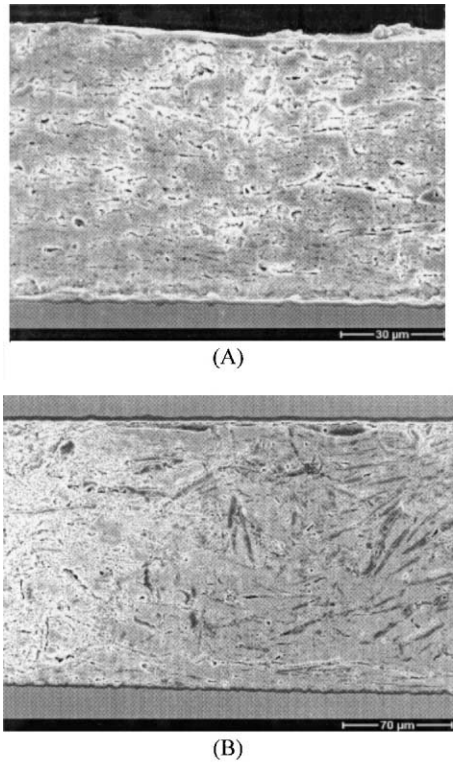


Fig. 8. Thickness of coatings produced from the mixed ethanol and acetylacetone suspension as a function of deposition period at an applied potential of 40 V.

metal substrates. Experimental studies showed that the absence of Al in the green form coating would lead to peeling off of the coatings during oxidation and sintering. The presence of Al did not only compensate the volume shrinkage of green form coatings, but also promoted the adherence of the coatings to the metal substrates. Fig. 7 shows SEM images of polished cross sections of three coatings, prepared using different suspension media, after sintering. By EDS analysis the dark phase was identified as alumina (Al_2O_3) and the grey phase as YSZ. In all cases, a thin alumina layer was formed between the coating and the metal substrate, which is probably due to the preferential oxidation of aluminium in the metal substrate. The microstructure of the sintered coating is dependent on the density of the deposited green form precursor. The coating produced from the mixed ethanol and acetylacetone suspension was more uniform with a lower porosity than for those deposited using either mixed ethanol and distilled water or pure ethanol. The higher density of the coating produced from the mixed ethanol and acetylacetone suspension can be attributed to a combination of the higher density of the green form and enhanced sintering at 1200°C due to the smaller particle size in the ball milled powder for this suspension medium. However, further study is needed to understand the relationship between the particle size, packing density of the green form and quality of the sintered coatings.

The thickness of composite coatings produced from the mixed ethanol and acetylacetone suspension can be readily controlled by varying the either the time period or the applied voltage used in electrophoretic deposition. As an example of this, Fig. 8 shows the thickness of coatings produced from the mixed ethanol and acetylacetone suspension, measured by SEM, as a function of deposition period at an applied potential of 40 V.

Fig. 9 shows SEM images of the cross section of PSZ/Al sintered coatings deposited on a Fecralloy substrate by EPD, using the mixed ethanol and acetylacetone suspension, at an applied voltage of 40 V for time periods of 3 and 5 min. The oxidation and sintering conditions were the same as for the specimens shown in Fig. 7, where the deposition time was 1 min. The thicker green forms, produced by longer deposition times, have sintered at the relatively low temperature, 1200°C, to well adhered, uniform, relatively dense coatings. The difference in microstructure of alumina (black) might be caused by the difference in shapes of aluminium before the oxidation. No cracks were detected within the coatings after sintering which suggests that the reaction bonding process was effective in a low-shrinkage ceramic composite layer. The relatively high density and uniformity of these coatings makes then suitable for application as thermal barrier or anti-corrosion protection layers for metal substrates in high temperature components. However, denser coatings should be made for anti-corrosion protection, whereas thicker coatings should produced for thermal protection.



(A)

(B)

Fig. 9. Scanning electron microscopy images of the cross section of PSZ/A1 green forms deposited on a Fecralloy substrate by EPD using an applied voltage of 40 V for (A) 3 and (B) 5 minutes after sintering.

4. Summary

(1) Electrochemical processing is a feasible low cost method to fabricate composite green forms which allows the use of a lower sintering temperature to produce a controlled microstructure and high sintered density of the composite coatings. These coatings may be

used as thermal barriers or to give anti-corrosion protection for the metal substrate.

(2) In order to prepare a stable suspension and fabricate a compact green form, it is important to select a suitable suspension medium for the powders used. Solvents in suspensions function as a medium to suspend and disperse the ceramic and metal particles. Mixed organic solvents were used here to make colloidally stable suspensions containing PSZ and Al particles. The results show that well-dispersed particles are necessary to produce densely packed green deposits. Green forms, which are uniform in thickness and of good quality, were obtained in a suspension using a mixture of ethanol and acetylacetone. The selection of organic solvents and the ball milling process control the density of green ceramic composite coatings produced by EPD. Further study of the relationships between the selection of suspension medium and the stability of the suspension, the stability of the suspension and the density of the green form, the density of the green form and the microstructure of sintered coating is required. This should allow the EPD conditions to be controlled to tailor the microstructure of the final sintered coating to the application.

(3) The addition of Al to the green form composites not only leads to the formation of crack-free composite coatings, but also promotes sintering of ceramic coatings at relatively low temperatures. The oxidation of the Al powder in the green form is affected by the thermal processing profile. It is important to choose suitable oxidation and sintering temperatures to optimise the density of coatings produced by this method.

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