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# Fabrication of composite coatings using a combination of electrochemical methods and reaction bonding process

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**Abstract**

The major difficulty in fabricating ceramic coatings on metal substrates using the electrophoretic deposition process (EPD) is problems caused by the volume shrinkage during the sintering of the green form ceramic coatings produced by EPD. Numerous cracks normally form in the EPD coating during sintering. In this work, we have developed the reaction bonding process to fabricate crack-free and dense ceramic coatings, where the volume shrinkage is compensated by the volume expansion due to the oxidation of aluminium in the green form coatings during sintering in air. Both EPD and electroplating were used here to produce green form coatings which contain aluminium particles and, in some cases, an intermediate nickel layer. During the subsequent heat treatment, melting and oxidation of the metals in the green form coating promote densification during sintering. By these means, relatively dense composite coatings have been fabricated on metal substrates. 

*Keywords:* $Al_2O_3$,$ZrO_2$; Composites; Electrophoretic deposition; Reaction bonding; Sintering

## 1. Introduction

Ceramic coatings are currently of much interest for applications in high-temperature and highly corrosive environments. Formation of ceramic coatings by electrochemical means 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 (ELD), 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. First, 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 overcome 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. The RBAO process can be modified in various ways by incorporating metal and ceramic additives to change the

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final composite composition, to accelerate the reaction, to further compensate for the sintering shrinkage, etc.[8,9] Moreover, the fine particle size of $Al_2O_3$ formed by oxidation could lead to a lower sintering temperature, compared with that for conventional processing of $Al_2O_3$.

In this work, the EPD process or sequential ELD and EPD processes were developed to deposit green form yttria stablised zirconia (YSZ)/Al composites, Ni + Al/YSZ composites or Ni + Al/SiC composites. The green form composites were firstly oxidised and then sintered in air at high temperature. Experimental results show that the addition of Al to the green form composites not only leads to the formation of crack-free composites coatings, but also promotes sintering of ceramic coatings at relatively low temperatures.

## 2. Experimental procedure

In this study, EPD was carried out under electric field between a platinum counter electrode (anode) and a substrate (cathode), distance between electrodes 15 mm, in a liquid solvent which contained a suspension of powder(s) of the material(s) to be deposited. EPD was carried out at room temperature using applied voltages in the range of 5–50 V and deposition times of 1–5 min. The substrate was a commercial Fecralloy foil (Fe-Cr-Al) (Goodfellow Cambridge Ltd. UK). Various ceramic and metal powders which include yttria-stabilised zirconia (8% Yttria) (YSZ, $<1$ μm) (PI-KEM K), aluminium (~1 μm) (Riedel-deHaen Germany) and silicon carbide (~1 μm) (PI-KEM UK) were used to produce stable suspensions in suitable solvents. YSZ and Al/YSZ powder suspensions were prepared by magnetic stirring of the mixture of ceramic and metal powders in a mixture of 60 vol% ethanol and 40 vol% water, with the pH controlled at approximately 3.5 by the addition of ethanoic acid. SiC powder was ball-milled for 24 h, to reduce the average particle size, before mixing with Al powder suspension in ethanol. All suspensions used here had powder concentrations in the range 30–100 g $l^{-1}$.

ELD of nickel was carried out at room temperature in a Watts-type electrolytic bath containing 300 g $l^{-1}$ nickel sulphate, 40 g $l^{-1}$ nickel chloride and 40 g $l^{-1}$ boric acid (Aldrich Chemical Co. UK) with the pH adjusted to 4.0 by the addition of sulphuric acid. ELD of nickel was carried out using a current density of 25 mA $cm^{-2}$ between the platinum anode and substrate cathode. The deposition time was 15 min.

After deposition the coatings were dried at room temperature prior to heat treatment. Oxidation and sintering were carried out at high temperature in air. The phases present in the sintered coatings were determined using X-ray powder diffraction (XRD) (Philips PW1050 X-ray Diffractometer, Cu$K_\alpha$ radiation). The microstructures of coatings were examined using optical microscopy, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) (Jeol JXA840 Microprobe).

## 3. Results and discussion

### 3.1. Fabrication of $YSZ/Al_2O_3$ Composite Coatings

The green form Al/YSZ composite coating was electrophoretically deposited on a Fecralloy substrate from a suspension containing 60 g $l^{-1}$ YSZ and 30 g $l^{-1}$ Al powders using an applied voltage of 10 V for 1 min. The specimen with the green form composite coating was placed in a tube furnace in air and heated at a rate of 3°C $min^{-1}$ to 660°C and held at this temperature for 60 min to allow oxidation of Al to occur. The temperature was then increased at 3°C $min^{-1}$ to 1300°C and held for 60 min in air for sintering. Fig. 1 shows the cross-section of the sintered coating. By EDS analysis the dark phase was identified as $Al_2O_3$ and white phase was identified as YSZ. A thin alumina layer was formed between the coating and the metal substrate, which is probably due to the oxidation of the metal substrate. X-ray diffraction analysis confirms the presence of α-$Al_2O_3$ and cubic or tetragonal YSZ [Fig. 2(A)]. The irregular shape of the alumina particles suggests that alumina may have been formed by the oxidation of liquid aluminium. Some porosity exists in the coating, however no crack was found on examination of the surface morphology of the coating [Fig. 3(a)]. Fig. 3(b) shows an optical micrograph of polished surface of a YSZ coating, prepared by EPD of a YSZ suspension containing 60 g $l^{-1}$ YSZ powder using a voltage of 10 V for 1 min and then sintering of the YSZ green form coating at 1200°C in air for 60 min. Numerous cracks were formed in the coat-

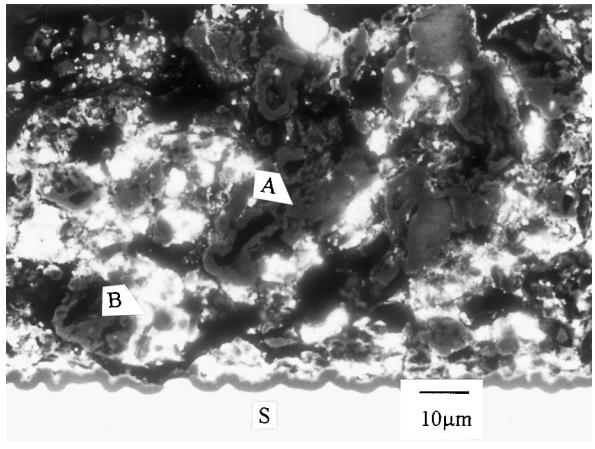


Fig. 1. SEM micrograph of a cross-section of Al/YSZ composite coating after heating at 660°C for 60 min and sintering at 1300°C for 60 min in air. A: $Al_2O_3$; B: $ZrO_2$; S: substrate.

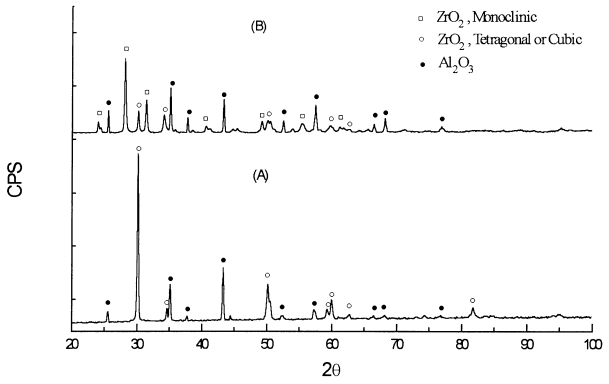


Fig. 2. X-ray diffraction pattern of Al/YSZ composite coating after heating at 660°C for 60 min and sintering at 1300°C (A) or 1500°C (B) for 60 min in air.

ing because of the shrinkage of the coating during sintering. It is apparent that the addition of Al to the green form coating enhanced the densification process due to the presence of liquid aluminium and compensated for volume shrinkage due to the volume expansion associated with the $Al \rightarrow Al_2O_3$ reaction. It should be noted that the oxidation of aluminium normally takes place below a temperature of 1000°C when no sintering occurs. The newly formed $Al_2O_3$ from oxidation can fill in the voids in the green form composites.

The high porosity in the coating is due mainly to the incomplete densification of the coating, since it was sintered at a relatively low temperature. Higher sintering temperatures are required to increase the final density of the coatings. Fig. 4 shows the cross-section of an Al/YSZ composite coating deposited from the same EPD cell using the same deposition conditions for fabricating the coating shown in Fig. 1, but heated to 660°C for 60 min and then sintered at 1500°C for 60 min in air. Although the sintering temperature (1500°C) is slightly higher than the substrate melting point (1480–1490°C), the alloy substrate was well protected by the composite coating without deformation during sintering. There was no diffusion of ceramic particles into the alloy substrate. In comparison with the specimen sintered at 1300°C (Fig. 1), the density of the coating is higher and less alumina is present in the coating [Fig. 4(a)]. However, the alumina layer between the metal substrate and the coating is much thicker than that in the specimen sintered at 1300°C. This suggests that some of liquid aluminium was transported to the coating/substrate interface and was oxidised to form alumina. There is some zirconia present in the alumina layer [Fig. 4(b)], which indicated the alumina particles from oxidation were sintered together with some YSZ particles to form a thick alumina layer containing YSZ at the interface. The alumina layer is denser than the zirconia matrix coating. There is no evidence of crack formation in the composite coating. XRD analysis shows that at least three phases are present in the coating, $\alpha$-$Al_2O_3$, cubic or/and tetragonal zirconia, and monoclinic zirconia [Fig. 2(b)]. It appears that increasing the sintering temperature to 1500°C had the effect of promoting the tetragonal-monoclinic transformation in the zirconia phase. This is probably due to the increase of sintering temperature causing significant grain growth of the individual tetragonal zirconia particles which would enhance the spontaneous transformation to monoclinic zirconia during cooling to room temperature after sintering.[10]

### 3.2. Fabrication of composite coatings at low temperature

We have developed a novel technique of combination of ELD and EPD to produce metal/ceramic composite coatings where lower sintering temperatures are required.[5] Here the ELD of Ni and subsequent EPD of YSZ/Al green composites were carried out to promote chemical reaction between nickel and aluminium which could enhance sintering at a relatively low temperature. A layer of pure Ni was electroplated onto a Fecralloy substrate in a Watts-type bath, using a current density

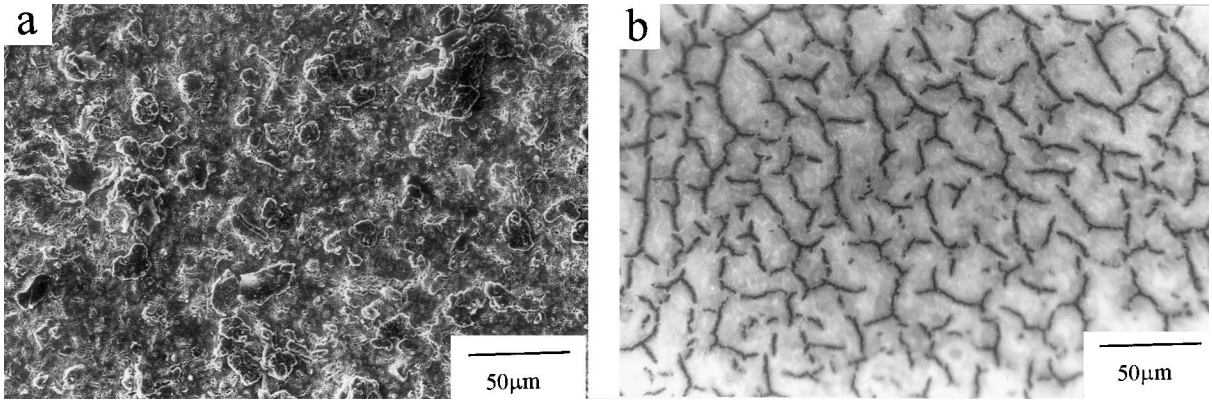


Fig. 3. Optical micrographs of surface morphology of (a) electrophoretic deposited Al/YSZ composite coating after heating at 660°C for 60 min then sintering at 1300°C for 60 min and (b) YSZ coating after sintering at 1200°C for 60 min.

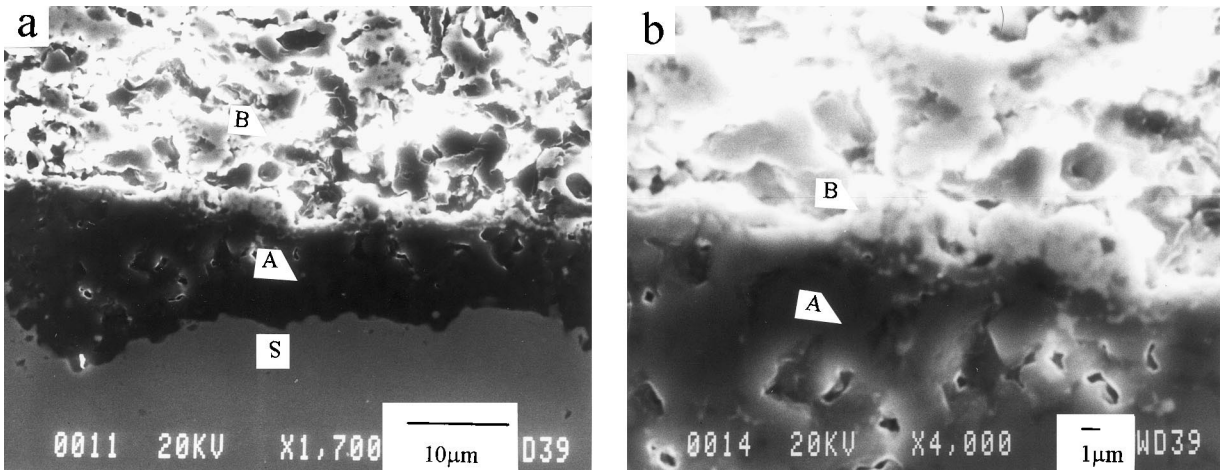


Fig. 4. (a) and (b) SEM micrographs of a cross-section of Al/YSZ composite coating after heating at 660°C for 60 min and sintering at 1500°C for 60 min in air. A: $Al_2O_3$; B: $ZrO_2$; S: substrate.

of 25 mA $cm^{-2}$ for 15 min. The Ni coated substrate was then placed in the EPD cell containing 60 g $l^{-1}$ YSZ and 30 g $l^{-1}$ Al powders in suspension. A composite Al/YSZ coating was deposited using an applied voltage of 10 V for 1 min. The specimen was heated to the melting temperature of Al (660°C) for 60 min in air and then sintered at 1350°C for 120 min in air. Fig. 5 is a SEM micrograph of a cross-section of the sintered specimen showing a multi-layer, dense composite film. The composite coating contains α-$Al_2O_3$ (A: black), $NiAl_2O_4$ (B: grey) and YSZ, tetragonal or cubic (C: white) (Figs. 5 and 6). This coating has a higher density than that sintered without the presence of the Ni layer, which was shown in Fig. 1. There are three layers formed at the interface between the composite coating and the metal substrate. The thin black layer beside the metal substrate is a layer of $Al_2O_3$ produced from the oxidation of the metal substrate. The white layer beside the composite coating is YSZ. The grey layer between the white and the black layers is $NiAl_2O_4$. It is assumed that both $NiAl_2O_4$ and $Al_2O_3$ layers are formed from oxidation of the deposited nickel and aluminium from the composite coating and the substrate alloy. However, it is difficult to explain the mechanism for formation of a layer of YSZ above the $NiAl_2O_4$ layer. Apparently the presence of Ni layer promotes the sintering of the composite coating, but further study is needed to determine the exact function of Ni in the sintering process.

A Ni coated substrate was placed in the EPD cell containing 50 g $l^{-1}$ SiC and 30 g $l^{-1}$ Al powders in suspension to deposit a composite Al/SiC coating using an applied voltage of 30 V for 1 min. The specimen was then heated and sintered under the same conditions as that for the Ni/Al/YSZ composite coating. Fig. 7 is a SEM micrograph of a cross-section of the sintered specimen showing a multi-layer, dense composite film. Five phases, $Al_2O_3$, $NiAl_2O_4$, NiO, SiC and $SiO_2$ were present according to analysis of the XRD spectrum of the composite coating (Fig. 8). The EDS analysis of the coating indicates that the inner thin dark layer adjacent

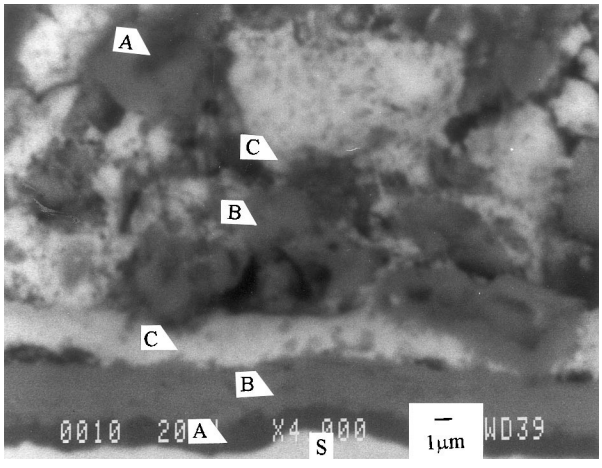


Fig. 5. SEM micrograph of a cross-section of Ni/Al/YSZ composite coating deposited by sequential ELD then EPD onto a Fecralloy substrate, after heating to 660°C for 60 min and sintering at 1350°C for 120 min. A: $Al_2O_3$; B: $NiAl_2O_4$; C: $ZrO_2$; S: substrate.

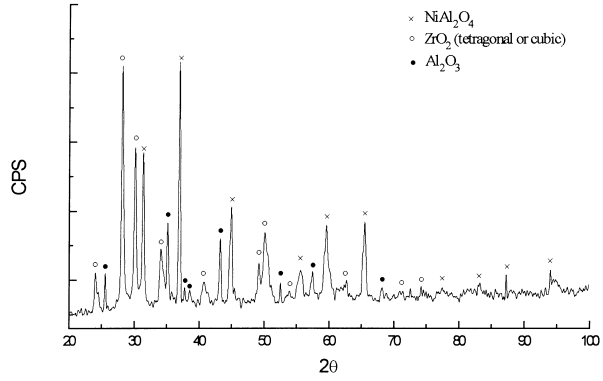


Fig. 6. X-ray diffraction pattern of Ni/Al/YSZ composite coating after heating at 660°C for 60 min and sintering at 1350°C 120 min in air.

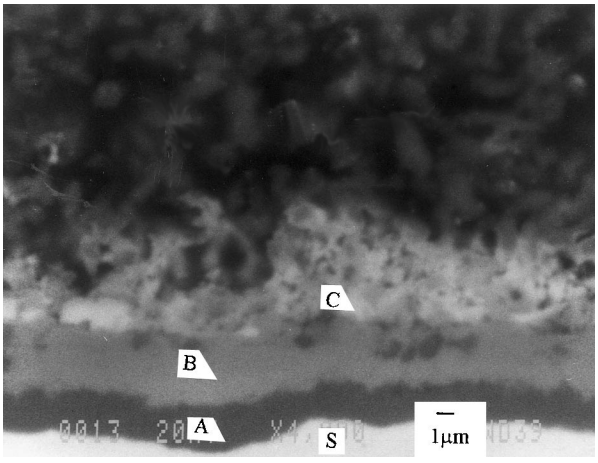


Fig. 7. SEM micrograph of a cross-section of Ni/Al/SiC composite coating deposited by sequential ELD then EPD onto a Fecralloy substrate, after heating to 660°C for 60 min and sintering at 1350°C for 120 min. A: $Al_2O_3$; B: $NiAl_2O_4$; C: NiO; D: SiC; E: $SiO_2$; S: substrate.

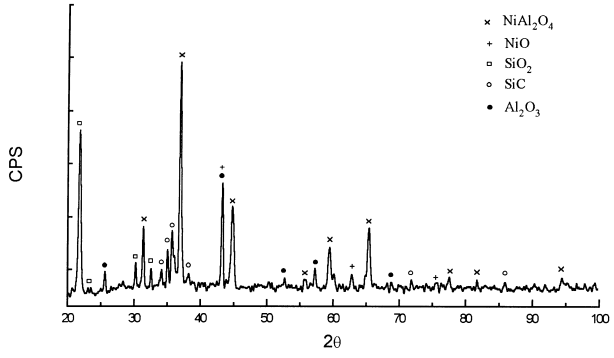


Fig. 8. X-ray diffraction pattern of Ni/Al/SiC composite coating after heating at 660°C for 60 min and sintering at 1350°C 120 min in air.

to the substrate (A) is $Al_2O_3$, the lighter grey region of interlayer (B) is $NiAl_2O_4$, and the white phase (C) beside the $NiAl_2O_4$ is NiO. The coating above the NiO layer is the mixture of SiC (D: black) and $SiO_2$ (E: grey). There is little alumina present in the mixture of SiC and $SiO_2$. Therefore, during heat treatment, liquid aluminium was transported to the surface of the nickel layer and reacted with nickel and oxygen to form nickel aluminate. The excess nickel there was oxidised into nickel oxide. Oxidation of SiC begins at temperatures $>820$°C and the oxidation of the SiC particles occurs only on their surfaces.[9] The $SiO_2$ layer surrounding the SiC particles grows with increasing temperature. The oxidation reaction of SiC in a compact is normally suppressed at temperatures above 1300°C.[9] This is attributed to the fast densification in this temperature region with corresponding increased density and reduced pore size. However, the presence of liquid aluminium in the SiC/Al composite coating may promote the oxidation of SiC. Again, the volume expansion associated with the oxidation of Al, Ni and SiC compensated for the volume shrinkage during sintering so that a dense and fracture-free composite coating was obtained.

## 4. Conclusions

Reaction-bonded ceramic coatings on metal alloy substrates have been prepared by EPD or sequential ELD and EPD, followed by oxidation and sintering processes. By controlling the composition of the ceramic or metal suspension, the deposition and sintering conditions, we have obtained a well adhered, relatively dense, crack-free ceramic coating on a metal substrate. The sintering process can be enhanced by the application of a reactive metal layer which allows the use of a lower sintering temperature and results in an increased sintered density of the composite coatings.

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