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Characterisation of ceramic coatings sintering using residual stress measurements

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Abstract

Yttria stabilised zirconia (YSZ) containing a few per cent of aluminium was deposited on metal substrates by using electrophoretic deposition (EPD). After sintering at 1150–1300 °C, YSZ matrix coatings containing isolated Al_2O_3 particles were produced on metal substrates. The constraint applied by metal substrates affected the sintering of the coatings. To characterise sinterability of the YSZ/Al_2O_3 composite coatings, the residual stress applied to the Al_2O_3, termed as micro-stress here, has been measured using Cr^{3+} fluorescence spectroscopy after the removal of metal substrates. It was found that the residual stresses increased with the increase in sintering temperature and attrition milling time. The relation between the density of the coatings and the micro-stresses can be expressed by a simple analytical equation. In addition, residual stress measurements in the coatings with the addition of cordierite glass as sintering aid further proves that the residual stress can be used to show the degree of sintering. Therefore Cr^{3+} fluorescence spectroscopy is a very useful technique in characterising the sintering of the YSZ/Al_2O_3 composite coatings.
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Keywords: Coatings; Fluorescence spectroscopy; Residual stress; Sintering; YSZ/Al_2O_3

1. Introduction

Application of ceramic coatings to metallic substrates is highly desirable in many industry applications. Electrophoretic deposition (EPD) is a simple and cheap processing technique for the fabrication of green ceramic coatings. To obtain ceramic coatings, the green coatings need to be sintered at relatively low temperature. Unlike a free standing ceramic compact whose sintering is determined by the properties of the green compact, the sintering behaviour of ceramic coatings on metal substrates is dependent not only on the green coating, but also on how the coating responds to the substrate constraint due to the adhesion of ceramic coatings to metal substrates. In-plane tensile stress results from constrained sintering, which would change the densification rate, causing non-uniform shrinkage, delamination and cracks.[1–3] Therefore the stresses arising either during sintering or on cooling from sintering temperature are an important issue regarding the sintering, defects formation and subsequent damage of the coatings. In order to investigate the sintering behaviour of ceramic coatings, an effective technique to measure sintering behaviour, for example, measuring the density of coatings, is essential. However, most of direct observations on sintering of coating have been based on an optical system that can be only used to detect the changes in coating thickness and curvature.[4–6]

YSZ/Al_2O_3 composite coatings have been produced by using electrophoretic deposition and low temperature sintering.[7,8] In this work, the YSZ/Al green coatings were prepared using EPD method and then the green coatings were sintered at 1150–1300 °C. During sintering, Al is oxidised into Al_2O_3 which is embedded in a matrix of YSZ. Due to the thermal mismatch between dispersing phase, Al_2O_3 and matrix, YSZ, residual stresses acting on Al_2O_3 particles arise when the sintered specimen was cooled from sintering temperature. The residual micro-stresses can be conveniently detected using Cr^{3+} fluorescence spectroscopy, as the impurity Cr^{3+} in Al_2O_3 can emit characteristic fluorescence peaks by laser stimulation. The technique of the stress measurement using Cr^{3+} fluorescence spectroscopy has been well established and extensively used.[9,10] The stress is linearly proportional to the peak shift in fluorescence spectra. The dependence of the wavenumber shift ($\Delta\nu'$) of the *R* lines upon stress for a

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polycrystalline material without preferred orientation can be written as:[11]

$$\Delta\nu_{R1} = 7.59 \times \frac{(\sigma_{11} + \sigma_{22} + \sigma_{33})}{3}$$
$$\Delta\nu_{R2} = 7.61 \times \frac{(\sigma_{11} + \sigma_{22} + \sigma_{33})}{3} \quad (1)$$

where $\Delta\nu$ is the wavenumber shift and σ_{11},σ_{22} and σ_{33} are stresses along three different crystallographic directions in α-Al_2O_3 lattice, respectively. The units for stress (σ) and wavenumber shift ($\Delta\nu$) are GPa and cm^{-1}, respectively.[6]

It is proved in this paper that the residual micro-stresses are dependent on matrix density of a partially sintered composite. A quantitative relation is established to relate the coating density to micro-stress acting on dispersing Al_2O_3 particles. By measuring the residual stresses in the coatings prepared using different processing variables, it was found that Cr^{3+} fluorescence spectroscopy is a useful technique in characterisation of the sintering of the YSZ/Al_2O_3 coatings.

2. Experimental procedure

2.1. Sample preparation

Powder coatings were prepared using EPD method from suspensions. Suspensions were made by mixing solid powders (YSZ powder: HSY-8, Daiichi Kigenso Kagaku Kogyo, Japan; Al powder: <6 μm, Alpoco, UK) with solvent (acetylacetone, 2,4-Pentanedione, Aldrich, UK) and followed by attrition milling (01-HD, Union Process) for different times.

Two types of suspensions were prepared from the compositions shown in Table 1. Cordierite glass was added in order to examine whether the addition of the glass phase would enhance the sintering of the ceramic coating. The cordierite glass was made from melting of the cordierite powder (Hi-Por Ceramic Ltd, UK) at 1500 °C, followed by quenching from molten state to room temperature. The composition of the cordierite is 33.9–36.9% Al_2O_3, 12.5–14.5% MgO and 48.2–51.2% SiO_2. The cordierite glass powder of ~1 μm size was made by crushing, grounding and attrition-milling.

The suspension was made with composition of 2 g solid/100 ml-acetylacetone and then sonicated in an ultrasonic bath for 5 min before EPD. Fecralloy plates in the size of 20 mm×10 mm×1 mm (thick) was polished using grit 800 paper and rinsed using acetone. During EPD process, a magnetic stirrer kept stirring in order to maintain a uniform concentration in suspension. By applying an electrical field of 80 V/cm and using a deposition time of 1 min, powder coatings with a thickness of about 200 μm were prepared. Ceramic coatings adhering to Fecralloy substrate were obtained by sintering the powder coatings in a chamber furnace at 1150–1300 °C for 2 h.

For the purpose of comparison, bulk ceramic samples also were made from those suspensions. Dry powders were obtained by drying the suspensions at a temperature about 150 °C. Pellets in the size of ~ϕ13 mm in diameter and 5mm in thickness were prepared by uniaxial pressing at 100 MPa. Sintered pellets were obtained by firing those green powder compacts at 1150–1300 °C for 2 h.

In order to measure the residual micro-stresses without stress applied by the metal substrate, the metal substrate was removed by placing samples into hot hydrogen chloride acid (~150 °C), where the metal dissolved into acid. We term the coating after removal of metal substrate as the free-standing coating, while the coating with substrates as supported coating.

Table 1
The chemical compositions of the suspensions.

Suspension	YSZ (wt.%)	Al (wt.%)	Cordierite glass (CG) (wt.%)
YSZ/Al	95	5	–
YSZ/Al/CG	92	5	3

2.2. Micro-stress measurements

The instrumentation for Cr^{3+} fluorescence measurements consisted of a modified optical microscope, a laser system (He–Ne, 632.8 nm in wavelength, 15 mW in power), a double spectrometer (Glen Creston) and a charge coupled device camera (CCD, Wright instruments, Peltier cooled). A PC computer is used to collect data, but no computer control at gratings. Measurements were made using a ×50 objective lens at room temperature on the top surfaces of free-standing coatings and supported coatings. A collecting time of 0.1 s was used for all the measurements. The *R*-line spectra recorded were subsequently analysed using the commercial Renishaw WiRe software to obtain the peak shift data. The reference sample was a gently cold-pressed α-Al_2O_3 powder pellet that was pressed using a pressure of 30 MPa. Apart from the stress state in the materials, other factors such as temperature, beam focusing and the length of lens, etc. can also affect the peak shifting of fluorescence. During the measurements, efforts were made to keep all conditions as similar as possible. Reference sample was regularly measured to eliminate the influence of the unnoticed variations in measurement conditions. Each experimental value was an average of at least 20 experimental data. Our experiments confirmed that the peak shift obtained in comparison with the reference sample is highly repeatable in our experimental conditions.

3. Results and discussion

3.1. Fluorescence spectra and residual stresses

The typical fluorescence spectra for supported coatings, free-standing coatings and the reference sample are shown in Fig. 1. Both free-standing coatings and supported coatings show a left-shift as compared to the reference spectrum. However the supported coatings produced spectra with larger peak shifts than that by the free-standing coatings (Fig. 1). This implies that the Al_2O_3 particles are under a higher compressive stress in the supported coatings. Meanwhile supported coatings normally showed broader spectrum peaks. The peak widths (FWHM, the full width at half maximum) of supported coatings were 1–2 cm^{-1} broader than those of free-standing coatings. Since stress gradient can induce peak broadening,[12] the broader peaks may imply a higher degree of stress gradient in the supported coatings.

The Al_2O_3 particles in the YSZ/Al_2O_3 composite coating are under residual stresses from two different origins: one due to the difference in the coefficients of thermal expansion (CTE) between Al_2O_3 and matrix YSZ, another due to the CTE difference between the metal substrate and YSZ/Al_2O_3 composite coating (Fig. 2). Both stresses arise on cooling from the sintering temperature and both stresses are compressive, because the CTE of Al_2O_3 is smaller than that of matrix YSZ and the substrate. The residual stresses caused by the mismatch between Al_2O_3 particles and matrix YSZ exist locally around individual Al_2O_3 particles. So they are called micro-stresses. The stresses caused by the thermal mismatch between the substrate and top ceramic coating are present along the direction parallel to the metal/coating interface and present across the coating, so they can be called macro-stress. The stresses measured on freestanding coatings are micro-stresses and those on supported coatings are a superimposition of micro-stresses and macro-stresses. Therefore the difference in peak shift between a supported coating and its corresponding free-standing coating represents the residual macro-stress.

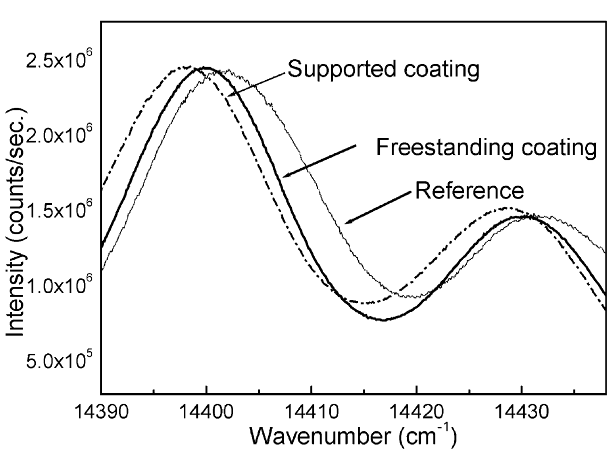

Fig. 1. Typical fluorescence spectra of free-standing and supported coatings, as compared to a reference spectrum; please note the intensities of spectra have been adjusted for the convenience of comparison.

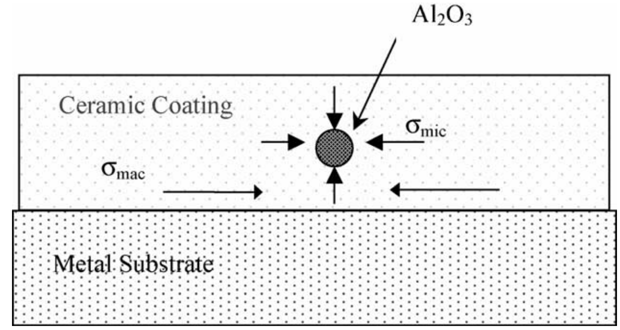

Fig. 2. Schematic of the residual stresses of an Al_2O_3 particle in the composite coating.

The micro-stresses were treated as hydrostatic, and according to Eq. (1), their dependence on peak shift can be written as:

$$\Delta\nu_{R1} = 7.59 \times \sigma$$
$$\Delta\nu_{R2} = 7.61 \times \sigma \tag{2}$$

The macro-stresses are biaxial and in the plane parallel to the interface, and according to Eq. (1), their dependence on peak shift can be written as:

$$\Delta\nu_{R1} = 5.060 \times \sigma$$
$$\Delta\nu_{R2} = 5.073 \times \sigma \tag{3}$$

3.2. Microstress–density relation

The micro-stress for a two-phase composite material with one phase as a dispersing phase another as a matrix phase can be written as:[13,14]

$$\sigma_{\text{mic}} = \frac{(\alpha_i - \alpha_{\text{m}})\Delta T}{\dfrac{2x(1-2\nu_{\text{m}}) + (1+\nu_{\text{m}})}{2E_{\text{m}}(1-x)} + \dfrac{1-2\nu_{\text{i}}}{E_{\text{i}}}} \tag{4}$$

where ν_i and E_i are the Poisson's ratio and Young's modulus of the dispersing phase; ν_m and E_m are the Poisson's ratio and Young's modulus of the matrix phase; α_i and α_m are CTEs of matrix and dispersing phase, respectively; ΔT is the temperature drop from the 'freeze' temperature. The freeze temperature refers to the temperature below which the stresses due to the mismatch CTE cannot be relaxed any more and starts to build up on further cooling.

For the YSZ/Al_2O_3 composite, Eq. (4) can be written as follows with input of the properties of both YSZ and Al_2O_3:[15]

$$\sigma_{mic} = \frac{4 \times 10^{-4} \Delta T \left[1 - \left(1 - \frac{\rho}{\rho_o}\right)^{2/3}\right]^S}{A + 0.299 \left[1 - \left(1 - \frac{\rho}{\rho_o}\right)^{2/3}\right]^S} \tag{5}$$

where

$$A = \frac{2x(1 - 2\nu_m) + (1 + \nu_m)}{2(1 - x)}$$

ρ is the density of a partially densified body and ρ_o the theoretical density.

To verify the Eq. (5), both micro-stresses and densities of the bulk YSZ/Al_2O_3 composites produced by sintering were measured. Composite pellets with different sintered densities were obtained either by using different sintering temperatures or different attrition milling times with experimental conditions shown in Table 2. The experimental data of the densities and stresses, plus fitting using Eq. (5), are shown in Fig. 3. Eq. (5) gives a very good fitting of the experimental data. The parameters 'A' and 's' obtained by fitting are 5.0 and 1.21 for the YSZ/Al_2O_3/CG composite, and 5.3 and 1.21 for YSZ/Al_2O_3 composites, respectively. Therefore Eq. 5 is suitable in describing the interrelation between the density and the micro-stress in a sintered composite material. Micro-stress measurements can be used to evaluate the degree of sintering of the composite materials.

Table 2
The sintering temperature and attrition milling time used to prepare composite pellets with different densities.

Sample[a]	YSZ/Al_2O_3				YSZ/Al_2O_3/CG			
	1	2	3	4	a	b	c	d
Sintering temperature (°C)	1150	1200	1250	1300	1300	1250	1300	1250
Attrition milling time (h)	80	80	80	80	56	56	56	16

[a] Sample denotation corresponds to Fig. 3.

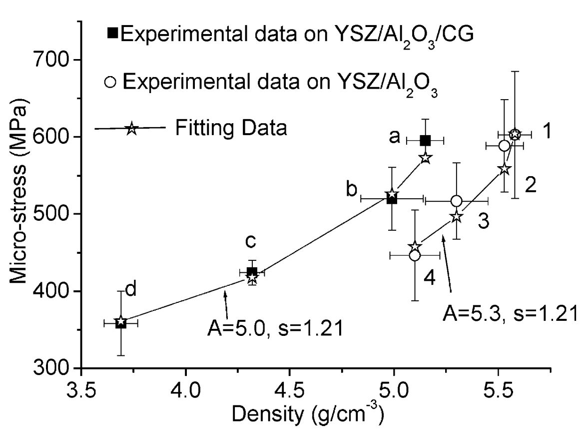

Fig. 3. Dependence of micro-stress on composite density; with error bars along x-axis representing the standard deviations of the densities from five samples prepared using same processing conditions, error bars along y-axis representing the standard deviation of the residual stresses from twenty fluorescence measurements on each sample.

3.3. Residual stresses in fired coatings

Fluorescence measurements were carried out at the surface of both free-standing coating and supported coatings, prepared using different attrition milling time or by sintering at different temperatures. In YSZ/Al_2O_3/CG coatings, cordierite glass was added. The dependence of the peak shift on the sintering temperature is shown in Fig. 4. All of the three coatings showed an increasing peak shift with increase in sintering temperature. The peak shifts measured on supported coatings show a similar trend to those measured on free-standing coatings. This suggests that the macro-stresses are not significantly affected by sintering temperature. The change of stress in the coatings produced with different milling times shows similar trend with the increase in sintering temperature. However, the coating with an addition of cordierite glass shows a different trend in the microstresses–sintering temperature relationship, although the stress also increased with increase in sintering temperature.

The increase in density resulted in an increase in micro-stresses [Fig. 3, Eq. (5)]. The increase in the micro-stresses with the sintering temperature can be attributed to the higher density as a result of a higher sintering temperature. Therefore, the micro-stress level can be an indicator of the degree of the sintering of coatings. The macro-stresses in sintered coatings can be approximated as:

$$\sigma_{mac} = \frac{\Delta\alpha \Delta T E_c}{(1 - \nu_c)} \tag{6}$$

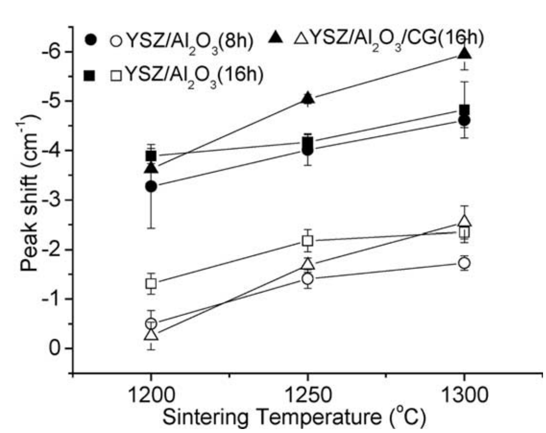

Fig. 4. The dependence of peak shift on the sintering temperature; the solid symbols representing the measurements on supported coatings and the hollow symbols representing the measurements on free-standing coatings, and the attrition milling time being given in the brackets.

where ν_c and E_c are the Poisson's ratio and Young's modulus of the coating; $\Delta\alpha$ is the difference in CTE between the coating and substrate and ΔT the temperature drop from the freeze temperature. The freeze temperature is the temperature from which stress is generated during cooling.

According to Eq. (6), macro-stresses should increase with Young's modulus of the coating, which in turn is supposed to increase as the coating density is increased. However, our experimental results showed that there is no direct dependence of macro-stress on the degree of sintering. Macro-stresses can be released by adhesive failure (delamination at the interface) and cohesive failure (spalling and micro-cracking within coating), and they also can be released by the creep of the metal substrate at high temperature, therefore the dependence of the macro-stresses on material properties is much more complicated than the description of Eq. (6).

The addition of cordierite glass obviously has changed the sintering behaviour of the powder coating. The melting point of the cordierite powder is about 1450 °C according to its specification from the manufacturer. When the temperature approaches nearer to the melting point of the glass, the viscosity would significantly decrease and thereby enhance the densification. For this reason we can see a steeper increase of the residual stresses with an increase in sintering temperature for the coatings with the addition of cordierite glass.

The dependence of residual stresses on attrition milling time is plotted in Figs. 5 and 6 for two different coatings, respectively. It is obvious that the micro-stresses increase with the attrition milling time. In contrast, the macro-stresses seem to follow a decreasing trend with attrition milling time. This might be due to a release of macro-stresses by adhesive or cohesive failure as mentioned earlier. Our visual observation found that increase in attrition milling time tended to result in more cracks and failure of the coating after cooling down from sintering temperature. This indicates that

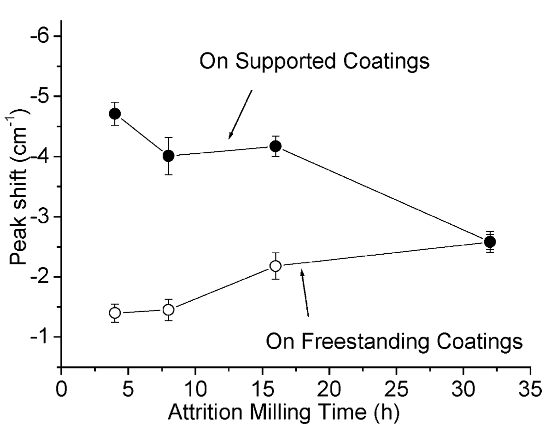

Fig. 5. Dependence of residual stresses of YSZ/Al_2O_3 on attrition milling time, the sintering temperature being 1250 °C.

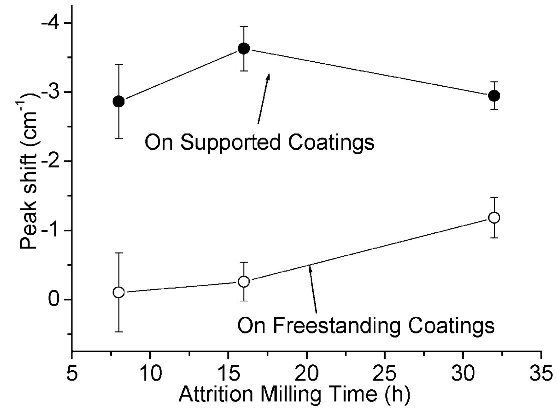

Fig. 6. Dependence of residual stresses of YSZ/Al_2O_3/CG on attrition milling time, the sintering temperature being 1200 °C.

extended attrition milling time may lead to a weak adhesion. The macro-stresses are partially or totally released. However, the reason why adhesion is affected by the attrition milling time is unclear so far. This implies that the residual stress in coatings can also be an indication of the coating failure or coating adhesion, which is very useful in the evaluation of the coating quality after fabrication and service.

Cr^{3+} fluorescence spectroscopy is a technique based on an optical system, with spatial resolution of about 1–2 μm. The fluorescence measurement is quick, simple and most importantly, non-destructive. In combination with other conventional techniques, this technique is capable of providing a lot of useful information that cannot be achieved by using other techniques.

4. Conclusions

The micro-stress acting on a dispersing phase (Al_2O_3) in a partially sintered YSZ/Al_2O_3 composite is dependent on the density of the material. The interrelationship between micro-stress and material's density has been established. The micro-stresses of the sintered YSZ/Al_2O_3 coatings increase with the density of coatings which are controlled by sintering temperature and attrition milling time. The residual stress in the coatings with an addition of cordierite glass show a different dependence on processing variables, indicating the function of the cordierite as sintering aids. The degree of sintering in coatings can be characterised by micro-stress measurements.

The residual stresses measured on supported coatings follow the same trend as those on free-standing coatings. Macro-stresses in coatings depend to a large extent on the mechanical integrity of the coatings. Residual stress measurements on supported coatings may reveal the adhesion status of a coating, as the poor adhesion would result in a release of macro-stresses, which would lead to an undue decrease in the residual stresses.

Therefore residual stress measurements by Cr^{3+} fluorescence spectroscopy are very useful in evaluation of the coating quality after fabrication and service.

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