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Thermal microstress measurements in Al_2O_3/SiC nanocomposites by Cr^{3+} fluorescence microscopy

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Abstract

Alumina/SiC 'nanocomposites' show significant property improvements compared with pure alumina. The improvements are thought to stem at least in part from the microstresses caused by the thermal expansion mismatch between alumina and SiC. These microstresses have been measured previously by neutron and X-Ray diffraction. This paper reports stress measurements using Cr^{3+} fluorescence microscopy of the alumina matrix. The results show that although fluorescence microscopy is less powerful than the diffraction techniques in terms of the range of information provided, it does provide an alternative method of measuring subsurface microstresses in these materials which is quicker, cheaper and higher in spatial resolution.

Keywords: Al_2O_3; Nanocomposites; Spectroscopy; Thermal expansion; Wear resistance

1. Introduction

Ceramic 'nanocomposites' formed by the addition of submicron SiC particles to an alumina matrix exhibit improvements in mechanical properties and greatly improved surface finish and resistance to severe wear conditions relative to unreinforced alumina of the same grain size.[1–7] Several mechanisms have been proposed to explain these improvements and though none has yet gained widespread acceptance, a common feature of most is that they rely in some way on the thermal microstresses which develop during cooling from processing temperatures owing to the thermal expansion mismatch between the alumina matrix and the SiC particles. It is therefore important to characterise and understand these stresses.

Measurements have been made previously using X-Ray diffraction[8] and neutron diffraction[9] and the results of these studies have provided detailed information about the microstresses in a small range of alumina/SiC nanocomposites. Although these diffraction techniques are very powerful, being able to distinguish between different phases and spatial and crystallographic directions, they also have some disadvantages which make them undesirable for the characterisation of a wider range of microstructures. The X-Ray diffraction technique is slow and the measurements can be affected by surface relaxation of the stresses. Neutron diffraction measures stresses deep in the bulk of the material but is also slow and is very expensive. Both techniques have poor spatial resolution relative to the scale of the microstructure.

Cr^{3+} fluorescence microprobe microscopy of alumina has been widely applied in recent years[10–13] and provides an alternative to these diffraction methods. Its chief advantages are that routine measurements can be made quickly and cheaply with a spatial resolution of $\sim$10 μm or better. Its disadvantages for this purpose are that it provides less detailed information than the diffraction techniques, and its ability to make subsurface measurements is also limited by the opacity of the sample. It has recently been shown, however, that essentially bulk measurements of thermal stresses in alumina particle reinforced glass can be obtained by focusing the laser spot on regions of the glass matrix between particles that intersect the surface.[13] The laser light used to excite the fluorescent radiation can then penetrate the glass matrix into the bulk of the material and the spectrum obtained comes mainly from alumina particles in the bulk of the material. It seems likely that effectively

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bulk measurements of the thermal microstresses in alumina/SiC nanocomposites can also be made in this way. The interaction volume of the laser light extends to ~10 μm below the surface with a typical experimental configuration. Since the depth to which significant surface relaxation of the thermal stresses occurs is of the order of the interparticle spacing (<1 μm) in the nanocomposites, much of the signal comes from matrix which is effectively in the bulk of the material. The aim of this short paper is to describe such measurements of the thermal stresses in alumina/SiC nanocomposites with various SiC volume fractions and to show that these compare favourably with results from previous diffraction measurements on similar materials.

2. Experimental

2.1. Material and specimen preparation

Alumina/SiC nanocomposites containing 2, 5 and 10 vol.% SiC were made by hot pressing mixed commercial powders (alumina: 200 nm, AKP50, Sumitomo, Japan, α-SiC: 200 nm, UF45, Lonza, Germany). The SiC was predispersed in distilled water for 20 min using an ultrasonic probe and attrition milled with the alumina in distilled water containing a dispersant (Dispex A40, Allied Colloids, UK). 0.25 wt.% MgO was added to the 2% SiC mixture to prevent abnormal grain growth. The mixed powders were freeze dried and hot pressed at 25 MPa in a graphite die under argon. A pure alumina specimen was also produced to act as a reference specimen. The hot pressing temperatures were chosen to give materials of similar grain size. Specimens were prepared for SEM examination by thermally etching polished surfaces at 1450–1500 °C in vacuum. TEM specimens were made by first excising 3 mm discs from 150 μm thick slices from the material. The discs were dimpled and then ion beam milled to perforation.

2.2. Cr^{3+} fluorescence measurements

The spectroscopic measurements were conducted using a Raman microscope (System 1000, Renishaw, UK) equipped with a He–Ne laser and filters to reduce the incident intensity. Preliminary experiments varying the incident intensity indicated that the effect of specimen heating was negligible with the filter setting used. A ×50/0.75 lens was used and the spot size focused at the specimen surface was ~2 μm in diameter. The confocal slit on the instrument was set to 10 μm and a strip of breadth 70 pixels was used to sample the spectrum with the CCD camera. Through focus intensity measurements on polished sapphire single crystals as described by Ma and Clarke[11] indicated that 50% of the signal came from within 30 μm of the surface with this experimental setup. This depth will have been reduced in the nanocomposites owing to their higher opacity.

Spectra were obtained from one fracture surface of each composition with an exposure time of 0.2 s per measurement. At least 25 measurements of peak position from different points were made on each sample. The alumina R_2 peak position (frequency, $\nu \approx 14\,434\ \mathrm{cm}^{-1}$) was determined by fitting the experimental spectra with mixtures of Lorentzian and Gaussian functions using commercial software (Grams/32, Galactic Industries, USA).

The difference in R_2 peak position, $\Delta\upsilon$, between spectra obtained from the nanocomposite and the pure alumina is caused by the thermal residual stresses in the nanocomposite. In order to convert this to a stress, the form of the stress state has to be known. Detailed neutron diffraction measurements of the thermal stresses in alumina/SiC nanocomposites[9] have shown that although some anisotropy is present in the form of crystallographic texture, alignment of elongated particles and thermoelastic anisotropy, its effect on the stresses is relatively small. Calculation of the volume averaged principal stresses for alumina grains orientated perpendicular and parallel to the hot pressing direction from the elastic strains measured by Todd et al[9] shows that all principal stresses were within 11% of the mean stress for the range of compositions used here, indicating that the volume averaged stress state was close to being hydrostatic. The stress state in the present nanocomposites was therefore assumed to be hydrostatic, which gives the following relationship between the hydrostatic stress in the matrix, σ_m, and $\Delta\upsilon$:[10]

$$\sigma_m = \frac{\Delta\upsilon}{2\Pi_a + \Pi_c}$$

where Π_a and Π_c are the piezospectroscopic coefficients relating frequency shifts to stress parallel and perpendicular to the basal plane respectively. The values used for the piezospectroscopic coefficients were $\Pi_a = 2.8\ \mathrm{cm}^{-1}\ \mathrm{GPa}^{-1}$ and $\Pi_c = 2.1\ \mathrm{cm}^{-1}\ \mathrm{GPa}^{-1}$.[14]

The mean stress in the particles, σ_p, can then be deduced from the internal stress equilibrium condition as:

$$\sigma_p = \frac{-(1-f)\sigma_m}{f}$$

where f is the volume fraction of SiC.

3. Results and discussion

The materials produced are summarised in Table 1, and Fig. 1 shows the microstructure of the 5 vol.% SiC nanocomposite, whose microstructural features are

Table 1
Materials used and fluorescence microscopy results. Figures in brackets represent the standard deviation of the measurements for the R_2 peak position and shift, and the standard deviation of the mean for the stresses

SiC (vol%)	Alumina grain size (μm)	R_2 peak position (ν cm^{-1})	R_2 shift (Δν cm^{-1})	σ_m (MPa)	σ_p (MPa)
0	2.5	14 434.123 (0.079)	–	–	–
2	3.0	14 434.401 (0.035)	0.278 (0.086)	36 (2.2)	−1 769 (109)
5	2.7	14 434.778 (0.045)	0.655 (0.091)	85 (2.4)	−1 616 (45)
10	2.0	14 435.433 (0.057)	1.310 (0.097)	170 (2.5)	−1 531 (23)

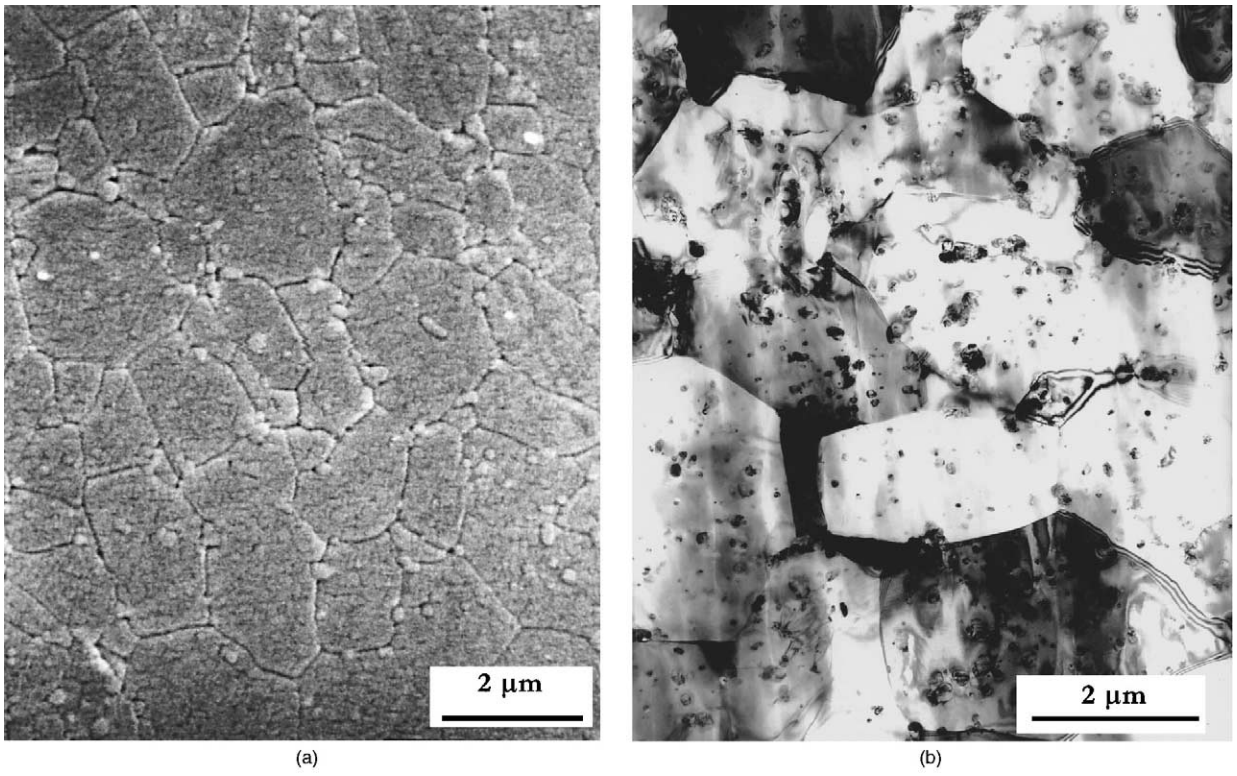

Fig. 1. (a) SEM and (b) TEM micrographs of the 5 vol.% SiC nanocomposite.

representative of all three nanocomposites. All grain sizes were in the range 2–3 μm, and all densities were at least 99.4% of theoretical. The materials were almost completely free from abnormal grain growth and SiC agglomerates. The SiC particles were uniformly distributed, with some on the alumina grain boundaries and others within the grains.

Table 1 also shows a summary of the fluorescence results. The hydrostatic stresses in the matrix were tensile, as expected from the sense of the thermal expansion mismatch, and increased with SiC content from 36 MPa for 2% SiC to 170 MPa for 10% SiC. The corresponding compressive stress in the SiC decreased from −1770 to −1530 MPa over the same range of compositions.

The stress results are compared with the neutron diffraction measurements of Todd et al.[9] and the X-ray diffraction measurements of Levin et al.[8] in Fig. 2. The predictions of the spherical particle/spherical shell model used in reference[9] are also plotted assuming a relaxation-free temperature reduction, ΔT, of 1300 °C and the elastic constants used in reference[9]. This value for ΔT has been chosen to give good agreement with the neutron diffraction measurements. Note that whilst the particle stresses in this work were inferred from measurements on the matrix, the diffraction measurements for the matrix and particles were made independently.

The present results show the trends as a function of volume fraction predicted by the elastic model and are close to the values from the diffraction studies. Nevertheless, the fluorescence stress measurements are systematically smaller in magnitude by ∼15% than the diffraction measurements. One reason for this is that some of the fluorescent radiation sampled comes from regions of matrix close to the surface compared with the interparticle spacing, where some of the thermal stress will have been relaxed. This must also apply to some extent to the XRD measurements of Levin et al.,[8] however, so it is likely that other systematic uncertainties such as the

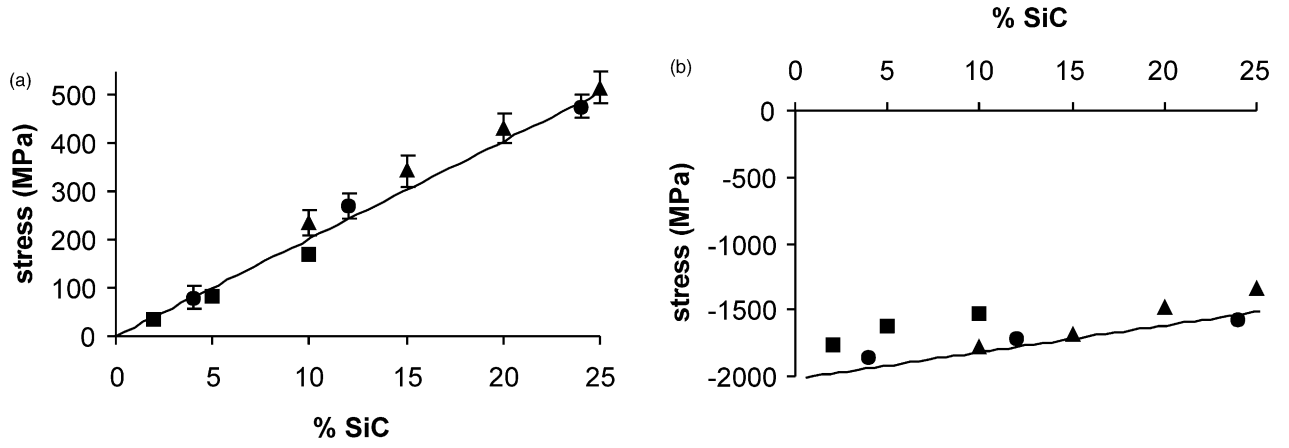

Fig. 2. Hydrostatic stresses in (a) matrix and (b) particles as a function of SiC content. Error bars have been omitted when smaller than symbols. ■ present work, ▲ Levin et al. ,[8]. Todd et al.,[9] —model.

values of the piezospectroscopic coefficients used, and the elastic constants used to convert the diffraction strain measurements to stresses contribute to the discrepancy. A further possibility is that the stresses really were smaller in our materials than in those used previously owing to a slower cooling rate, for example. Whatever its origin, it is important to note that the discrepancy between the fluorescence and diffraction measurements is small, and we conclude that the fluorescence stress values provide a reasonably accurate representation of the microstresses in the bulk of the nanocomposites.

The stress measurements so far have referred solely to the 'interphase' stresses which result from the thermal expansion mismatch between the alumina matrix and the SiC particles. The materials also contain 'intergrain' stresses caused by the thermal expansion anisotropy of alumina ($\alpha_c > \alpha_a$). The hydrostatic component of these stresses must be zero, but they cause a shift in R_2 peak position nevertheless because $\Pi_a \neq \Pi_c$. If these anisotropy stresses are the same in the alumina reference specimen and the nanocomposites, this shift is subtracted out in calculating $\Delta\nu$, and the stress measurements represent the interphase stresses only, as intended. Previous work [9] has suggested that the alumina anisotropy stresses are reduced in the nanocomposites. The reduction is small for the range of SiC contents used here, however, and we estimate the systematic error in the interphase stress measurements to be in the range +1.5 to +3 MPa for the materials used. This is comparable in size to the standard deviation of the stress values and is in the opposite sense to the systematic discrepancy between the present stress values and the diffraction measurements.

Although the effect of the anisotropy stresses on our *average* stress measurements is small, it is likely that the spread of R_2 peak positions arises in part from the differing relative orientations of the grains in the vicinity of each individual measurement. The alumina anisotropy stresses are of similar magnitude to the interphase stresses in the matrix [9] and can be assumed to fluctuate on a similar length scale to the spatial resolution of the fluorescence measurements, in contrast to the interphase stresses which fluctuate on the scale of the interparticle spacing. This may be why the standard deviation of the R_2 peak positions for the nanocomposites did not exceed the standard deviation of the alumina measurements despite the possibility of increased variation owing to local SiC volume fraction and orientation fluctuations.

4. Summary

Thermal microstresses in alumina/SiC nanocomposites containing 2, 5 and 10 vol.% SiC have been measured by Cr^{3+} fluorescence microscopy. The results agree well with previous diffraction measurements on similar materials. We conclude that fluorescence microscopy provides a method of assessing the level of bulk thermal microstress in alumina nanocomposites microstructures which, though less powerful than diffraction methods in terms of the range of information provided, is cheaper, quicker and better in spatial resolution.

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