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Preliminary Results on a Novel Fabrication Route for α-Al_2O_3 Single Crystal Monofilament-reinforced Reaction-bonded Mullite (RBM)

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Abstract

Owing to their excellent properties, continuous-fibre reinforced mullite-matrix composites are good candidates for applications in which oxidation resistance and damage tolerance at high temperatures (>1000°C) are required. To avoid fibre damage, near net-shape fabrication techniques of the composite are required. This has been achieved by using the reaction-bonding process which benefits the oxidation of metal powders producing volume expansion, and hence fully or partially compensating for the sintering-induced shrinkage. Starting materials include Al–Si alloy (80:20), Si metal, α-Al_2O_3 and mullite precursor powders. Due to the variety of starting compounds with different reaction and sintering kinetics, composite fabrication becomes a complex process. Differential scanning calorimetry (DSC) measurements, scanning electron microscopy (SEM) observations, and X-ray diffractometry (XRD) data show that effective milling of metal powder leads to a high degree of mullite formation (≈84%) at temperatures as low as 1500°C, although densification of the ceramic compacts remains rather low (≈45% of theoretical density).

Single crystal α-Al_2O_3 monofilaments were used to reinforce the reaction-bonded mullite (RBM) matrix. Although no intense reaction between the matrix and the fibres was observed at process temperature, strong bonding develops between uncoated fibres and the matrix. In order to produce a weaker fibre–matrix interface, which is necessary for improvement of the damage tolerance, the fibres were coated with ZrO_2 by means of high frequency sputtering. Microstructural observations of the fibre surfaces before and after the reaction-bonding process indicate that thick coatings (>10 μm) produce very weak bonding, insufficient for matrix–fibre load transfer due to shrinkage of the low density ZrO_2 layers. Thinner layers (1 μm) produce a better interfacial relation with suitable pull-out of fibres.

1 Introduction

Mullite is an excellent candidate for ceramic components requiring high temperature oxidation resistance.[1,2] However, due to the low strength and fracture toughness of mullite, continuous-fibre reinforcement is required if the material should be damage tolerant under cycling temperature conditions.

Fabrication of ceramic composites with continuous fibres is a complicated process, since volume shrinkage of the matrix during processing can give rise to fibre damage. Reaction bonding of metal powders has been suggested to be a suitable method to acquire near net-shape production of ceramics. Reaction-bonded silicon nitride (RBSN) and aluminium oxide (RBAO) are the best known examples of such materials, in which sintering-induced shrinkage is at least partially compensated by nitridation or oxidation yielding volume expansion of the starting metals and alloys.[3,4] Recently, some studies were devoted to fabricating mullite ceramics with this method (reaction bonded mullite; RBM), using Al–Si alloys or Al and Si metal and SiC powders as starting compounds.[3,4,7]

The aim of the present study was to produce continuous-fibre reinforced mullite matrix composites with long-term oxidation resistance, good high-temperature stability (≥1250°C), good thermal shock behaviour, and low creep rate. As a matrix, mullite meets these requirements. One possible way to increase the damage tolerance of the brittle mullite matrix is to use polymer-derived oxide-based fibres. However, most of the commercially available fibres are stable only up to 1250°C for long-term and up to 1400°C for short-term use.[5] Another approach to solve this problem is to use single crystal fibres. The present paper presents preliminary results on the fabrication of α-Al_2O_3 single crystal monofilament-reinforced mullite composites, making use of a modified reaction-bonding technique.

2 Materials and Experimental Methods

2.1 Processing of composites

2.1.1 Starting materials

Starting materials for mullite reaction bonding were Al–Si (80:20) alloy (24 wt%), mullite precursor (60 wt%), α-Al_2O_3 (14 wt%) and Si metal powders (2 wt%). The laboratory produced (nitrogen-atomized) Al–Si metal powder (Toyal, Osaka, Japan) had a particle size of d_{av} = 60 μm. To decrease the mullitization temperature of the system, a commercial mullite precursor produced from colloidal starting materials (Siral, Condea Chemie, Hamburg, Germany) was added. The as-received precursor was a nanometre-sized powder. It was calcined at 400°C in order to burn out the organic species and thereby reduce weight loss during composite processing. α-Al_2O_3 was a submicrometre-sized powder (99·995% Al_2O_3, AKP-50, Sumitomo, Tokyo, Japan), while the Si powder had an average particle size of 3 μm (Starck, Goslar, Germany).

For reinforcement of the composite, commercial single crystal corundum (α-Al_2O_3) continuous monofilaments (d = 125 μm), with the fibre axis being parallel to the crystallographic c-axis of α-Al_2O_3, were used (Saphikon, Milford, USA).

2.1.2 Coating of fibres

Fibres were coated with ZrO_2. Coatings were produced in argon atmosphere at about 150°C by using commercial ZrO_2 (+ 3% HfO_2) targets in a high frequency sputtering equipment (Balzers, Lichtenstein, Germany). For the coating procedure fibres were mounted between metal grids and were rotated (50 rev min^{-1}). Two types of coating experiment were carried out on the α-Al_2O_3 fibres, one having a duration of 15 min and the other a duration of 4 h. After a coating time of 15 min, the layer thickness was about 1 μm; it reached about 12–15 μm after 4 h of sputtering.

2.1.3 Composite fabrication

The principles of mullite matrix development and composite fabrication are given in Fig. 1. Mullite precursor, α-Al_2O_3 and Si metal powders were mixed with organic pressing aids in alcohol and wet-milled overnight. The Al–Si alloy powder was milled separately according to three different schedules in order to achieve a high degree of oxidation of the Al–Si metal powder at low temperature during reaction bonding:

- wet-planetary milling of the Al–Si alloy powder together with the other reactants;
- separate dry ball-milling of the Al–Si alloy powder, prior to mixing with the other reactants. To avoid the danger of flaming, the alloy powder was previously calcined in air at 350°C;
- dry ball-milling of the calcined Al–Si alloy powder as described above but after an attrition milling step in alcohol.

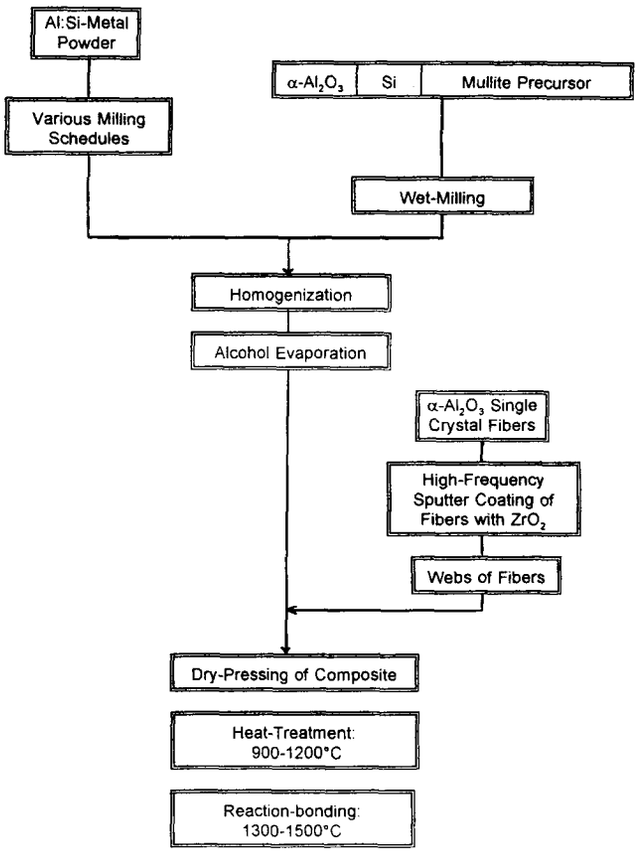

Fig. 1. Processing flow chart of reaction-bonded mullite matrix composites.

After homogenization of the powder mixtures, alcohol was evaporated in each case by a rotary evaporator. Fibres were arranged in webs by using a fixture which consisted of fine grooves of 100 μm. The fibre webs were fixed with glue at the fibre ends. Composite samples were prepared by uniaxial pressing of the fibre webs, which had been filled with the powder mixtures.

Composite powder compacts were heat-treated (300°C h^{-1}) at 900 and 1200°C for 5 h to promote volume oxidation of Al and Si particles. Reaction-bonding was performed at 1500°C (60°C h^{-1}) for 1 h.

2.2 Characterization methods

2.2.1 X-ray diffractometry (XRD)

X-ray powder diffraction studies were carried out at room temperature with a computer-controlled Siemens D5000 powder diffractometer using Cu K_α radiation. Diffraction patterns were recorded in the 2θ range of 10 to 80°, in a step scan mode (3 s / 0·02°, 2θ).

2.2.2 Differential scanning calorimetry (DSC)
DSC data were collected by a computer-controlled Netsch DSC 404 equipment with respect to a sapphire reference material considering baseline corrections of the DSC curves. Measurements were carried out in air up to 1400°C, with a heating rate of 10°C min^{-1}.

2.2.3 Microstructural investigations
Microstructural investigations were performed with a Philips 525M scanning electron microscope (SEM) on fracture surfaces of uncoated and ZrO_2-coated α-Al_2O_3 fibres and composites.

3 Results and Discussion

The investigation on the fabrication of α-Al_2O_3 single crystal monofilament-reinforced mullite composites was focused on two main activities: (i) development of the reaction-bonded mullite matrix and (ii) coating of α-Al_2O_3 single crystal monofilaments and subsequent fabrication of composites.

3.1 Development of the reaction-bonded mullite matrix

The main aims of matrix development were to achieve near net-shape production, low Al–Si alloy oxidation and low mullitization temperatures, homogeneous microstructures, and suitable densities. Near net-shape production requires compensation of the sintering-induced shrinkage of the green body by volume expansion of the starting metal powder caused by oxidation of the alloy and subsequent reaction of Al_2O_3 and SiO_2 to mullite.

The present study used an Al–Si metal alloy with an Al : Si ratio of 80 : 20, which is near to that of mullite (75:25). DSC measurements showed that the as-received Al–Si alloy powder melts at 584°C, whereas surface oxidation of particles starts immediately after melting and reaches to maximum at about 620°C. The sudden oxidation results in the formation of an oxide layer which slows down further oxidation of the Al–Si alloy particles. Volume oxidation of the Al–Si alloy takes place at about 900°C (Fig. 2). Si oxidizes in turn above 1200°C.[4]

Microstructural observations show that the melting of Al–Si alloy particles prior to oxidation is highly unfavourable, since this produces large, channel-like pores. We believe that the initial exothermal surface oxidation primarily forms a shell structure around the Al–Si alloy particles and consequently causes local temperature increase and melting of the Al–Si alloy left in the core. The melt diffuses out of the oxidized shell through grain boundaries and microcracks and wets the other existing particles, causing large voids in the shell centres. This may be prevented by achievement of complete oxidation of Al—Si particles prior to melting. Literature data report that this is possible if very fine (≤1 μm) metal powders are used.[7] Furthermore, addition of α-Al_2O_3 enhances oxidation of metal powders probably due to an increased oxygen partial pressure provided by alumina.[3]

DSC and XRD investigations showed that the milling procedure of the Al–Si alloy powders has a significant influence on the oxidation behaviour and on reaction processes. According to DSC measurements, wet-milling of the metal powder together with the other reactants has no significant effect on the oxidation behaviour (Fig. 2). Dry-milling of the precalcined metal powders prior to mixing with the other reactants results in an increase of particle surface area. In this case, the rates of surface and volume oxidation are similar (Fig. 3). Surface oxidation becomes more significant if metal powder is attrition-milled. Thereby, the melting and oxidation temperatures of the alloy have also been reduced to 578°C and 600°C, respectively (Fig. 3).

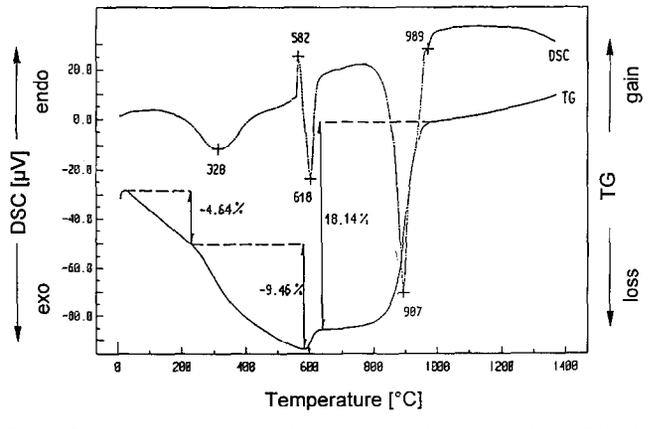

Fig. 2. DSC measurement and thermal gravimetry analysis (TGA) on powder wet-milled in air up to 1400°C (10°C min^{-1}) mixtures.

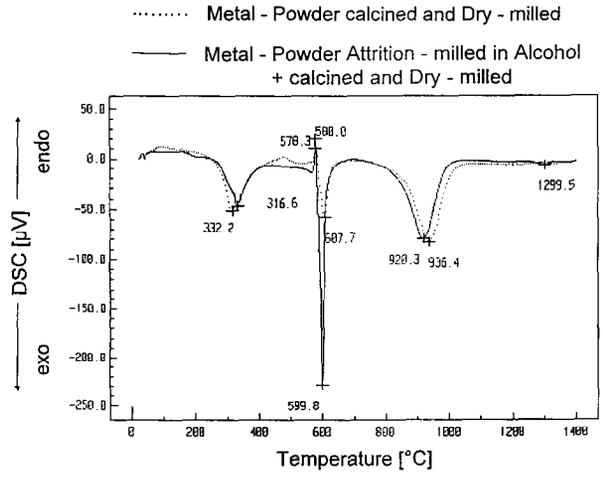

Fig. 3. DSC measurement on metal alloy, ceramic, precursor powder mixtures in air up to 1400°C (10°C min^{-1}), after dry-planetery and attrition-milling of metal powders.

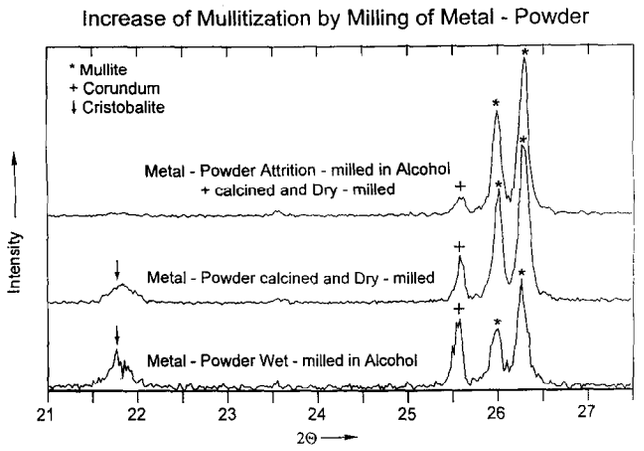

Fig. 4. XRD traces of metal alloy, ceramic and precursor powder compacts after various milling schedules and reaction-bonding processes at 1500°C .

XRD data show that the milling of Al–Si alloy powders greatly affects the rate of mullitization. Best results were obtained by attrition-milled metal powders (Fig. 4). Powder compacts, prepared by attrition-milling and subsequent reaction bonding at 1500°C, contain high mullite (84%) and low corundum (16%) contents. Dry- and wet-milled powders have lower mullite-to-corundum ratios and contain same cristobalite (Fig. 4).

Non-crystalline mullite precursors, transforming to mullite at temperatures above about 1200°C, were added to the starting powders. These low temperature-produced mullite crystals may act as nuclei for reaction-bonding induced mullitization, thus increasing the mullite formation rate at a given temperature with respect to samples without precursor addition in the starting material. Precursor additions to the green bodies also have a strong influence on the volume stability during processing. Precursor additions of 40 wt% led to a slight total volume expansion of the sintered samples (2–15 vol%). Precursor additions of > 60 wt% produce volume shrinkages (~10–16 vol%). In order to achieve a near-zero volume shrinkage, precursor contents between 45 and 55 wt% may be considered. The experiments also showed that the processing temperature of the RBM compacts can be reduced by more than 100°C, by addition of ~40 wt% mullite precursor. This may be an essential point, if polycrystalline fibres are used for the reinforcement instead of α-Al_2O_3 single crystal fibres, since the former are unstable at processing temperatures ≥ 1300°C.

3.2 Coating of α-Al_2O_3 single crystal fibres and fabrication of composites

Preliminary experiments were carried out to identify the fibre stability, during processing, and to develop suitable fibre coatings. Fibre coatings are essential to produce the necessary fibre–matrix interaction which on the one hand enables load transfer from the matrix to the fibre, and on the other gives rise to energy-consuming crack deflection and pull-out effects. Frequently used coating materials are SiC, C or graphite-type BN, which may initiate favourable fibre debonding by sliding processes parallel to the respective {0 0 1} crystallographic planes.[8] However, due to poor oxidation resistance, these coatings are not suitable for long-term use in oxidizing atmospheres.

In this study α-Al_2O_3 fibres were coated with ZrO_2 by using high frequency sputtering technique. After 4 h of high frequency sputtering, the thickness of the ZrO_2 layers on the fibres was ~12–15 μm. The layers exhibit columnar microstructure with ZrO_2 growing perpendicular to the fibre surface (Fig. 5). Between individual ZrO_2 columns small pore-like channels occur. The webs of coated fibres were compacted with matrix powder mixture and die-pressed prior to reaction bonding at 1500°C. After processing the thickness of ZrO_2 layers was reduced to 7 to 8 μm, due to sintering of the low density ZrO_2 coatings. This

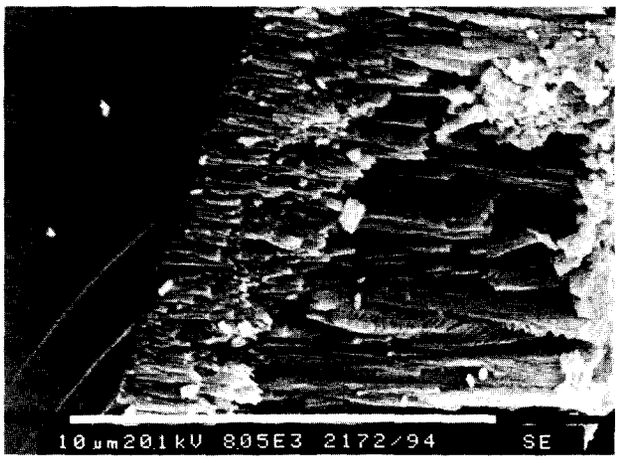

Fig. 5. High frequency sputtered ZrO_2 layer (4 h) on single crystal α-Al_2O_3 fibres, before reaction bonding.

Fig. 6. High frequency sputtered ZrO_2 layer (4 h) on single crystal α-Al_2O_3 fibre, after reaction bonding at 1500°C.

Fig. 7. High frequency sputtered ZrO_2 layer (15 min) on single crystal α-Al_2O_3 fibre, before reaction-bonding process.

effect is reinforced by the strong thermal contraction of ZrO_2 (higher expansion coefficient), caused by cooling down the composite from processing to room temperature (Fig. 6). Thereby, gaps up to 5 μm wide are formed between the fibres and matrix, producing low or even insufficient interfacial fibre–matrix bonding at room temperature.

Short time high frequency sputtering experiments (15 min) deposit thin ZrO_2 layers (≈ 1 μm) on the α-Al_2O_3 fibres (Fig. 7). The interfacial gaps produced by shrinkage of the ZrO_2 coating after processing in this case are almost negligable. In spite of the very thin ZrO_2 layers on the fibres, no reaction between the fibres and the matrix has been observed.

Our preliminary study on the fabrication of the ZrO_2-coated α-Al_2O_3 single crystal monofilament-reinforced mullite composite stresses its potential as a high temperature oxidation resistant, damage tolerant material. However, further intensive work is needed in order to improve RBM matrices, fibre coatings and related fibre–matrix interactions, and the fabrication of composites. These investigations should include a careful mechanical characterization of the composites, extending to strength measurements, damage tolerance studies and fibre push-out tests at room temperature and at high temperatures.

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