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Short communication

Alumina/silicon carbide composites fabricated via *in situ* synthesis of nano-sized SiC particles

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Abstract

Alumina/silicon carbide composites have been fabricated by a new technique involving the *in situ* synthesis of nano-sized SiC particles. A mixture of alumina powder and silicon carbide precursors was prepared in an aqueous suspension. Green bodies were formed by cold isostatic pressing of granules obtained by freeze granulation, and pressureless sintered at 1750 °C for 4 h in an argon atmosphere. Mullite (10–20 vol%) formed in addition to SiC during sintering. The SiC particles were located predominantly to the interior of the mullite and alumina matrix grains.
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1. Introduction

The addition of smaller volumes (5–10 vol%) of a nano-sized reinforcing agent may give a significant increase in creep resistance, strength and toughness of Al_2O_3 ceramics [1–10]. There are, however, wide differences between the results presented by different researchers because of differences in fabrication and testing procedures, and the reproducibility has in some cases been poor. The mechanisms behind the observed improvements in mechanical properties with these small additive volumes are not fully explained. It has been suggested that the SiC nano-particles restrict Al_2O_3 grain growth, and that this is a major factor behind the improvements [9,10]. Also, different models for strengthening and toughening of ceramic nanocomposites have been proposed [1,11–15].

A homogeneous and defect free composite microstructure is a prerequisite for optimum mechanical performance. In order to achieve this, it is essential to form a homogeneous and non-agglomerated mixture of the starting materials, and to retain the homogeneity during forming of green bodies [16]. It may prove difficult to obtain a homogeneous distribution of the additives, and to control the size of the nanoparticles, when the starting powder mixture is formed by milling different powders together in a liquid medium. There is a risk of agglomeration, and liquid transport of finer particles will tend to demix the powder mixture during removal of the liquid. Colloidal powder processing followed by freeze granulation and calcination will, on the other hand, give granules that retain the homogeneity of the aqueous suspension [17]. These granules may then be pressed into green bodies.

This short communication describes the fabrication of Al_2O_3/SiC nanocomposites by a new technique involving the *in situ* synthesis of nano-sized SiC particles. Homogeneous green bodies containing Al_2O_3 powder particles and SiC precursors were obtained by compressing granules formed by freeze granulation.

2. Experimental procedures

2.1. Fabrication

A mixture of alumina powder and silicon carbide precursors was prepared in an aqueous suspension. The Al_2O_3 starting powder (AKP 30, Sumitomo, Japan) was milled in water together with a silica sol (Bindzil NH3/220EKA Chemicals) for 1 h using Si_3N_4 milling balls. A carbon source (formaldehyde resin, Fenorex 6446, Dynea, Finland) was added to this mixture, and the so obtained aqueous suspension was stirred for

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1 h before a pressing aid (3 wt% PEG 400) was added. After additional stirring for 1 h, the mixture was sieved (100 μm) and freeze granulated by spraying into liquid nitrogen. This was followed by freeze drying, and the granules were sieved (500 μm) prior to compaction by cold isostatic pressing (300 MPa).

The green bodies were placed in a protective SiC powder bed and pressureless sintered in an argon atmosphere at 1750 °C for 4 h. The heating rate was 5 °C/min, with the exception of the temperature regime 1000–1200 °C where a reduced temperature increase rate (1 °C/min) was used in order to facilitate the formation of SiC.

The amount and relative fractions of the SiC precursors were such that a dense sintered body would contain 5 vol% SiC. SiC formation by carbothermal reduction of silica is a multi-step process which may be modelled according to [18]:

$$SiO_2 \quad (s,1) + 3C \quad (s) \leftrightarrow SiC \quad (s) + 2CO \quad (g) \qquad (1)$$

In order to drive the reaction towards SiC formation, the slurries were prepared with an excess amount of the carbon source, corresponding to 60 and 70 wt% rest carbon with respect to the amount of formed SiC.

The open porosity of the sintered materials was determined by Archimedes principle using distilled water.

2.2. *Structural analysis*

The overall phase assemblage and homogeneity of the sintered materials were assessed by X-ray diffractometry (XRD) and scanning electron microscopy (SEM) of polished sections. The fine scale microstructure was studied by transmission electron microscopy (TEM) of thin foils prepared by standard techniques. Elemental compositions were determined by energy dispersive X-ray spectroscopy (EDX). Elemental profiles acquired by the EDX system attached to the TEM were used for the evaluation of peak areas in the quantification of the EDX spectra.

3. Results and discussion

The amount of excess carbon in the starting powder mixture had a clear effect on the porosity of the sintered material. The open porosity decreased from 7.9 to 6.3% when the excess carbon was increased from 60 to 70%. Electron microscopy also revealed the presence of a smaller volume fraction of closed porosity in both materials.

Excess carbon has previously been found to promote the SiC formation [21]. Reaction (1) proceeds in two steps [18]:

$$SiO_2 \quad (s, \quad 1) + C \quad (s) \leftrightarrow SiO \quad (g) + CO \quad (g) \qquad (2)$$

$$SiO \quad (g) + 2C \quad (s) \leftrightarrow SiC \quad (s) + CO \quad (g) \qquad (3)$$

Carbon catalyzes the reduction of SiO_2 to SiO (2), and participates in subsequent SiC formation (3). A reduced porosity with a higher amount of excess carbon may, hence, be related to a more complete reaction (3). Residual carbon was not identified in these microstructures.

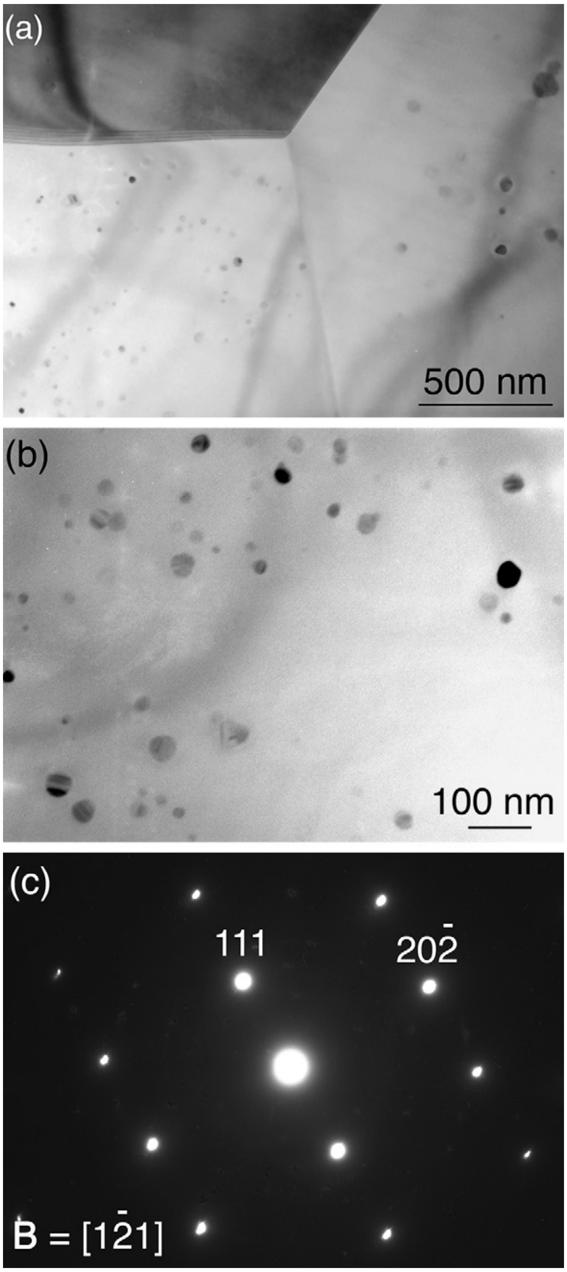

Fig. 1. Triple grain junction (a) and SiC particles (b) in the material fabricated with 70% excess carbon. (c) Electron diffraction pattern from a larger (~100 nm) 3C–SiC particle.

X-ray diffraction showed that both SiC and mullite had formed during the sintering process. This was also confirmed by SEM and TEM. Imaging together with EDX point analysis in the TEM showed that the SiC was present as a fine dispersion of nano-sized particles, see Fig. 1. The SiC particles were homogeneously distributed in the microstructure, and predominantly present inside the mullite and alumina grains. Only a limited number of the particles were located at the grain boundaries or at the walls of residual pores. Around 50% of the SiC particles in the material fabricated with 60% excess carbon had a size less than 50 nm, and around 80% were less than 100 nm in size, see Fig. 2. The SiC particle size was, hence,

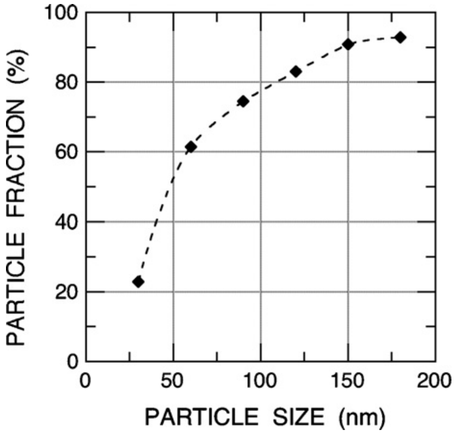

Fig. 2. Cumulative fraction of SiC particles against particle size in the material fabricated with 60% excess carbon.

reduced significantly as compared to Al_2O_3/SiC microstructures fabricated through conventional powder processing [19].

Electron diffraction from larger SiC particles showed that these were of different polytypes. The cubic 3C structure (β-SiC, see Fig. 1(c)), and the hexagonal 6H and rhombohedral 15R structures were identified. The presence of β-SiC is in agreement with previous observations that reaction formed SiC often has the cubic β-SiC structure [18,20–22]. The differences in free energy of formation between the different SiC polytypes are, however, very small [23]. As a consequence, the synthesis of SiC often produces a mixture of different polytypes which may coexist over a wide temperature range [23].

The grain size of the mullite as well as the Al_2O_3 matrix was typically around 3–4 μm. X-ray mapping in the SEM showed that the mullite was evenly distributed in the Al_2O_3 matrix, see Fig. 3. The area fraction of mullite, as calculated from EDX elemental maps, varied between 10 and 20%, and appeared to be the same in the two materials fabricated with different amounts of excess carbon. Assuming a homogeneous microstructure, the volume fraction of mullite would be the same as this area fraction.

The mullite grains contained between 65 and 71 mol% Al_2O_3 as shown by EDX in the TEM. The lower end of this range is close to the composition of $2Al_2O_3{\cdot}SiO_2$ (2:1 mullite). The solid solution range of mullite may, however, be extended to higher concentrations of Al_2O_3 (up to 76 mol%) under metastable conditions [24].

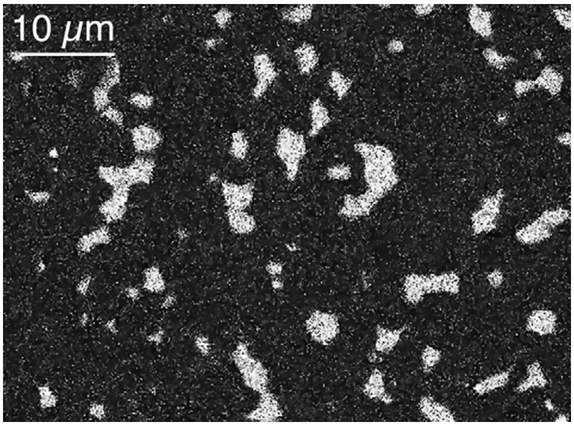

Fig. 3. Silicon map (EDX) of a polished section through the material fabricated with 70% excess carbon. The mullite appears with bright contrast.

The lowest eutectic temperature in the SiO_2–Al_2O_3 system is at 1587 °C and 5 mol% Al_2O_3 [24]. Solid state reactions between the two oxides at temperatures below that would be extremely slow. This strongly suggests that a liquid phase formed during sintering, and that mullite grew from this liquid. The crystallisation of mullite would then result in a solid solution around 2:1 mullite [24]. The mullite compositions determined by EDX in the TEM were in this range.

The presence of mullite grains in the microstructures shows that not all of the SiO_2 was consumed in the formation of SiC. The onset of SiC formation has been reported to be in the temperature range 1200–1500 °C [7,18,20,21,25]. It may, hence, be expected that a certain amount of SiC had formed before the formation of a Si–Al–O liquid and a subsequent crystallisation of mullite.

4. Concluding remarks

The results highlight the potential of forming a homogeneous distribution of nano-sized SiC particles *in situ* during sintering of an Al_2O_3 powder compact containing SiC precursors. This fabrication technique makes it possible to obtain a significantly reduced size of the reinforcing agent as compared to Al_2O_3/SiC composites fabricated through conventional processing of commercial powders.

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