

Al₂O₃–SiC composites prepared by warm pressing and sintering of an organosilicon polymer-coated alumina powder

Dušan Galusek^{a,b,*}, Jaroslav Sedláček^a, Ralf Riedel^b

^a Vitrum Laugaricio-Joint Glass Centre of the Institute of Inorganic Chemistry, Slovak Academy of Sciences, Alexander Dubček University of Trenčín, and RONA, j.s.c., Trenčín, Slovak Republic

^b Institute of Materials Science, Darmstadt University of Technology, Darmstadt, Germany

Received 18 March 2006; received in revised form 4 September 2006; accepted 10 September 2006

Available online 2 November 2006

Abstract

Al₂O₃/SiC micro/nano composites were prepared by axial pressing of poly(allyl)carbosilane-coated submicrometre alumina powder at elevated temperature (called also warm pressing, or plastic forming) with subsequent pressureless sintering in the temperature interval between 1700 and 1850 °C. Warm pressing at 350 °C and 50 MPa resulted in green bodies with high mechanical strength and with markedly higher density than in green bodies prepared by cold isostatic pressing of the same powder at 1000 MPa. The sintering of warm pressed specimens moreover yielded the composites with higher final density (less than 4% of residual porosity) with the microstructure composed of micrometer-sized alumina grains ($D_{50} < 2 \mu\text{m}$) with inter- and intragranular SiC precipitates. High sintering temperatures ($>1800^\circ\text{C}$) promoted the formation of intergranular platelets identified by TEM as 6H polytype of α -SiC. The maximum hardness ($19.4 \pm 0.5 \text{ GPa}$) and fracture toughness ($4.8 \pm 0.1 \text{ MPa m}^{1/2}$) were achieved in the composites containing 8 vol.% of SiC, and sintered for 3 h at 1850 °C. These values are within the limits reported for nanocomposites Al₂O₃/SiC by other authors and do not represent any significant improvement in comparison to monolithic alumina.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Al₂O₃; SiC; Al₂O₃/SiC; Precursors-organic; Mechanical properties

1. Introduction

Warm pressing or plastic forming is traditionally used as the method of forming of ceramic green bodies at elevated temperature, using mixtures of ceramic powder (e.g., alumina), and thermoplastic, or thermosetting organic polymer. After decreasing the temperature the polymer hardens and provides the green body with desired handling strength. Usually, the polymer is not intended as a permanent additive, and is completely removed (burnt out) before sintering.

The discovery of metallorganic precursors, i.e., the polymers, which upon suitable thermal treatment (pyrolysis) convert to ceramics with high yield, opened new possibilities for warm pressing. Here the warm pressing is used as the means of shaping the pre-ceramic polymers by heating them to the temperature where particles of the polymer can be deformed by viscous flow, or above their melting point, and pressing

them into a die of desired geometry.^{1–6} After cooling down to ambient temperature a polymer “green body” is obtained. The method has been successfully applied for shaping of precursors of aluminium nitride,¹ silicon carbonitrides,^{4–6} and silicon boron carbonitrides.^{2,3,6} In most cases the warm pressed green bodies have much higher density than the bodies prepared by, e.g., cold isostatic pressing (CIP) of polymer powders. This is explained by plastic deformation of polymer particles so that the porosity in green body is partially eliminated by mutual sliding of polymer particles and by viscous flow. Moreover, the authors reported different behaviour of warm pressed bodies in the course of their conversion to ceramics. Compared to CIP-ed polymers the ceramic materials derived from warm pressed bodies achieve higher density after pyrolysis, the formation of cracks and pores in the course of pyrolysis is less extensive, and the ceramic yield is higher. Such behaviour is the consequence of formation of chemical bonds among the individual polymer particles and of higher degree of cross-linking due to extended exposure to elevated temperature in the course of the warm pressing.

* Corresponding author.

E-mail address: galusek@tuni.sk (D. Galusek).

Another attitude utilises the fact that pre-ceramic precursors can be used as plastification aids or binders in their polymeric state, while leaving ceramic residue after pyrolysis.⁷ In this case ceramic powders like SiC whiskers can be mixed in usual way with substantial amount of a pre-ceramic polymer like polycarbosilane, extruded, warm pressed, or shaped by another suitable technique, and subsequently pyrolysed to yield a ceramic–ceramic composite.^{8,9} These include short fibre reinforced silicon carbide,⁸ or reaction bonded silicon nitride obtained by nitridation of silicon carbide precursor.⁹

Present work describes slightly modified way of utilisation of pre-ceramic polymers in preparation of Al₂O₃ matrix composites with submicrometre SiC inclusions. The traditional preparation route consists of mixing the alumina and SiC powders in a suitable aqueous or non-aqueous media, drying, green body shaping and high temperature densification, usually with the assistance of applied pressure. However, especially with very fine-grained (submicrometre) powders, which are required for preparation of nanocomposites it is difficult to prevent agglomeration of the submicrometre SiC particles, and to ensure homogeneous mixing of SiC and Al₂O₃. The presence of agglomerates then impairs sintering, resulting in formation of voids and cracks in sintered composites. Moreover, sintering without pressure is difficult, requires high sintering temperatures and long times, and usually results in microstructure with relatively coarse alumina grains (mean grain size ~5 µm).¹⁰

Alternative processing routes described in the literature include so-called “hybrid” route, which utilises SiC-forming organosilicon polymers, such as polycarbosilanes.^{11–14} This technique is usually based on coating of alumina particles with dissolved polymer, followed by drying, cross-linking, pyrolysis and densification. The method allows formation of alumina-based nanocomposites with ultrafine particles of SiC (~12 nm) located either intra-^{11,12} or intergranularly¹³ and with high mechanical strength. As a disadvantage, in all cases reported, hot pressing was necessary to densify the composites completely. Moreover, the thermal decomposition of organosilicon polymers usually yields not only SiC, but also free carbon, which is known to impair mechanical properties of the composite.¹⁵ Development of the polymer – poly(allyl)carbosilane – which under suitable thermal processing conditions at 1400–1500 °C yields β-SiC with no residual carbon, and is now commercially available, overcame the latter obstacle.¹⁶

In the present work we describe the preparation of alumina–SiC composites from green bodies shaped by warm pressing of a poly(allyl)carbosilane-coated alumina powder, with subsequent pyrolysis and pressureless sintering. The influence of the volume fraction of the polymer, and the conditions of sintering on densification are studied in more detail.

2. Experimental

In all experiments liquid poly(allyl)carbosilane SP-M10 (StarFire Systems, Watervliet, NY) was used as the source of SiC. Upon heating in inert atmosphere (Ar) the polymer transforms directly to amorphous ceramics with SiC stoichiometry with high ceramic yield (75–80 wt.%, depending on tempera-

ture). The polymer-to-ceramic conversion is accompanied by evolution of hydrogen and of small amounts of hydrocarbons. At higher temperature the amorphous ceramic crystallises and yields β-SiC. The polymer is soluble in aprotic solvents and can be handled in ambient environment.

An ultra pure (purity 99.99%) alumina powder Taimicron TM-DAR (Taimei, Japan) with the nominal particle size 200 nm was coated with the polymer by vigorous stirring of a suspension of 20 g of the powder with the polymer dissolved in 40 ml of water-free cyclohexane in sealed glass flask under Ar for 2 h. The amount of polymer was calculated in order to obtain powders containing the equivalent of 3, 5, or 8 vol.% of SiC. The solvent was removed by evaporation at decreased pressure (approximately 200 Pa) at ambient temperature. The polymer-coated powders were then sieved through a 100 µm PE sieve, filled into a steel die with heating mantle and uniaxially pressed at 50, 100, or 250 MPa and at 350 °C for 1 h to form cylindrical pellets with the height and diameter of 6, and 12 mm, respectively. The green density was calculated from the weight and dimensions of warm pressed pellets.

The pellets were then pyrolysed for 1, or 2 h in flowing Ar at 1000 or 1200 °C, and their density after pyrolysis calculated from the dimensions of pellets. The pellets were then placed in a high temperature electric furnace with graphite heating elements and sintered without pressure under Ar for 3, 5, or 8 h at various temperatures between 1550 and 1850 °C. The pellets were protected with powder bed containing 50 wt.% Al₂O₃, 25 wt.% SiC and 25 wt.% C (soot). The sintered pellets were cleaned from the residua of powder bed, and surface porosity sealed by spraying the pellets with polymerising coating. Preliminary measurements with specimens of known density proved that application of the thin polymer film does not influence measured density values. The density of sintered specimens was then determined by Archimedes method in water.

The specimens were cut, polished to 1 µm finish, and then etched chemically for 3 min in concentrated phosphoric acid at 250 °C. SEM examinations were carried out at both fracture surfaces and the polished and chemically etched cross-sections using a Philips XL30 high-resolution scanning electron microscope equipped with EDX analyzer (Philips, Eindhoven, The Netherlands). The parameters of microstructure (mean size of alumina grains, size and fraction of inter- and intragranular SiC particles) were determined from SEM micrographs with the aid of computer image analysis software Lucia v. 4.82, (LIM Praha, Czech Republic).

The total SiC content after pyrolysis and sintering step was calculated from the content of carbon, as determined by the LECO C200 carbon content analyzer (LECO Corp., St. Joseph, MI), assuming a stoichiometric conversion of the polymer with no free carbon.

Simultaneous thermal analysis was carried out on the simultaneous thermal analysis (STA) equipment, Netzsch STA 429, (Netzsch-Gerätebau GmbH, Selb, Germany), coupled with mass spectrometry (Balzers MID) in the temperature range 20–1500 °C.

Mechanical properties, i.e., hardness and fracture toughness were measured by Vickers indentation of polished specimens at

Download English Version:

<https://daneshyari.com/en/article/1476800>

Download Persian Version:

<https://daneshyari.com/article/1476800>

[Daneshyari.com](https://daneshyari.com)