Al$_2$O$_3$–SiC composites prepared by warm pressing and sintering of an organosilicon polymer-coated alumina powder

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Abstract

Al$_2$O$_3$/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 ($D_{50} < 2\,\mu$m) with inter- and intragranular SiC precipitates. High sintering temperatures (>1800 °C) promoted the formation of intergranular platelets identified by TEM as 6H polytype of α-SiC. The maximum hardness (19.4 ± 0.5 GPa) and fracture toughness (4.8 ± 0.1 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 Al$_2$O$_3$/SiC by other authors and do not represent any significant improvement in comparison to monolithic alumina.
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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.

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 Al_2O_3 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 Al_2O_3. 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 $\sim$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 ($\sim$12 nm) located either intra-[11,12] or intergranularly[13] 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 temperature). 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.% Al_2O_3, 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
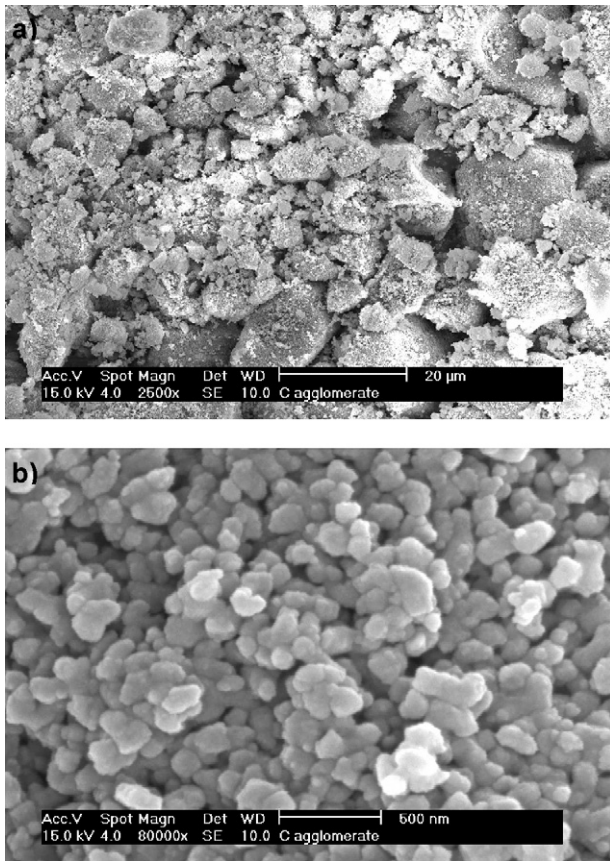
Fig. 1. Agglomerates of polymer-coated powder (a) and more detailed view of an agglomerate consisting of submicrometre alumina particles glued together with the polymer (b).

the maximum indentation loads of 10 and 100 N, respectively. The fracture toughness was calculated from the length of radial cracks by the method described by Anstis et al.[17]

3. Results and discussion

The polymer-containing alumina powder consisted of agglomerates with the size of up to 30 μm (Fig. 1a), which were composed of submicrometre alumina particles glued together with the polymer (Fig. 1b). Warm pressing of the powder at the pressures of 100 and 250 MPa yielded heavily cracked green bodies. The pressing at 50 MPa, however, yielded glossy crack-free specimens with relative density markedly higher than the green density of cold isostatically pressed pellets (CIP at 1000 MPa) prepared from the pure alumina powder or from the polymer-containing powder with the added amount of polymer equivalent to 5 vol.% SiC (Fig. 2). Moreover, the green density (both absolute, and relative, expressed with respect to the true density of the polymer-containing powder calculated by the rule of mixtures) increased linearly with increasing volume fraction of the polymer, achieving nearly 65% at 8 vol.% of the polymer. The results suggest that warm pressing facilitates densification of the green body by viscous flow of the polymer, and by mutual sliding and rearrangement of alumina particles in the course of pressing. Moreover, some pore space is filled with the cross-
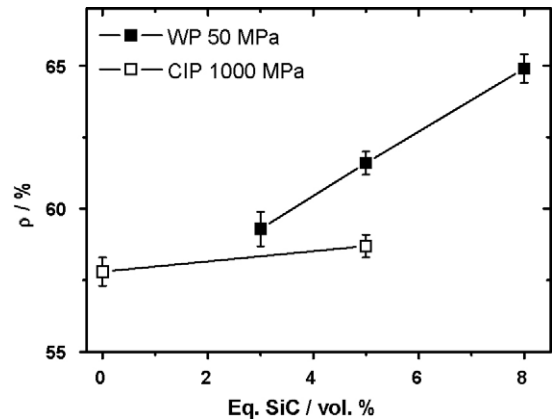

Fig. 2. Relative density of green bodies prepared by warm pressing and cold isostatic pressing of polymer-coated alumina powder.

linked polymer after warm pressing (the temperature and time of warm pressing increase the degree of cross-linking of the polymer), thus further increasing the green density.

The density of CIP-ed pellets decreased markedly after 1 h pyrolysis at 1200 °C (from 2.25 to less than 2.0 g cm^{-3}; Fig. 3). Taking into account that the density of amorphous ceramic residua after pyrolysis is higher than the density of the polymer (approximately 2.0 and 0.99 g cm^{-3}, respectively) such decrease cannot be explained merely by the loss of volatile compounds in the course of thermal treatment, which accounts for only about 20% mass loss. It is therefore suggested that the low-molecular weight oligomers, and gaseous by-products of the pyrolysis of low-cross-linked polymer accumulate in the green body and cause formation of cracks in the pellet. These were directly observed by SEM (Fig. 4a): the cracks are present both among the individual powder agglomerates and within them, and are believed to be one of the reasons of poor sinterability of CIP-ed bodies (61.7% relative density after 3 h sintering at 1550 °C, compared with 71.3% of the warm pressed body sintered under the same conditions). No evidence for swelling or bubble formation within pyrolysed pellets was found. It is suggested that the content of the polymer was too low to decrease the viscosity of the system to an extent, which would facilitate
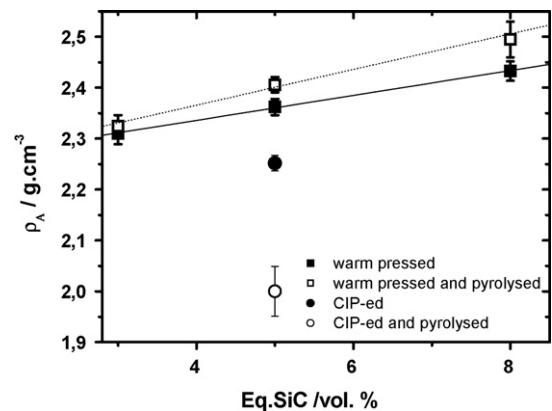

Fig. 3. Absolute density of specimens prepared by warm pressing before (■) and after (□) pyrolysis (1 h at 1200 °C), and by cold isostatic pressing at 1000 MPa before (●) and after (○) pyrolysis performed under the same conditions.
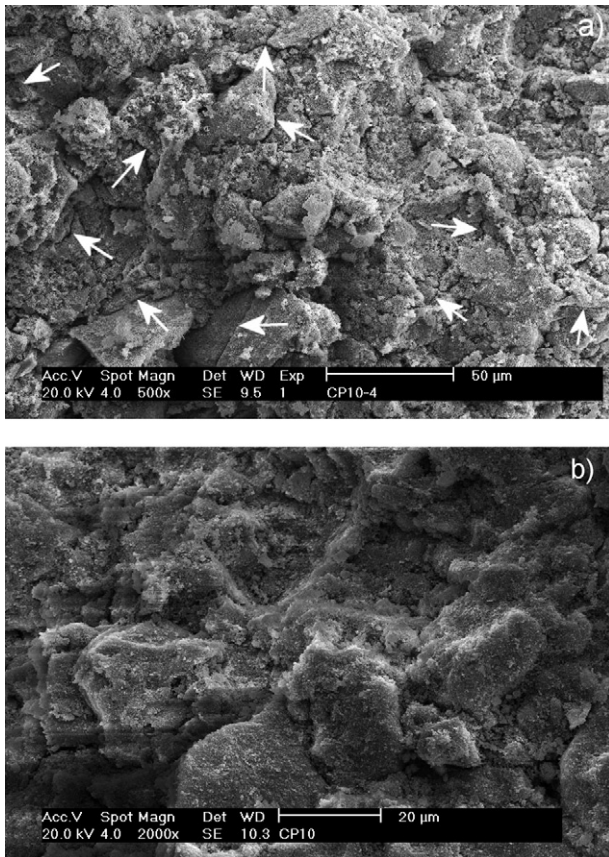
Fig. 4. The microstructure of the specimen containing the amount of polymer equivalent to 5 vol.% of SiC and CIP-ed at 1000 MPa, after 1 h pyrolysis at 1000 °C. The cracks among, and within individual powder agglomerates are marked with white arrows (a). The original morphology of powder agglomerates is well preserved in CIP-ed body even after pyrolysis (b).

formation of bubbles under the given pressure of gaseous pyrolysis by-products.

The second, and probably more important, reason of poor sintering ability of CIP-ed specimens is that the original morphology of agglomerates was preserved both through CIP-ing and pyrolysis (Fig. 4b), resulting in differential shrinkage and formation of interagglomerate pores in sintered bodies.

Unlike the CIP-ed samples, the pyrolysis of warm pressed pellets resulted in further increase of absolute (volumetric) density, which was more pronounced in specimens with higher volume fraction of the polymer. The pyrolysis was accompanied by a relative volume change of pellets by about 28%, irrespective of the volume fraction of the polymer. Such shrinkage can be attributed to shrinkage of the polymer in the course of its decomposition and ceramisation. However, the relative densities remain at the same level as in warm pressed specimens, e.g., 64.9% in the specimen with added amount of the polymer equivalent to 8 vol.% of SiC. This result suggests that the mass loss during pyrolysis is compensated by the density increase in the course of ceramisation of the polymer, but not by sintering of alumina. The temperature used during the pyrolysis is high enough to facilitate densification of the pure alumina powder: the dilatometric studies indicate the onset of shrinkage of the pure alumina at 990 °C. However, coating of powder with the polymer
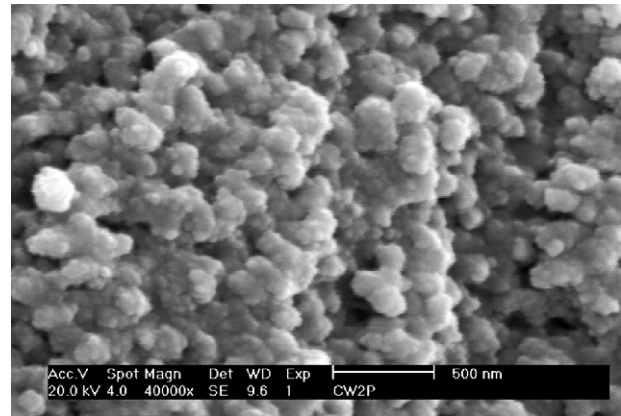

Fig. 5. The microstructure of warm pressed specimen containing the amount of polymer equivalent to 5 vol.% of SiC, after 1 h pyrolysis at 1000 °C.

prevents direct contacts between individual alumina particles, blocking the diffusion paths. The onset of densification is then shifted to correspondingly higher temperatures (1220 °C). No clear influence of the conditions of pyrolysis could be therefore detected on the density of pyrolysed specimens. Slight increase of the relative density from 64 to 66% TD was observed when increasing the time and temperature of pyrolysis of the specimens containing the equivalent of 8 vol.% of SiC from 60 to 120 min and from 1000 to 1200 °C, respectively.

The pyrolysed bodies consisted of fine alumina grains (approximate size 200 nm). As mentioned above, the temperature of pyrolysis is too low to facilitate the formation of necks between adjoining alumina particles coated with the polymer. The contacts among individual grains seen in Fig. 5 are therefore mediated by an amorphous product of pyrolysis with the SiC stoichiometry. Careful inspection of the fracture surface of the pyrolysed body shown in Fig. 5 revealed the presence of nanometer-sized globular precipitates of amorphous SiC with the average diameter 46 ± 8 nm at the surface of alumina grains.

The conditions of pyrolysis were found to have profound influence on sintering ability of pyrolysed bodies (Fig. 6). The results of simultaneous thermal analysis published in our previous paper indicate that conversion of the polymer to ceramic is completed at temperatures between 800 and 900 °C.[18] The
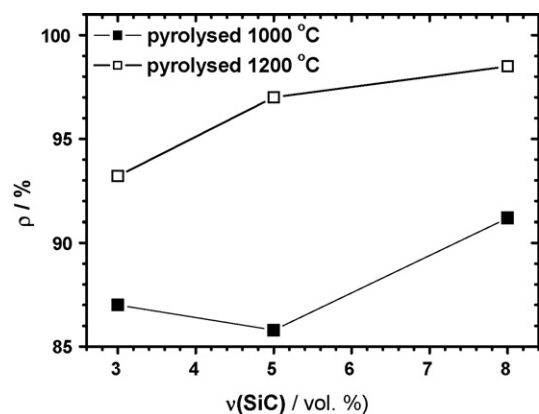

Fig. 6. Relative densities of warm pressed specimens pyrolysed at 1000 and 1200 °C, after 5 h sintering at 1800 °C.

ceramic product can be described as a random Si–C network, which then crystallises at higher temperatures to form β-SiC. The crystallisation is completed at approximately 1500 °C. However, the results obtained in this work indicate that gases can develop at temperatures significantly exceeding 900 °C, and thus impair the densification process significantly. In order to verify the assumption, the warm pressed specimens with added amounts of polymer equivalent to 3, 5, or 8 vol.% SiC were pyrolysed for 2 h at 1000 °C or 1 h at 1200 °C, using an optimised heating schedule, and subsequently sintered for 5 h at 1800 °C. The samples pyrolysed at 1200 °C sintered readily, and relative densities between 95 and 99% could be achieved (Fig. 6). The lower pyrolysis temperature (1000 °C) reduced the sintering ability of the composite, so that the densities of only 94% TD or less were achieved at all volume fractions of SiC. The SEM examinations revealed also marked differences of microstructure of sintered materials. Fig. 7 shows the SEM micrographs of the specimens sintered after pyrolysis at 1000 (a), and 1200 °C (b), both containing 8 vol.% SiC. The specimen pyrolysed at higher temperature contains only few isolated pores much smaller than the size of the alumina grains, homogeneously distributed throughout the body. The pores in the

specimen pyrolysed at 1000 °C are more frequent, with diameters approaching the size of the alumina grains, and localised mostly in the centre of the pellet. This is considered as an evidence of both the incomplete pyrolysis at 1000 °C, and further reactions taking place at higher temperatures, as will be discussed below.

The previously published results of STA of the polymer-coated alumina powder containing the equivalent of 10 vol.% of SiC[18] show the weight loss of 0.7% in the temperature interval between 1254 and 1500 °C. The coupled mass spectrometry confirmed the evolution of gaseous species with the mass $z = 2$ a.u., with the traces of species with $z = 16$, 17, 18, 28, and 44 a.u. These can be attributed to hydrogen ($z = 2$), water vapour fragments from the reaction of hydrogen with the silica formed by partial oxidation of the polymer in the course of coating ($z = 16$, 17, 18), carbon monoxide ($z = 28$) and silicon monoxide ($z = 44$) from carbothermal reduction of silica, which is known in some cases to proceed at temperatures <1300 °C.[19,20] The gases are then entrapped within the pores and hinder their closure. The higher temperature of pyrolysis enables all mentioned reactions to come to end before the pore closure commences at higher temperatures, and provides the time for better outgassing of the pellet. Higher pyrolysis temperature is then prerequisite for successful densification of a composite.

A set of experiments was also carried out using the optimised heating schedule[21] in order to prepare the composite by a one-stage process, where cross-linking, pyrolysis, and sintering take place during one continuous heating experiment. The temperature dependence of the relative sintering density of the composites containing 3, 5, and 8 vol.% SiC (in the following text denoted as CW3, CW5, and CW8) is shown in Fig. 8. The relative density increased markedly with sintering temperature at all volume fractions of SiC. However, the temperatures required to attain the relative densities above 90% in most cases exceed 1750 °C and 3–5 h dwell time. The increase of sintering temperature is tremendous, as the pure Taimicron TM DAR alumina powder sinters to nearly theoretical density after only 1 h dwell at 1350 °C. This increase of the temperature required to achieve high density is explained by the fact that the composites are prepared from polymer-containing powders, with alumina par-
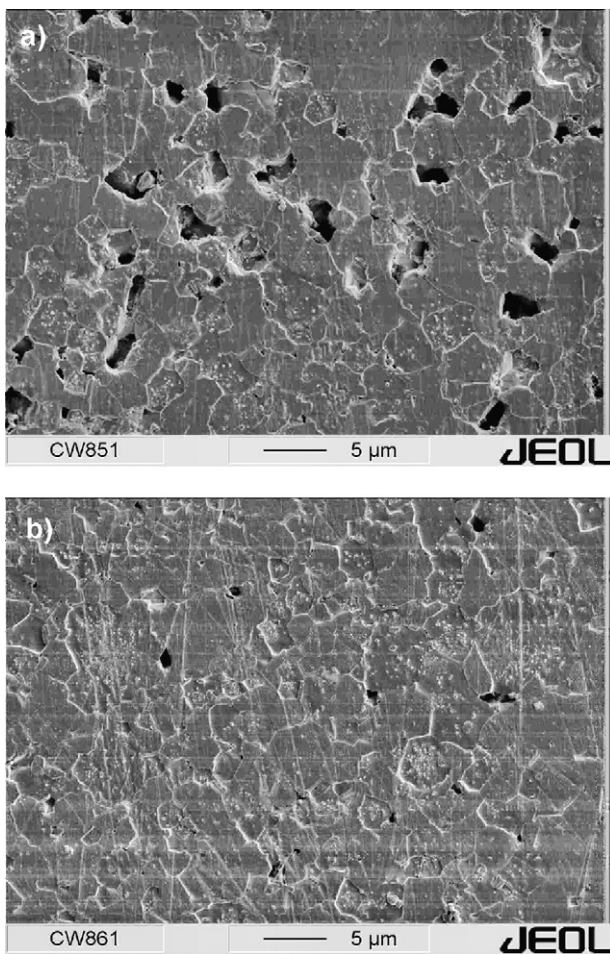

Fig. 7. SEM micrographs of warm pressed specimens containing 8 vol.% of SiC, pyrolysed 2 h at 1000 °C (a) and 1 h at 1200 °C (b), after subsequent 5 h sintering at 1800 °C.
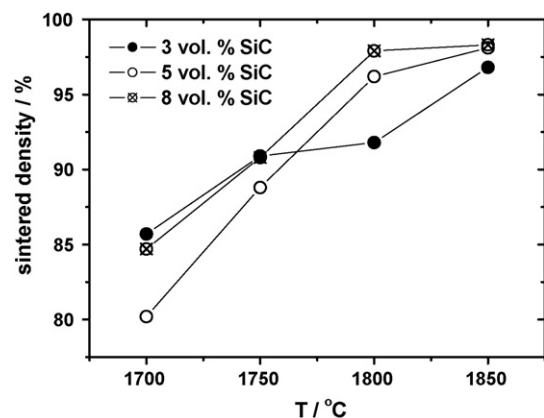

Fig. 8. Relative density of sintered specimens as a function of sintering temperature.

ticles covered with a discontinuous layer of SiC precipitates. The presence of precipitates/layer of SiC then reduces contact area among alumina particles, and impairs diffusion processes responsible for densification. Moreover, the polymer, which assists densification in the course of warm pressing by facilitating the rearrangement of alumina particles and by filling the pore spaces among them, transforms to a rigid covalently bonded ceramic substance during pyrolysis, which might effectively prevent rearrangement of alumina particles in the initial stage of sintering.

Interestingly, the relative density of composites sintered under identical conditions does not always follow the usually observed fact that higher volume fraction of second phase equals more difficult densification. At the sintering temperatures of 1700 and 1750 °C the lowest densities were achieved for the CW5 composite. At 1800 and 1850 °C the CW8 composite was the densest, while the material CW3 achieved the lowest density, although the difference at 1850 °C is small. All specimens, irrespective of the volume fraction of SiC, achieved relative density >96% after 3 h sintering at 1850 °C.

The SEM micrographs of the specimens sintered at 1800 °C are shown in Fig. 9. The microstructures shown indicate that the grain boundary mobility, and hence the grain growth, were significantly affected by the volume fraction of SiC in the material. This result is in accord with the classic work of Lange and Hirlinger,[22] who studied the influence of second phase inclusions on densification and grain growth of Al_2O_3–ZrO_2 composites. From the assumption that all grain corners have to be occupied by a second phase inclusion to prevent grain growth they estimated the minimum volume fraction of the second phase sufficient to prevent grain growth to approximately 5 vol.%. At lower volume fractions of the second phases the grain growth is not inhibited, while at higher volume fractions the grain growth can be entirely suppressed. Indeed, the quantitative characterisation of the microstructure of sintered composites revealed some trends in grain size–temperature–SiC volume fraction dependences. The mean size of alumina grains increases with the temperature of sintering (Table 1), and the grain size distribution tends to broaden. The trends are best visible in specimens

with the 3 vol.% of SiC. At higher volume fractions of SiC (5 and 8 vol.%) the increase of grains size and grain size distributions broadening is less pronounced, and the microstructures of CW5 and CW8 composites are much finer than the microstructure of CW3. These results confirm a significant grain boundary mobility retarding action of SiC inclusions, especially at low temperatures, and at higher SiC volume fractions. The aspect ratio of intergranular SiC increases with the temperature of sintering (Fig. 9b and c), and many grain boundaries in materials sintered at $T \geq 1800$ °C contain platelets of second phase situated parallel to alumina–alumina grain boundaries. The particles are in the figures marked by black arrows: their edge-on location parallel to grain boundaries gives them the apparent look of particles with whisker-like morphology, but the TEM investigation confirmed the presence of platelets of 6H polytype of α-SiC. The breakaway of a particle with such geometry from the grain boundary is energetically very demanding, and the particle therefore acts as an effective pinning site. The formation of SiC particles with platelet morphology suggests that at high temperature the cubic β-SiC, which is known to crystallise directly from the polymer, transforms to hexagonal α-SiC. Such transformation in strongly covalently bonded SiC usually occurs by dissolution–reprecipitation mechanism through grain boundary melt. As the presence of any significant amount of melt is very unlikely in this case, we suggest that the phase transformation proceeds by evaporation–condensation mechanism. This hypothesis is further supported by the fact that the platelets are formed only at high temperature (>1800 °C), where the partial pressures of corresponding entities could be sufficient to facilitate such process.

The mechanical properties (hardness and fracture toughness) of composites with the residual porosity <4% are summarised in Table 2. Slight increase of hardness with sintering temperature can be attributed to decrease of residual porosity. The fracture toughness increased moderately from 4.5 ± 0.1 to 4.8 ± 0.1 MPa m$^{1/2}$ if the volume fraction SiC increased from 5 to 8%. However, the anticipated significant improvement of mechanical properties was not achieved. The measured values of hardness fall well into the interval reported for monolithic

Table 1

Microstructure characteristics of pressureless sintered composites with various volume fractions of SiC

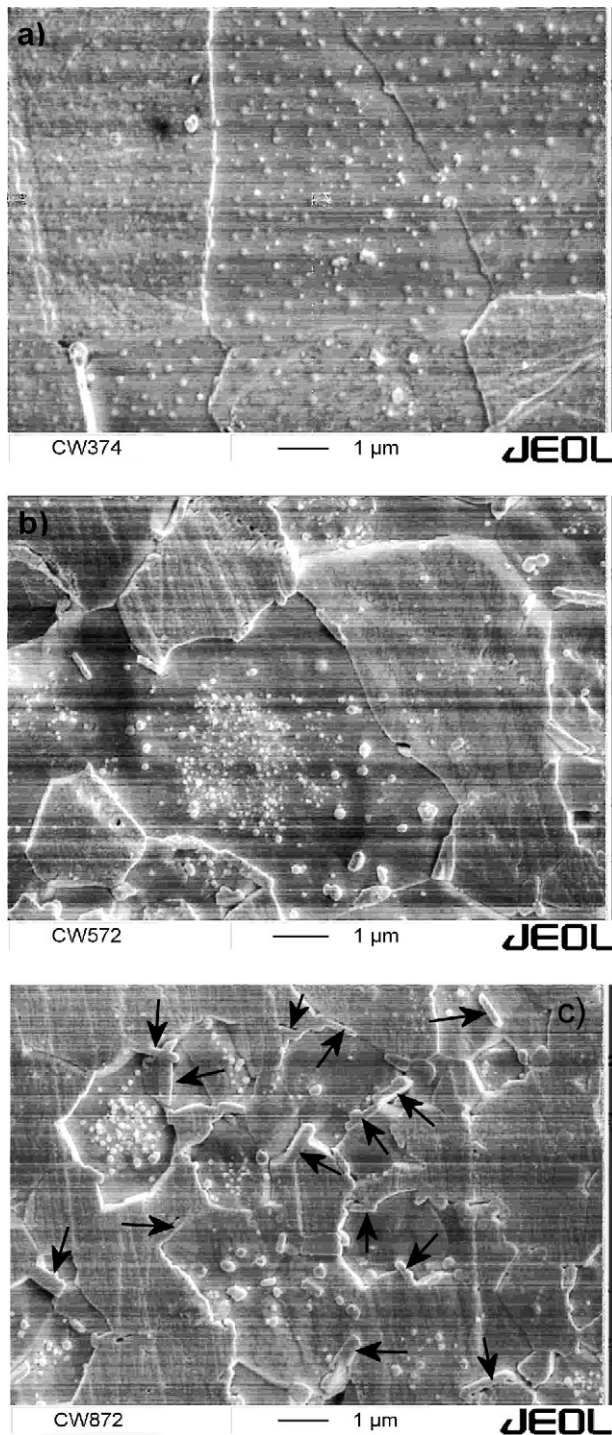| Sintering	SiC (vol.%)	$D_{50}(Al_2O_3)$ (μm)	$D_{50}(SiC_{intra})$ (nm)	$D_{50}(SiC_{inter})$ (nm)
1700 °C/5 h	3	1.5	125	n.m.
	5	0.9	86	118
	8	n.m.	70	118
1750 °C/5 h	3	1.9	123	201
	5	1.0	114	207
	8	0.8	96	184
1800 °C/5 h	3	2.0	161	251
	5	1.2	159	154
	8	1.0	88	214
1850 °C/3 h	3	n.m.	n.m.	n.m.
	5	1.5	88	143
	8	1.2	89	186

D_{50}, mean grain size.

Fig. 9. SEM micrographs of the composites with 3 vol.% (a), 5 vol.% (b) and 8 vol.% (c) of SiC, sintered 5 h at 1800 °C using the optimised one-stage heating regime.[21]

Table 2
Hardness and indentation fracture toughness of the composites sintered to less than 4 vol.% of residual porosity

Sintering	SiC (vol.%)	HV10 (GPa)	K_{IC} (MPa m$^{1/2}$)
1800 °C/5 h	5	18.6 ± 0.4	4.5 ± 0.1
	8	18.8 ± 0.3	4.7 ± 0.1
1850 °C/3 h	3	n.m.	n.m.
	5	19.2 ± 0.4	4.5 ± 0.2
	8	19.4 ± 0.5	4.8 ± 0.1

with previously published data,[23–25] markedly improved with respect to monolithic polycrystalline alumina with comparable grains size. A detailed summary of the results is in preparation.

4. Conclusions

Al$_2$O$_3$–SiC composites have been successfully prepared by warm pressing of poly(allyl)carbosilane-coated submicrometre alumina powder followed by pressureless sintering in the temperature interval between 1700 and 1850 °C. The composites sintered at the temperature ≥ 1800 °C were densified to less than 4% of residual porosity, and their microstructure was composed of micrometer-sized alumina grains ($D_{50} < 2\,\mu m$) with homogeneously distributed nanometer-sized SiC precipitates located both inter- and intragranularly. High sintering temperatures (1850 °C) promoted the formation of intergranular grains of second phase with platelet morphology situated parallel to grain boundaries. High sintering temperatures required to attain composites with low residual porosity are attributed to strong pinning effect of SiC precipitates. No significant influence on mechanical properties was detected, and the hardness and fracture toughness of the composites are comparable to those of monolithic alumina.

Acknowledgements

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alumina, and are most likely decreased by the presence of approximately 3 vol.% of residual porosity. The fracture toughness is slightly higher than the toughness of monolithic aluminas (typically 3–4 MPa m$^{1/2}$) and is comparable to the values usually reported for Al$_2$O$_3$–SiC micro-nanocomposites. However, our recent results indicate that the resistance of polymer-derived alumina–SiC nanocomposites to abrasive wear has, in accord

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