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Liquid Phase Sintering of Al_2O_3/SiC Nanocomposites

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Abstract

Al_2O_3/SiC nanocomposites are usually prepared by hot pressing or using high sintering temperatures, viz. 1700°C. This is due to the strong inhibiting effect of the nano-sized SiC particles on the densification of the material. Liquid phase sintering (LPS) can be used to improve densification. This work explored two eutectic additive systems, namely $MnO_2.SiO_2$ (MS) and $CaO.ZnO.SiO_2$ (CZS). The additive content in Al_2O_3/5 wt% SiC nanocomposite material varied from 2 to 10 wt%. Densities of up to 99% of the theoretical value were achieved at temperatures as low as 1300°C. Characterisation of the materials by XRD, indicated the formation of secondary crystalline phases in addition to Al_2O_3 and SiC. SEM and TEM analysis showed the presence of a residual glassy phase in the grain boundaries, and an increase in the average grain size when compared to nanocomposites processed without LPS additives.

Keywords: nanocomposites, Al_2O_3, SiC, liquid phase sintering, sintering.

1 Introduction

Al_2O_3/SiC nanocomposites have been extensively investigated over the last 10 years as a result of promising mechanical properties, such as strength,[1–3] creep resistance[4,5] and wear resistance.[6,7] The proposed microstructural design consists of grains of an alumina matrix reinforced by nano-sized (< 200 nm) SiC particles.[1] If an homogeneous dispersion of the SiC particles in the alumina has been attained by careful processing,[8–10] achieving high density materials has been difficult, and high sintering temperatures or hot pressing have been found necessary.[1–10] This is a result of the presence of the SiC nano particles which inhibit grain boundary diffusion.[8]

Liquid phase sintering, LPS, offers an alternative method of overcoming the lack of densification.[11] Although LPS has been used for the production of a number of technical ceramics, no specific work on the LPS of Al_2O_3/SiC nanocomposites has been found in the literature. However, this is a potentially attractive route for obtaining dense materials, especially if the related application involves only low temperatures. In this situation, the influence of any residual glassy phase can even be positive. For instance, glassy silicate phases between the grain boundaries were found to cushion the high residual stresses of alumina, improving the wear resistance.[12] Additionally, it is interesting to observe the microstructural behaviour of this material when sintered in the presence of a large amount of liquid phase, since two competing mechanisms will take place, viz. hindrance of densification and grain growth by the nano-sized SiC particles, and microstructural coarsening by the liquid phase.

2 Experimental

2.1 Additives

The additive systems used in this work, $MnO_2.SiO_2$ (MS) and $CaO.ZnO.SiO_2$ (CZS), were prepared before being added to the Al_2O_3 and SiC powders. $CaCO_3$, as precursor for CaO, and commercial MnO_2, ZnO and SiO_2 powders (Aldrich), all having particle sizes smaller than 1 μm, were dispersed in water according to the eutectic composition given in Table 1. The powders were mixed in an attritor for 1 h, dried at 100°C overnight, passed through a 180 μm sieve and calcined for 2 h at 600°C.

2.2 Powder preparation for sintering

Commercial Al_2O_3 (A-16 Alcoa, average particle size 0·5 μm), SiC (UF-45 Lonza, average particle

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Table 1. Characteristics of the additive systems used in this work

Code	*Composition (wt%)*	*Eutectic temperature (°C)*
CZS	16% CaO, 50% ZnO; 34% SiO_2	1170
MS	63% MnO, 37% SiO_2	1251

size 200 nm) and the pre-mixed additive powders were attrition milled in distilled water (ratio powder/water = 1) for 1·5 h to form a homogeneous (solids 95% Al_2O_3, 5% SiC) slurry. The amount of sintering additive used varied from 2 to 10 wt%. After the separation of the slurry from the balls, 0·5 wt% of PVA was added as binder. The material was flocculated by adding HCl, thereby increasing the slurry viscosity, and finally dried for 24 h at 100°C in an oven. Flocculation of the matrix powder was found to prevent the segregation and agglomeration of the SiC nanoparticles and the additives. The blend was broken up using a pestle and mortar and passed through a 180 μm sieve, pressed uniaxially to 50 MPa and isostatically to 200 MPa to form cylindrical pellets and calcined in air at 600°C for 5 h using a box furnace (EDG-1800).

2.3 Sintering and characterisation

Sintering was carried out in a closed furnace with graphite elements (Thermal Technology Inc, USA), under an Argon atmosphere. The pellets were surrounded by a mixture of the loose Al_2O_3 and SiC powders from which they were made in order to reduce evaporation losses and contamination from the furnace atmosphere, and were heated to between 1300 and 1400°C for nanocomposites with LPS additives and to between 1300–1700°C for nanocomposites without additives. The dwell time was 2 h and the heating rate was approximately 25°C/min. Fully dense materials for use as a reference were obtained by hot isostatic pressing (American Isostatic Presses Inc, USA) at 1300–1400°C at 200 MPa in argon.

Sintered densities, *D*, were measured using the Archimedes method. X-ray diffraction (Kristaloflex D500), was used to check for the presence of extra phases arising from the crystallisation of glassy phases and possible oxidation or reaction of the SiC with the additives. For microstructural observation, the samples were polished using diamond paste to a 1 μm finish. Thermal etching was carried out in argon at 1300–1380°C depending on the amount of liquid phase additives added. In addition, some samples were chemically etched with a 10 vol% HF aqueous solution for 10 to 60 s. The etched sections were gold coated and examined using SEM (Carl Zeiss 940A). EDS and X-ray mapping was used to analyse the composition of the sample. The average grain size was measured by the linear intercept method. TEM analysis (Philips CM 120) was carried out on carbon coated thin samples prepared by argon-ion milling.

2.4 Observation of the solid/liquid interaction

In order to observe the type of interaction between the liquid formed by the additives and the Al_2O_3 matrix, pellets of both materials were pressed in cylindrical shape and placed on top of each other, according to the schematic diagram shown in Fig. 1. The pellets were heated to 1400°C for 1 h in argon, to allow the liquid to melt. After cooling, cross sections of the pellets were polished to 1 μm finishing and analysed by SEM, to observe the wetting, penetration and reactivity behaviour of the liquid formed with the matrix.

3 Results and Discussion

3.1 Solid/liquid interaction

Figure 2 shows SEM micrographs of polished cross sections of the pellets used to observe the solid/liquid interaction. Both additive systems wetted and reacted with the alumina matrix. The existence of reaction indicated that the systems were far from thermodynamic equilibrium. However, the liquid formed from MS [Fig. 2(a)] seemed to have very low viscosity. It penetrated deep into the matrix, destroying the interface between the pellets (see the corresponding schematic drawing). In contrast, the liquid formed from CZS [Fig. 2(b)] did not penetrate the matrix showing that it had high viscosity and that its reactivity with alumina was small. These observations suggested that the MS additive could yield better improvements in the densification of alumina based systems than the CZS additive.

3.2 Densification

Figure 3 presents the results of densification of the Al_2O_3/SiC nanocomposites as a function additives content, for 1300 and 1400°C. Each result is the average of three specimens. A great improvement

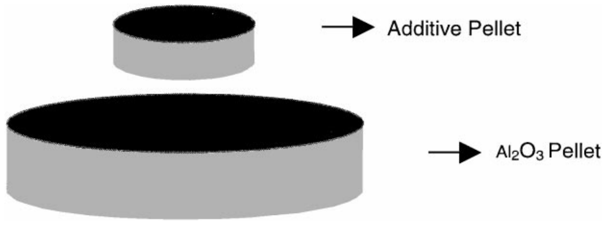


Fig. 1. Schematic drawing illustrating the experiment used to observe the solid/liquid interaction.

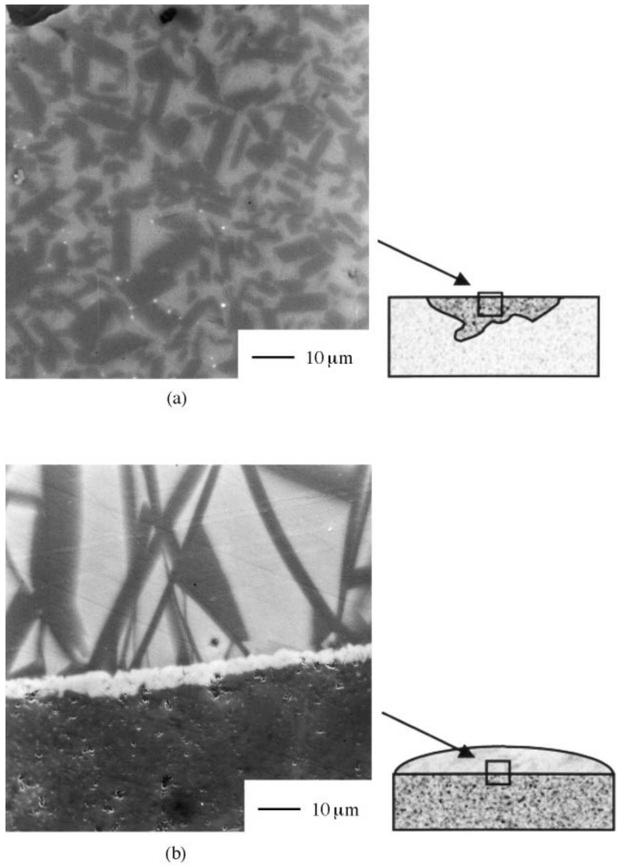


Fig. 2. SEM micrographs of polished cross sections of the interfacial region in the solid/liquid interaction experiment, (a) MS and (b) CZS. In both cases the liquid formed wetted and reacted with the matrix.

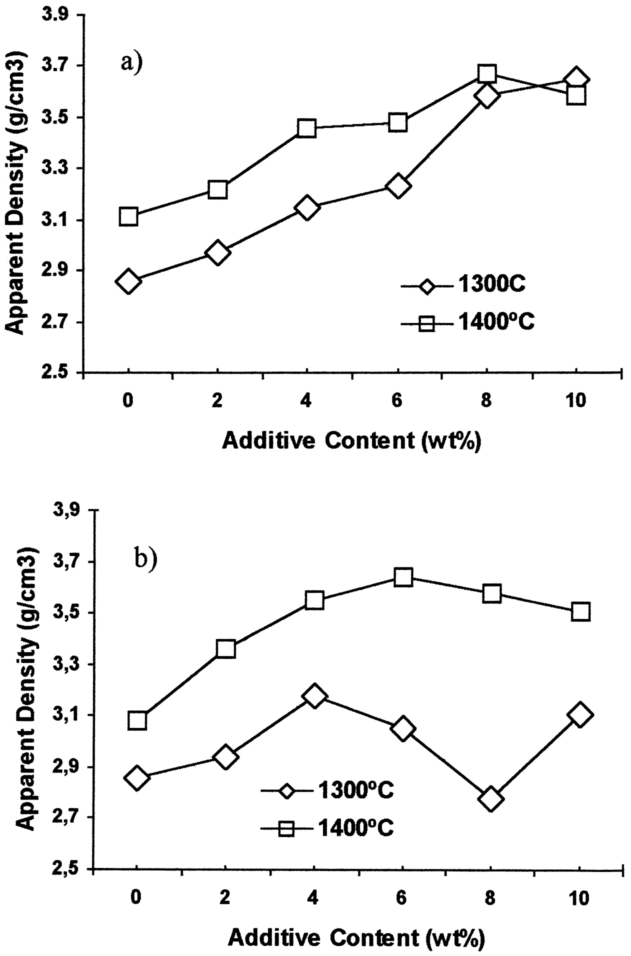


Fig. 3. Apparent density of Al_2O_3/SiC nanocomposites as a function of LPS additive content, for 1300 and 1400°C; (a) MS and (b) CZS.

in density was obtained as the additive content and the temperature increased. Maximum densities were reached with 10 wt% MS and 4 wt% CZS at 1300°C, and 8 wt% MS and 6 wt% CZS at 1400°C. In these cases, the apparent porosity was always smaller than 1%. The increase in densification with liquid content occurred partly by the effect of the liquid phase in allowing the rearrangement of the particles in the first stage of the LPS process. In this situation a wetting liquid creates an attractive force between the particles, putting the particle contacts in compression.[11] This effect is so strong that complete densification is possible by rearrangement if enough volume fraction of liquid is present (usually higher than 25 wt%).[11] The effect of increasing the sintering temperature on the densification is due to several mechanisms. For instance, it reduces the liquid viscosity, increases the solid solubility in the liquid, accelerates the diffusion mechanisms that control the dissolution and reprecipitation of the solid, and favours the pore elimination that occurs in the last stage of the process. However, excesses of both liquid and temperature reduced the densification of the material. In this condition grain and pore growth are favoured.[11]

The results of Fig. 3 are given in absolute values, since the theoretical density of the materials could not be easily calculated either by the rule of mixtures or by picnometry. The former would be confused by the presence of secondary phases, formed during sintering, which were not quantitatively determined. Picnometry needs fine powders, which could not be obtained either by crushing the material, due to the high hardness of the sintered pellets, or by sintering loose powders, due to the effect of the furnace atmosphere in the powder. Therefore, the values of theoretical density for nanocomposites prepared by LPS were obtained by HIPping sintered samples at 1400°C. The HIPped samples were assumed to be fully dense, since higher temperatures did not improve the final density. For the two compositions which gave the highest sintered density, i.e. 10 wt% MS and 6 wt% CZS the values obtained were 3·65 and 3·75 $g\,cm^{-3}$, respectively. Calculating the relative density, using the results shown in Fig. 3, the nanocomposite with 10 wt% MS reached 99% of the theoretical density at 1300°C, and with 6 wt% CZS the density was 96% at 1400°C. Comparing these results with those of materials prepared without the addition of LPS additives (see Table 2) achieving a density 96% of theoretical value would need temperatures of around 1600°C, whereas a density of 99% would require temperatures of around 1700°C. A reduction of more than 400°C in the sintering temperature can, therefore, be obtained by using 10 wt% MS LPS additives. The better results observed with additions of MS in comparison to CZS, can be explained by the lower viscosity and higher reactivity of the liquid formed, as described in Section 3.1.

3.3 XRD and microscopy analysis

Figure 4 shows the XRD patterns for compositions with the highest concentration of additives, viz. 10 wt%. All diffractograms showed SiC, confirming that this phase neither reacted extensively with the liquid formed by the additives nor oxidised. This is an important observation, since the presence of the nano SiC phase is responsible for the improvements in the mechanical properties observed in nanocomposite materials.[1–6] The diffraction patterns of Fig. 4 also showed the existence of crystalline phases for both compositions, i.e. $CaSiO_3$ for materials with CZS, and Al_2SiO_{13} for materials with MS. However, results from the literature, for similar systems, predicted the formation of more than one secondary phase.[13] The fact that this was not observed in this work suggested that there was not enough time for them to form or that their amount was below the detection limit of the equipment.

Table 2. Densification of Al_2O_3/SiC nanocomposites as a function of temperature: materials without LPS additives

Sintering temperature (°C)	*1300*	*1400*	*1500*	*1600*	*1700*
% of theoretical density	75	80	90·5	95·5	98·5

Figure 5 shows SEM micrographs of thermally etched polished samples (a) 10 wt% MS/1300°C and (b) 6 wt% CZS/1400°C. Comparing these to materials without LPS additives sintered at 1300 and 1400°C, shown in Fig. 6(a) and (b), respectively, it can be observed that LPS materials presented larger average grain size, wider grain size distribution, a morphology consisting of equiaxed and elongated grains. The coarsening of the microstructure took place despite the presence of nano SiC particles in the materials. For solid state sintering, these particles are observed to hinder grain growth, by pinning the matrix grain boundaries.[3,14] It is evident, that a compromise between the two mechanisms was obtained, i.e. grain growth occurred but it was not as strong as it would have been if the SiC nano-particles had not been present in the material. Table 3 shows the measured average grain size for these compositions.

Figure 7 shows TEM micrographs of the LPS nanocomposite materials. Glassy phase pockets were observed in the grain junctions of both materials

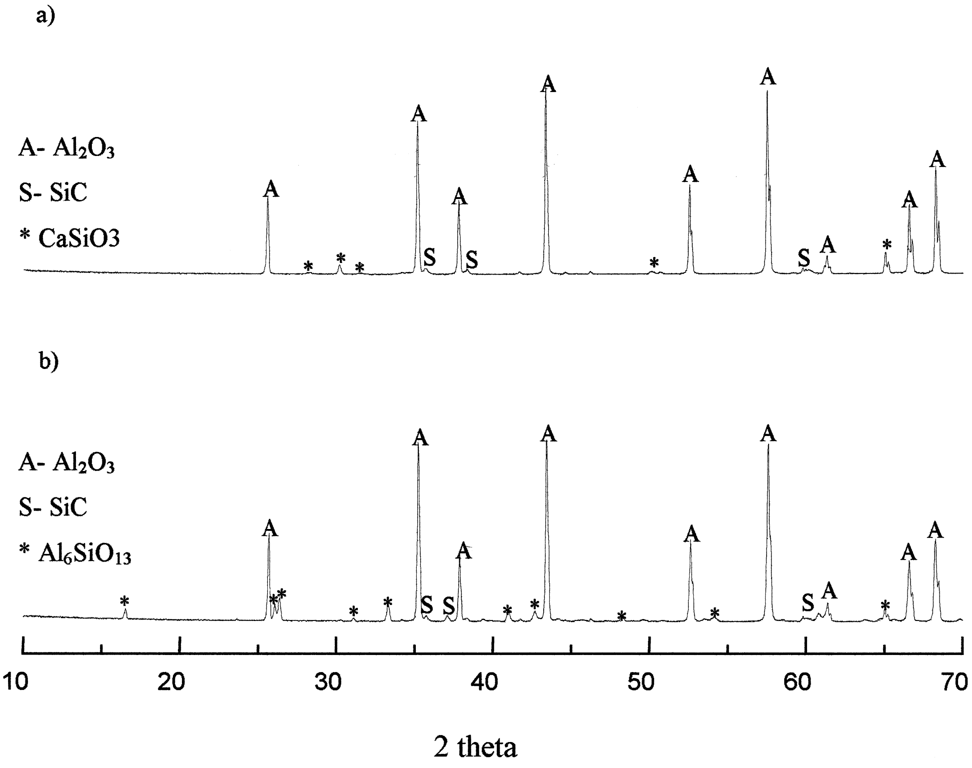
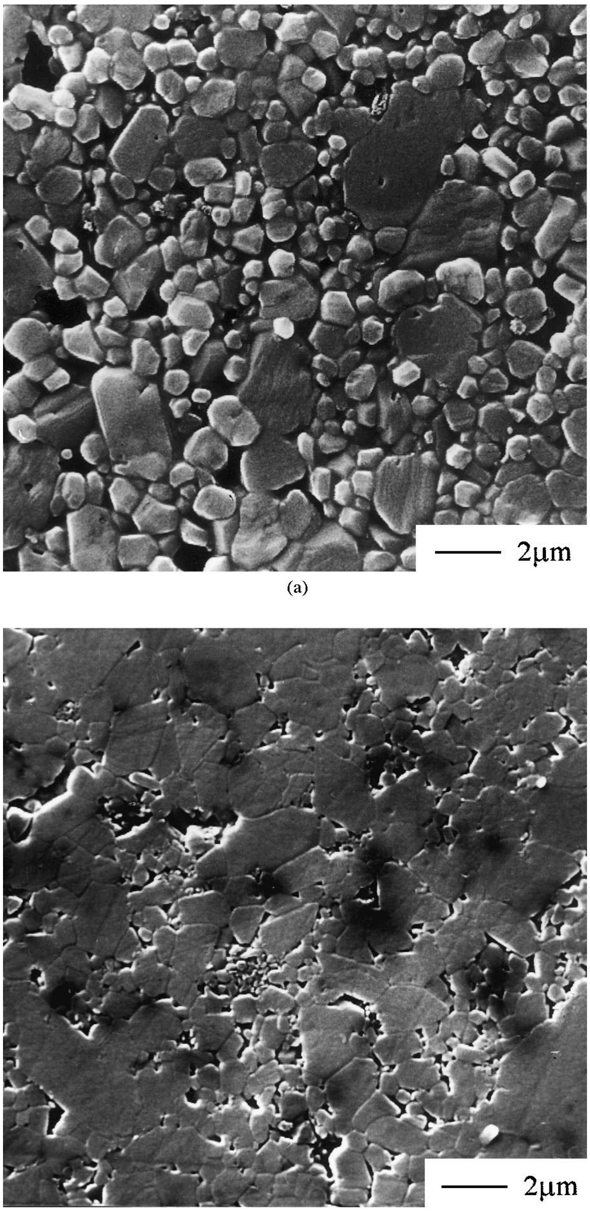


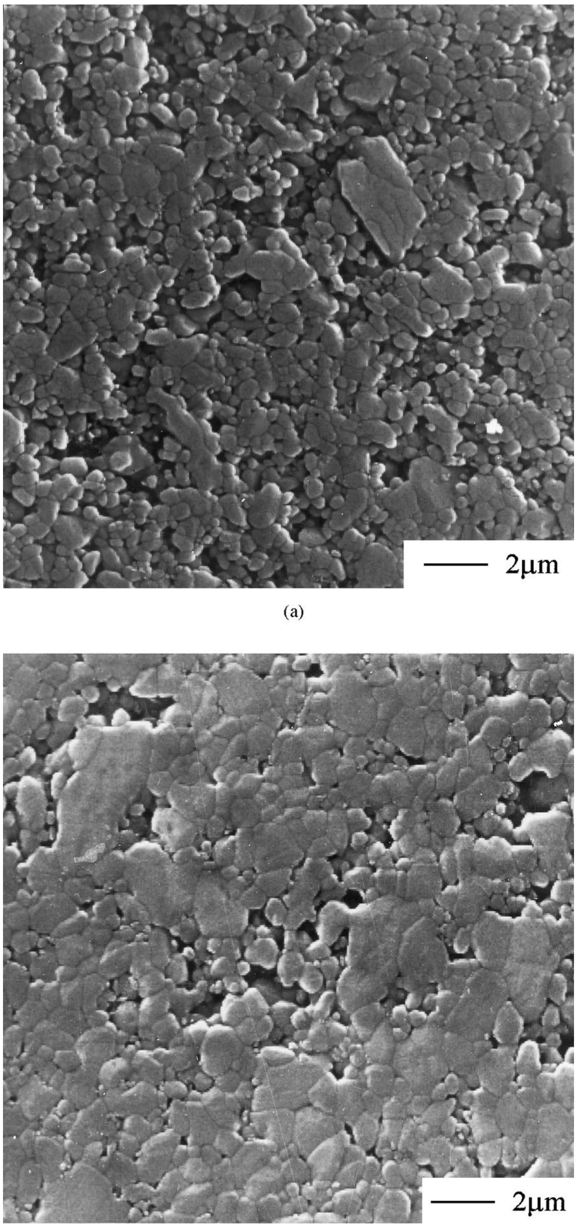
Fig. 4. XRD of the LPS nanocomposites: (a) 10 wt% CZS and (b) 10 wt% MS. Both materials exhibited extra phase in addition to Al_2O_3 and SiC.



(a)

(b)

Fig. 5. SEM micrographs of thermally etched nanocomposite material (a) 10 wt% MS sintered at 1300°C and (b) 6 wt% CZS sintered at 1400°C.



(a)

(b)

Fig. 6. SEM micrographs of thermally etched nanocomposite material without LPS additives: (a) sintered at 1300°C and (b) sintered at 1400°C.

(see the arrows). This was more visible, at this magnification, for the nanocomposite with 10 wt% MS [Fig. 7(a)], probably due to the higher content of liquid present in this case. The heterogeneity of the grain morphology is apparent, with grains with aspect ratio around 5[15] and abnormal grains present in the materials. The TEM micrographs also showed the location of the SiC nano-particles in respect to their sizes. SiC particles smaller than 200 nm were predominantly situated inside the alumina grains, whereas larger SiC particles retain intergranular positions. This has been observed in other work.[1–6,8–10,14] Figure 8 shows an SiC particle embedded in the glassy phase, indicating its stability in the liquid formed. More extensive TEM analysis also identified some agglomerates of SiC particles, which indicated the difficulty in dispersing the powders, when the sintering additives are used. This in conjunction with the glassy phase, may be responsible for the growth of abnormal, platelet and elongated grains in the LPS nanocomposites.

Table 3. Average grain size for some materials investigated in this work

Additive content	*Sintering temperature (°C)*	*Grain size* (μ*m*)
—	1300	0·75
—	1400	1·18
10 wt% MS	1300	1·80
6 wt% CZS	1400	1·70

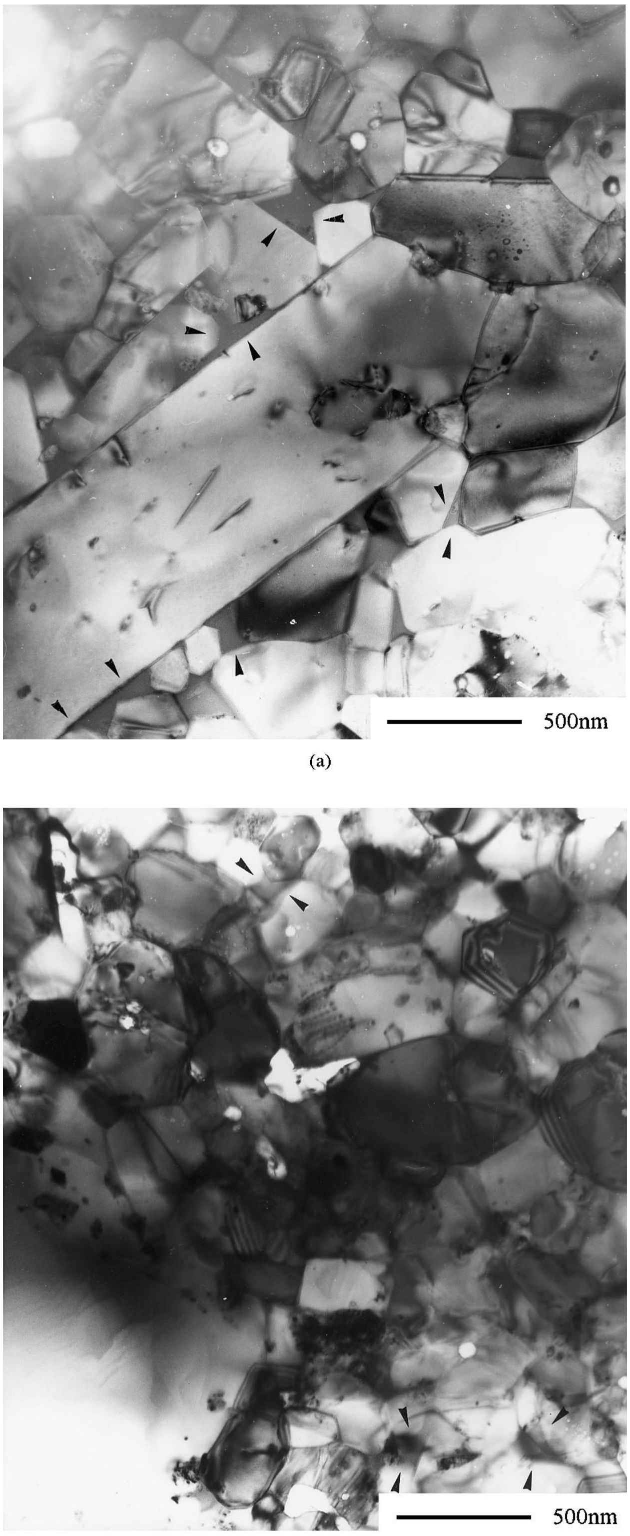


Fig. 7. TEM micrograph of nanocomposite material: (a) 10 wt% MS and (b) 6 wt% CZS. The arrows show glassy phase pockets.

Erosion wear tests, carried out in these samples and described in detail elsewhere,[16] have shown that the LPS materials have wear resistance values comparable to nanocomposite materials prepared by HIP at 1600°C, despite the presence of residual glassy phase and abnormal grain growth in the LPS nanocomposite materials.

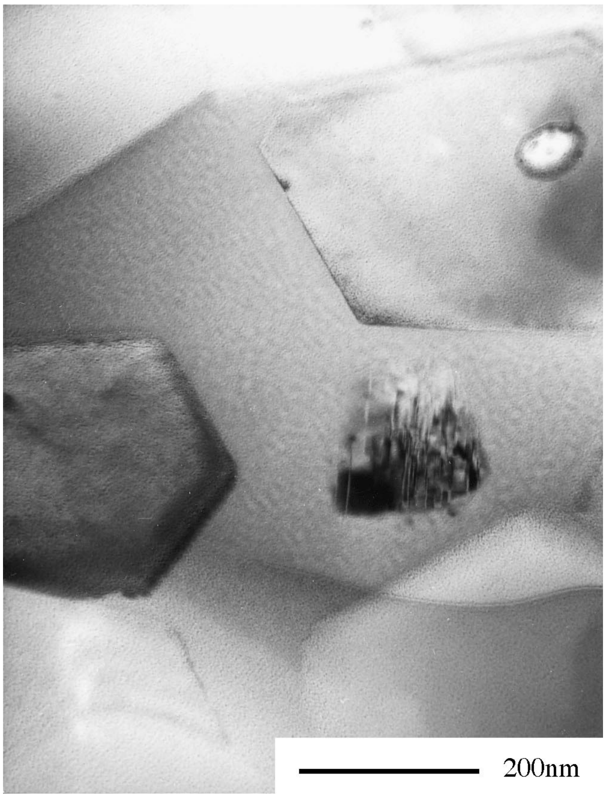


Fig. 8. TEM micrograph of nanocomposite material with 10 wt% MS, showing an SiC particle embedded in a vitreous phase.

4 Conclusions

This work shows that liquid phase sintering (LPS) can be used to prepare dense Al_2O_3/SiC nanocomposites, at temperature as low as 1300°C. For the additive systems investigated, the best densification results occurred for additions of $MnO_2.SiO_2$. This agreed with SEM analysis of the liquid/solid interactions which showed that this system was more reactive and less viscous than $CaO.ZnO.SiO_2$ in the presence of alumina. Parallel to the improvement in densification, LPS of the nanocomposites caused some microstructural changes when compared to nanocomposites prepared without LPS, i.e. (i) grain growth of the alumina matrix grains, (ii) formation of residual crystalline and glassy phases, (iii) formation of elongated, platelet and abnormal grains and (iv) a heterogeneous distribution of the nano-sized SiC particles.

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