

# Processing of Al<sub>2</sub>O<sub>3</sub>/SiC Composites in Aqueous Media

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(Received 15 September 1995; revised version received 28 August 1996; accepted 29 August 1996)

## Abstract

Two processing routes for the composite system Al<sub>2</sub>O<sub>3</sub>/SiC (SiC content ranging from 2.5 to 25 vol%) in water have been developed, using SiC powder with a chemically modified surface. For each system, slurry properties were optimised by measuring adsorption isotherms and rheological behaviour. Slurries with high solid loadings (47 vol%) and homogeneous SiC distribution could be realised. Green bodies of high densities (up to 62% of theory) for various SiC contents were prepared by slip casting into a porous mould and drying in air. Pressureless sintering was conducted under different atmospheres (N<sub>2</sub> or Ar) and temperatures (1690 to 1950°C). Sintering conditions to obtain high densities strongly depend on the SiC content and on the processing route of the composite. Best results for one processing route were obtained for 10 and 15 vol% SiC samples, each reaching densities of 97.5% of theory when sintered for 1 h in N<sub>2</sub> at 1880°C. A sample prepared by the other developed system, containing 5 vol% of SiC could be densified up to 98.2% of theory when sintered for 1 h in N<sub>2</sub> at 1800°C. © 1996 Elsevier Science Limited.

Zwei Prozeßtechniken zur Herstellung von Al<sub>2</sub>O<sub>3</sub>/SiC Kompositen über wäßrige Schlicker wurden unter Verwendung von oberflächenmodifiziertem SiC entwickelt (der SiC Anteil lag dabei zwischen 2.5 und 25 vol%). Die Schlickerparameter für jedes System wurden durch die Bestimmung von Adsorptionsisothermen und die Untersuchung der rheologischen Eigenschaften optimiert, wodurch hohe Feststoffgehalte (47 vol%) und eine homogene SiC Verteilung resultierten. Schlickerguß in eine poröse Form und anschließendes Trocknen an Luft ergab Probekörper mit hohen Gründichten (bis zu 62% des theoretischen Wertes). Sintern erfolgte drucklos in verschiedenen Atmosphären (N<sub>2</sub> oder Ar) zwischen 1690 und 1950°C. Die ermittelten Sinterdichten variierten stark mit dem SiC Gehalt und waren von der verwendeten Prozeßtechnik abhängig.

*Eine Probe mit 5 vol% SiC, welche nach der ersten Technik hergestellt wurde, erreichte eine Dichte von 98.2% der Theorie (1800°C, N<sub>2</sub>, 1 h), während Probekörper mit 10 oder 15 vol% SiC, hergestellt nach der zweiten Verarbeitungstechnik, auf jeweils 97.5% relativer Dichte gesintert werden konnten (1880°C, sonst gleiche Sinterbedingungen).*

## Introduction

The interest in the Al<sub>2</sub>O<sub>3</sub>/SiC system has grown rapidly within the last few years. SiC as a second phase can be incorporated into an Al<sub>2</sub>O<sub>3</sub> matrix either as whisker,<sup>1-4</sup> platelet<sup>5</sup> or particle.<sup>6-13</sup> As an alternative to these techniques, Al<sub>2</sub>O<sub>3</sub> and SiC composite materials have been produced from mixtures of aluminosilicates and carbon as precursor materials.<sup>14</sup> In most cases, mechanical properties were found to be improved by the second phase compared to the pure matrix material leading to different proposals for the strengthening mechanism. Outstanding values of the fracture strength were reported for a particulate (5 vol% SiC/Al<sub>2</sub>O<sub>3</sub>) reinforced 'nano'-composite (1520 MPa compared to 350 MPa for the pure Al<sub>2</sub>O<sub>3</sub>).<sup>6</sup> To obtain good homogenisation, the powders in these particle/particle systems were mixed in organic media (e.g. EtOH, ball milling) and were then hot pressed under N<sub>2</sub>.<sup>6-10</sup> Investigation of several organic dispersants revealed large differences in their ability to stabilise the powder slurries.<sup>12</sup> By choosing an unsuitable medium (e.g. hexane) agglomerates form, which severely inhibit densification in the sintering process, as confirmed by theory.<sup>15</sup> It is shown,<sup>12</sup> that by pressureless sintering high densities (up to 99% for a composite containing 5 vol% SiC) can be reached by using the best of all investigated organic dispersants (MeOH). Sintering temperatures for a composite material were generally found to be higher than for pure Al<sub>2</sub>O<sub>3</sub>. It is known,<sup>16</sup> that second-phase particles can inhibit grain growth of a matrix,

which according to classical sintering theory<sup>17,18</sup> should lead to an enhancement of densification. In the case of the  $\text{Al}_2\text{O}_3/\text{SiC}$  system it appears however, that retardation of densification is so dominant over the inhibition of grain growth, that an overall reduction in the densification rate results. This behaviour is not fully understood at the moment. The intention of the present work is to examine ways for powder processing and homogenisation by using aqueous media and carefully adjusting and controlling the slurry properties. It is shown, that it becomes possible to produce  $\text{Al}_2\text{O}_3/\text{SiC}$  composites without the need for hot pressing. This opens up the opportunity for an economic manufacturing of this material.

### Experimental Procedures

The zeta-potential of both components (SiC: H. C. Starck, UF 45, 200 nm;  $\text{Al}_2\text{O}_3$ : Sumitomo, AKP 53, 200 nm) can be rendered nearly identical by chemically modifying the SiC surface using functional silanes (e.g. aminoethyl-aminopropyl-trimethoxy-silane).<sup>19</sup> Details for preparation can be found elsewhere.<sup>20</sup> It is now possible to stabilise the two components of the composite in the same way, using a short (MW = 1000) polyacrylic acid (PAA) in water.<sup>21,22</sup> Adsorption isotherms of PAA were determined, using suspensions with 20 or 10 vol% solid loadings ( $\text{Al}_2\text{O}_3$ , SiC-mod, respectively). Each sample was prepared in exactly the same way by first adding a known amount of PAA into an aqueous solution which is stirred magnetically. By using NaOH as a base, the acidic solution was then adjusted to the desired pH value (between 7.2 and 9.6). Afterwards the powder was added slowly (79.4 g of  $\text{Al}_2\text{O}_3$  or 32.1 g of SiC-mod, total volume of each sample = 100 ml) and the pH value was constantly monitored and controlled within  $\pm 0.1$  pH units. For a necessary correction in the acidic direction hydrochloric acid (HCl) was used. When all of the powder was added to the water/PAA solution, the suspension was stirred magnetically and the pH value controlled until no further change could be detected (up to 2 h stirring was necessary). Each sample was then left on a mechanical shaker for 24 h to ensure equilibrium of the interaction between the polymer and the powder surface. Control of the pH value after this treatment showed that in some samples the pH value still shifted up to 0.2 pH units (towards a more basic value for  $\text{Al}_2\text{O}_3$  and towards a more acidic value for SiC-mod). For analysis, the pH-values after 24 h of shaking have been used for classification of the data points in the adsorption isotherms. For a given pH (e.g. 8.2

in the  $\text{Al}_2\text{O}_3$  adsorption isotherm) not all the samples are necessarily exactly at this point, but as close as possible ( $\pm 0.1$  pH units). The suspensions were then centrifuged, the PAA-containing supernatant adjusted to pH 12 (using 1 N NaOH) and titrated with 0.5 N HCl. Comparison with a calibration line (measured earlier) gives the amount of PAA left in the water and consequently the PAA adsorbed on the powder surface. For calibration, known amounts of PAA in aqueous solutions were titrated with 0.5 N HCl, beginning at pH 12 (adjusted with 1N NaOH) and ending at pH 1.5. The first derivative of the titration curve shows two peaks and their distance is linearly related to the amount of PAA in the slurry.<sup>22</sup>

Several suspensions at different pH values were prepared for each component separately in order to determine the rheological behaviour as a function of the pH value. As above, the samples were prepared by adding  $\text{Al}_2\text{O}_3$  or SiC-mod into an aqueous solution with the desired pH value and containing the appropriate amount of PAA to cover the whole powder surface. These values are pH-dependent and are taken from the adsorption isotherms. The solid loading of each of these samples was 50 or 15 vol% ( $\text{Al}_2\text{O}_3$ , SiC-mod, respectively, with a volume of 40 ml per sample). The pH value was controlled during and after the addition of the powder in the same way as above ( $\pm 0.1$  pH units from the adjusted pH value). The suspensions were stirred for 2 h, when no more pH change could be detected and were then examined in a cylinder rheometer (Physica Rheolab MC 20). The viscosity at a given shear rate was taken from the measured rheological curves and depicted in a diagram, using the pH value as *x*- and the viscosity as *y*-axis; thus, in each of the diagrams (one for  $\text{Al}_2\text{O}_3$ , one for SiC-mod) one data-point represents one suspension.

In another process, a small nonionic organic molecule (SOM) was used as a dispersing agent. The amount of SOM needed was optimised by measuring the viscosity as a function of concentration of the SOM for each component separately. The suspensions for these examinations had solid loadings of 40 and 20 vol% for SiC-mod and  $\text{Al}_2\text{O}_3$ , respectively (using 30 g powder each). For this system, control of the pH value was not as strictly necessary as above. The only requirement is staying in the acidic region around pH 5. To prepare the samples, aqueous slurries containing the SOM and some drops of acetic acid (HAc) were stirred magnetically and the powder added slowly. To improve dispersion, the samples were frequently ultrasonicated for 1 min, then stirred again. The pH value was always controlled, adding HAc when necessary. As above,

rheological data of each suspension were measured and viscosity at a given shear rate determined, which was found to be dependent on the amount of SOM used for stabilisation.

The PAA-stabilised slurries for various SiC contents were prepared, using the above determined optimised parameters of pH value and PAA content. Again, the pH value was controlled exactly, this time using *n*-butylamine and acetic acid to avoid the presence of chloride and alkali in the samples and only small deviations from the ideal pH value were allowed ( $\pm 0.1$  pH-units). Homogenisation was conducted for 2 h in a roller mill, causing a small shift in the pH value (up to 0.1 pH units towards a higher pH value). SOM-stabilised slurries were prepared at pH 5, using the optimum amount of SOM determined earlier. Slurries were homogenised in a vibratory mill for several hours (preferably for 4 h). The pH values are shifted considerably (up to 1.3 pH units towards a more basic region) by milling, but this change does not affect the slurry properties. For both slurry systems, dispersion of the particles after milling was measured by a ultrafine particle analyser (UPA 150, Microtrack).

Green bodies with varying SiC/ $Al_2O_3$  ratios were prepared with both techniques by slip casting in a porous gypsum mould. Green densities were measured in mercury. Sintering was conducted under flowing Ar or  $N_2$  in a graphite furnace. Weight loss and densities of the sintered ceramic were determined (Archimedes' method). By evacuating the sample, pouring water over it, weighing under water and in air, open porosity is measured as well. Optical microscopy of a polished cross-section was used to examine the distribution of SiC in  $Al_2O_3$ .

## Results and Discussion

Chemical modification of the SiC surface shifts the isoelectric point (IEP) from pH 3 to 9.5<sup>19</sup> (compared to 9.0 of the  $Al_2O_3$ ) (Fig. 1).

The adsorption isotherms for the modified SiC (Fig. 3) and the  $Al_2O_3$  (Fig. 2) indicate the changing conformation of the PAA molecule with varying pH value. At low pH, the functional acidic groups of the PAA are not fully dissociated, thus the PAA is set in a coiled conformation. With increasing pH, dissociation increases, leading to repulsive negative forces, uncoiling the PAA chain. As a consequence, at low pH more PAA is needed to cover the powder surface than at higher pH, which is clearly visible in the adsorption isotherms (Figs 2, 3; wt% refers to the total amount of powder). To get a better understanding

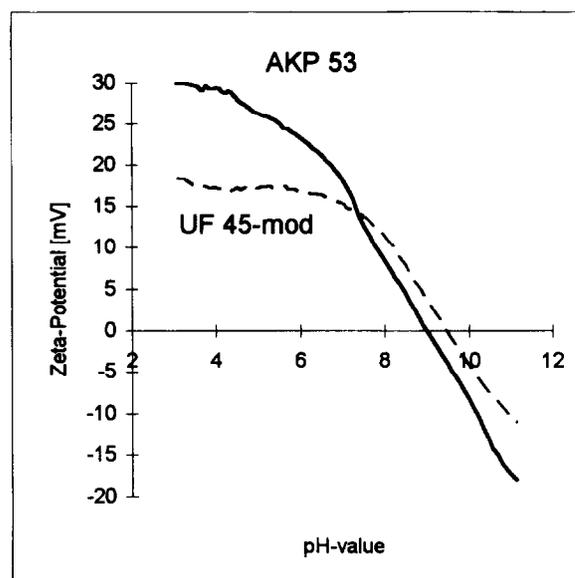


Fig. 1. Zeta potentials of SiC-mod and  $Al_2O_3$ .

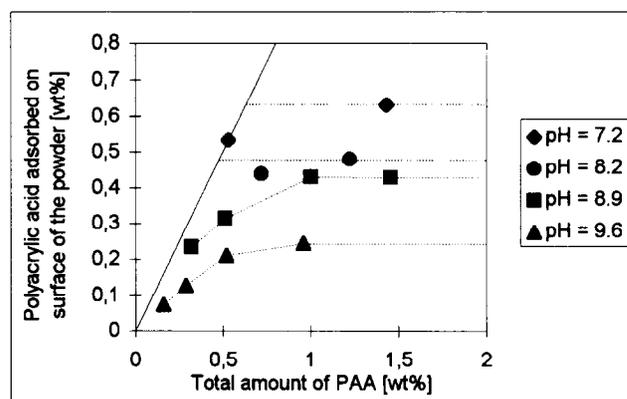


Fig. 2. Adsorption isotherm of  $Al_2O_3$ .

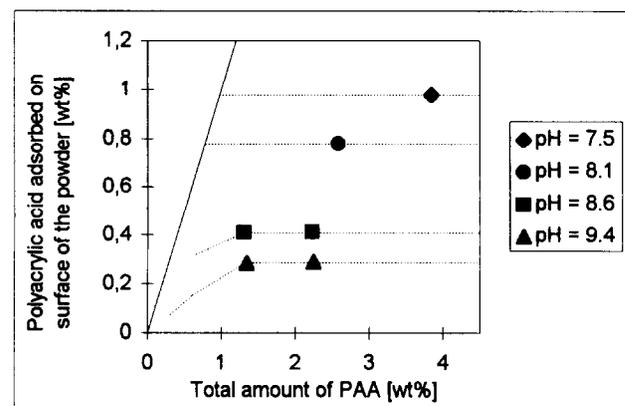


Fig. 3. Adsorption isotherm of SiC-mod.

of the interaction between powder and polymer, one also has to consider the pH-dependent surface charge of the powder (Fig. 1). Below the IEP, each powder is positively charged, thus allowing a strong attraction to the negatively charged PAA. Above the IEP, the force of attraction changes (both powder and PAA are negatively charged now), but still PAA can be found on the powder surface.<sup>21,22</sup>

The diagonal drawn in the adsorption isotherms is a hypothetical line, marking the points where the amount of added PAA equals the amount of PAA on the surface of the powder. When adding a large surplus of PAA into a slurry of  $\text{Al}_2\text{O}_3$  or SiC-mod, the amount of PAA adsorbed on the powder surface was found to be nearly constant (Figs 2, 3; points located as far away from the diagonal as possible). One could now expect that this amount is sufficient to cover the powder surface and optimally stabilise the slurry. To emphasise this idea, some extrapolated horizontal lines have been drawn into the diagrams on the basis of the data points determined for a surplus of added PAA. The experiments show, though, that when adding less PAA to the solution, the data points do not follow the extrapolated horizontal lines but decrease to lower values. For clarity, a look at Fig. 2 reveals the experimental facts. At a given pH of 8.9, approximately 0.4 wt% of PAA can be found on the powder surface when adding  $\geq 1$  wt% PAA into the solution, thus 0.6 wt% PAA is left in the liquid and not adsorbed. When decreasing the amount of added PAA (0.5 wt%), only about 0.3 wt% PAA is located on the powder surface. Further decrease of the PAA content leads to even less PAA on the powder, which results in solidification of the slurry as stabilisation cannot be realised any more. These solidifications could be found for all the data points close to the diagonal when shaking the sample slurries for 24 h. The difficulty is now to find the optimum amount of PAA needed for stabilisation. As has been explained, the values determined from the intersection of the extrapolated horizontal lines with the diagonal at a given pH are not sufficient for complete coverage of the powder surface because they are only valid for a large surplus of PAA. On the other hand, these hypothetical values characterise the adsorption saturation for a specific powder at a given pH and are as such reproducible and important data. As a consequence, when working with these hypothetical values to stabilise PAA slurries, a surplus of 20% (based on experimental experience) has to be added to avoid solidification. The data points of pH 8.9 in Fig. 2 can once again provide a good example: the adsorption saturation is located close to 0.4 wt% (extrapolated value). When providing only this amount of PAA in the slurry, solidification would result, as has been found experimentally. Increasing the total amount of PAA to about 0.5 wt% leads to a stable slurry. As can be seen in Fig. 2 only about 0.3 wt% of PAA is expected to be located on the powder surface, an amount which lies below the adsorption saturation, but is still high enough to ensure a stable slurry. It is interesting to note

that, even when using two or three times more PAA than necessary for stabilisation, the rheological slurry properties should not be affected, as the PAA used has only a molecular weight of 1000.<sup>21,22</sup>

The rheological examination of the pure  $\text{Al}_2\text{O}_3$  slurries (50 vol% solid loading) showed a minimum viscosity at pH 9 (equals the IEP of  $\text{Al}_2\text{O}_3$ , see Fig. 1) regardless of the applied shear rate (Fig. 4, each data point is one suspension) whereas the SiC-mod slurries did not show any minimum (Fig. 5). Instead, the viscosity decreases steadily with increasing pH. The pure SiC-mod slurries showed a strong increase in viscosity with rising solid loading, only allowing 15 vol% of solid content.

From the adsorption isotherms and the rheological data the optimal parameters for slurry preparation were determined to be pH 9.2 and 0.5 wt% of PAA for both components. Composite slurries with 5, 15 and 25 vol% SiC/ $\text{Al}_2\text{O}_3$  could be realised (44, 40, 35 vol% solid loading, respectively). The reason for a decreasing solid loading with increasing SiC content is a specific interaction of the SiC-mod with the PAA, which causes an increase in viscosity and a strong pseudoplastic behaviour of the slurry. As the slurry has to meet the requirements of slip casting, a minimum of 35 vol% of solid loading has to be realised, thus

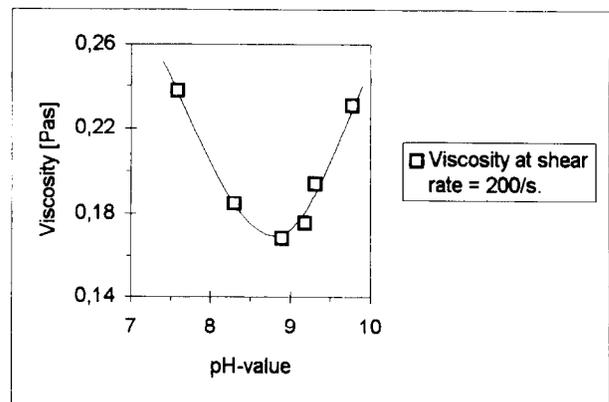


Fig. 4. Viscosity as a function of the pH value for a PAA slurry of  $\text{Al}_2\text{O}_3$  (50 vol% solid loading).

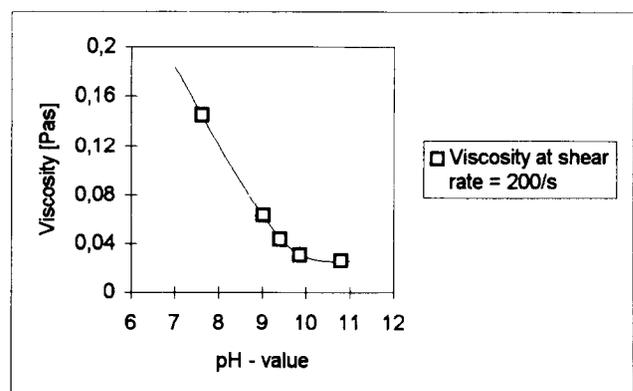


Fig. 5. Viscosity as a function of the pH value for a PAA slurry of SiC-mod (15 vol% solid loading).

limiting the system to 25 vol% SiC only. Higher SiC contents would require slurries with lower solid loadings than 35 vol% and thus are not interesting for this application (Figs 6, 7). The green densities were found to decrease with increasing SiC content (see Fig. 11). Pressureless sintering in  $N_2$  at  $1800^\circ C$  yielded samples of 98.2, 90.8 and 76.8% theoretical density for 5, 15 and 25 vol% SiC/ $Al_2O_3$ , respectively. Optical microscopy revealed large agglomerates of SiC in the sample (up to  $5 \mu m$ ) as well as large areas (up to  $20 \mu m$ ) with no SiC at all (Fig. 21). It was thus necessary to develop a new way to stabilise the aqueous slurry to ensure homogeneous distribution of both components.

A small organic molecule (SOM) at pH 5 was found to give excellent results for slurry prepara-

tion. Examination of rheological behaviour as a function of the pH value for several 40 vol% pure SiC-mod slurries revealed a minimum of viscosity at 2.5 wt% SOM (referring to the total amount of powder, Fig. 8). The same amount of SOM was found to optimally stabilise pure  $Al_2O_3$  suspensions. The solid loading of composite slurries could easily be increased to 47 vol% regardless of the SiC content (Fig. 10) and the resulting slurries did not show the pseudoplastic properties of comparable PAA slurries (Fig. 9). Green densities were improved, too, compared to the PAA slurries (62, 61, 60% for 5, 15, 25 vol% SiC, respectively see Fig. 11). In a vibratory mill, the viscosity of the composite slurries decreased for the first 4 h and did not change any further afterwards (Fig. 12). The measured size of the particles in the slurry did not change during this milling procedure (Fig. 13), indicating that the rheological change observed is only due to a homogenisation effect.

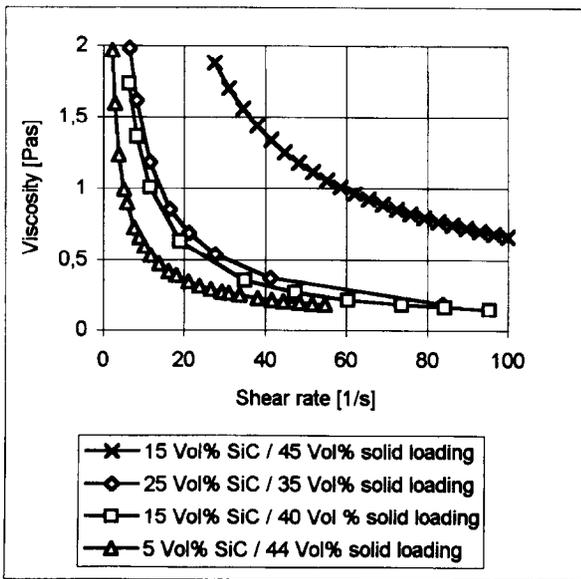


Fig. 6. Viscosity as a function of solid loading and SiC content of PAA slurries stabilised at pH 0.2. Increasing the SiC content causes strong rise in viscosity.

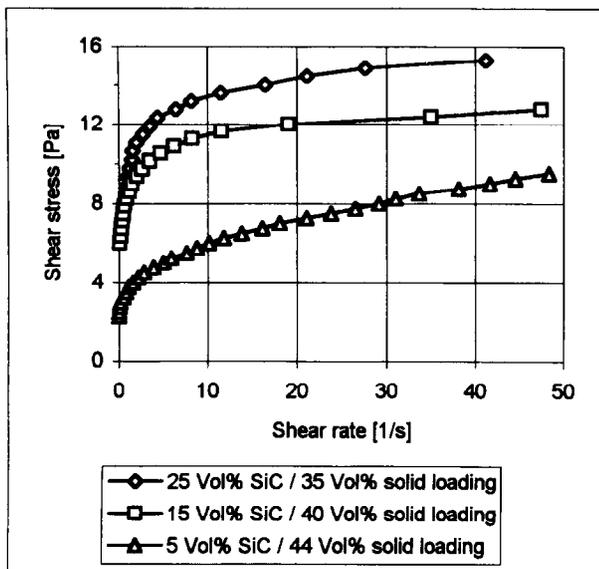


Fig. 7. Shear stress as a function of SiC content and solid loading of a PAA slurry at pH 9.2.

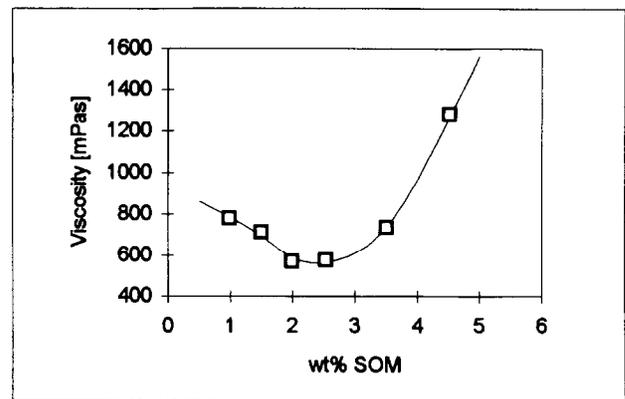


Fig. 8. Viscosity at  $52 s^{-1}$  as a function of the SOM concentration for a SiC-mod slurry with 40 vol% solid loading (wt% referring to the total amount of powder).

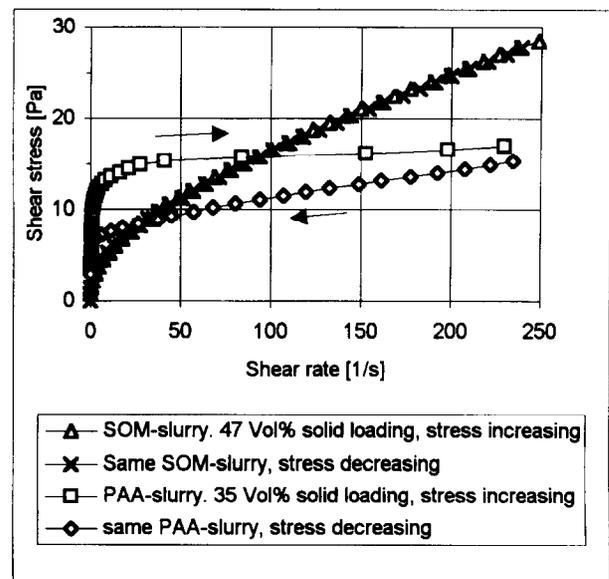


Fig. 9. Comparison between two slurries with 25 vol% SiC/ $Al_2O_3$ . The pseudoplastic behaviour of the PAA slurry is visible.

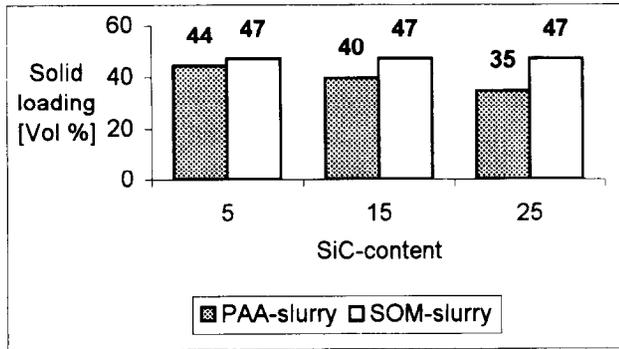


Fig. 10. Maximum possible solid loadings of composite slurries as a function of SiC content.

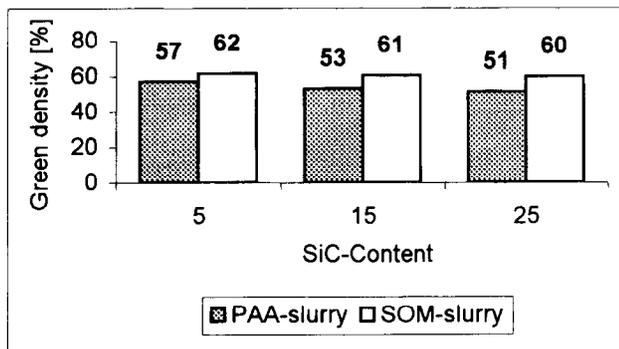


Fig. 11. Green densities of composite samples as a function of SiC content.

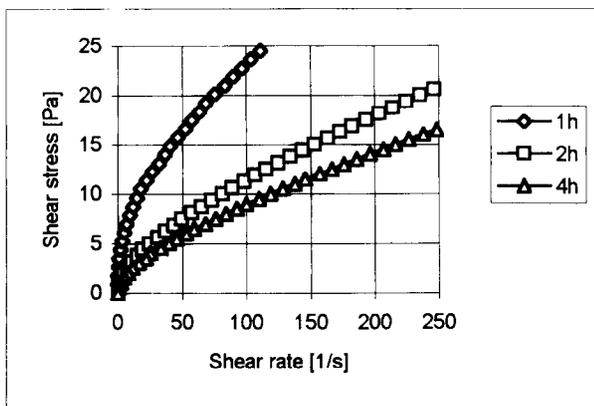


Fig. 12. Shear stress as a function of milling time in a vibratory mill for a SOM slurry with 5 vol% SiC and 47 vol% solid loading. Milling longer than 4 h does not further change rheology.

Increasing the SiC content in the slurry led to a higher viscosity (Fig. 14), though the solid loading did not have to be decreased as for PAA slurries with comparable SiC contents (Fig. 7). It is thus possible to make composite slurries of any desired composition with 47% solid loading. All composite slurries were milled for 4 h to ensure homogeneity and discs of 5.5 cm diameter were prepared by slip casting.

Sintering of samples prepared from SOM slurries was conducted under  $N_2$  or Ar at various temperatures (with different SiC contents: 0, 2.5, 5, 10, 15, 25 vol% SiC). A sintering map can be

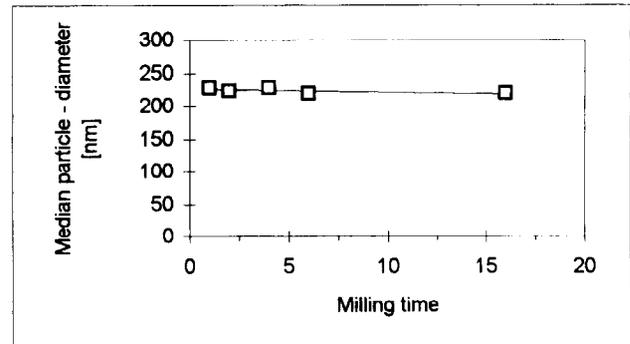


Fig. 13. Particle size distribution in SOM slurries (47 vol% solid loading) as a function of milling time.

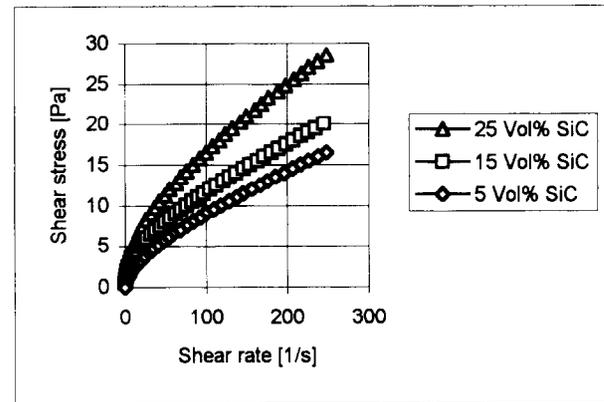


Fig. 14. Shear stress as a function of SiC content for SOM slurries, each containing 47 vol% of solid loading. All slurries are homogenised 4 h in a vibratory mill.

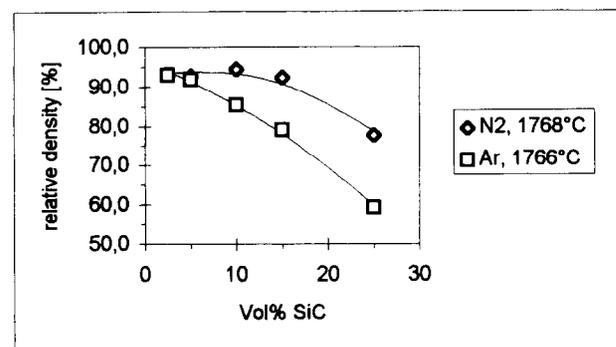


Fig. 15. Relative densities as a function of SiC content and sintering atmosphere at 1767°C. Samples were prepared from a SOM slurry.

drawn from these results. For each composite the density when sintered in  $N_2$  was different, compared to sintering in Ar (for 1767°C see Fig. 15). It is interesting to note that the difference between relative densities increases with increasing SiC content and that for this temperature (1767°C), all the relative densities were higher in  $N_2$  than in Ar. Increasing the temperature when sintering in Ar does not change the relative densities considerably (Fig. 16), thus it shows that densification is limited to below 95% of theory and is even lower for high SiC contents (only around 60% of theory for 25 vol% SiC). Extensive studies of sintering

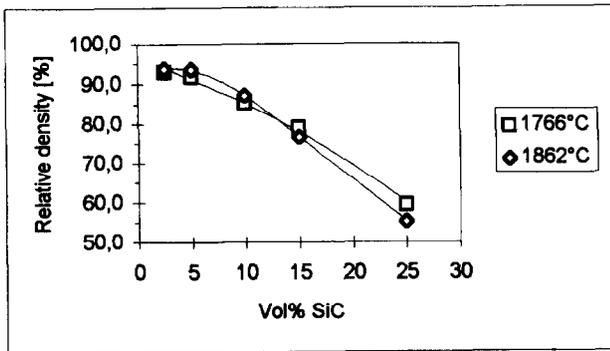


Fig. 16. Relative densities as a function of temperature when sintering in Ar. Samples were prepared from a SOM slurry.

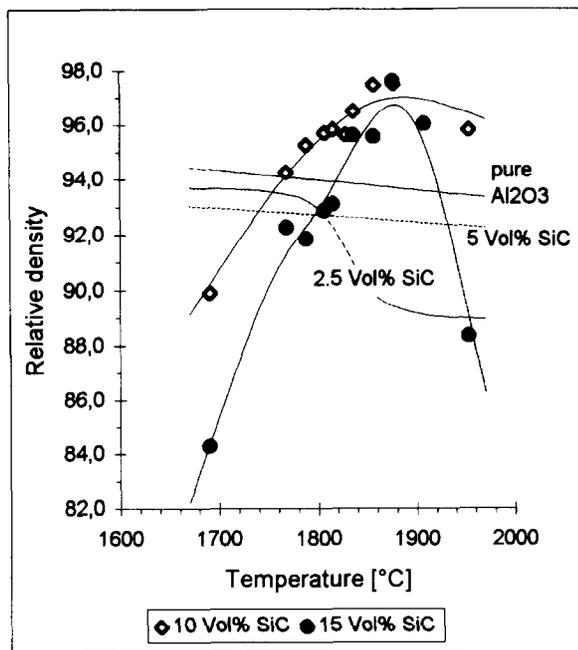


Fig. 17. Densities after sintering in  $N_2$  for 1 h as a function of temperature and SiC content. Samples were prepared from a SOM slurry. For clarity, data points are only shown for 10 and 15 vol% SiC samples.

conducted under flowing  $N_2$  show surprising results (Fig. 17). While the relative densities of pure  $Al_2O_3$  and samples containing 5 vol% of SiC do not change considerably with temperature and are generally low (values around 94 and 93% of theory), samples containing 2.5 vol% SiC show a strong decrease in relative densities when exceeding temperatures of about 1840°C. High densities can be obtained for 10 and 15 vol% SiC content, reaching peak values of 97.5% of theory when sintered at 1880°C for 1 h in  $N_2$ . Samples with 25 vol% SiC never yielded densities better than 80% (Fig. 15). When sintering at very high temperatures (1950°C), all the samples showed visible deformation effects on the surface, indicating the existence of evaporating components. The thermodynamics of the  $SiC/Al_2O_3$  composite system<sup>23,24</sup> has to be considered when trying to conduct sintering at high temperatures without pressure

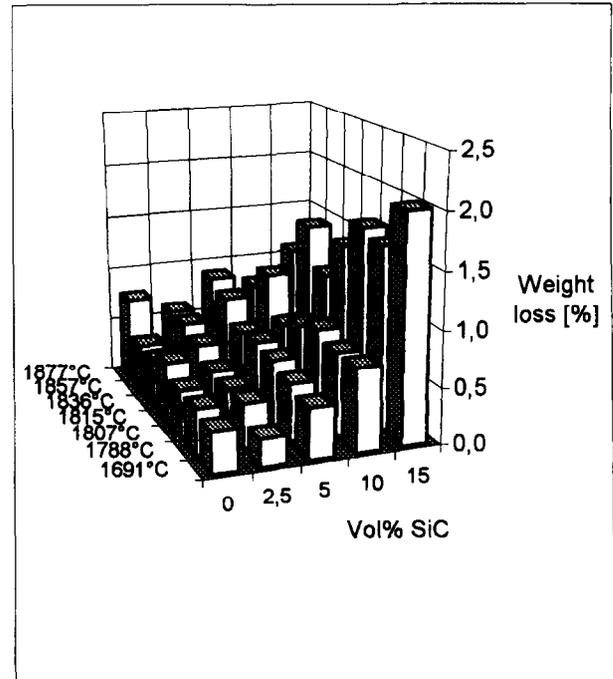


Fig. 18. Weight loss when sintering in  $N_2$  as a function of SiC content and temperature. Samples were prepared from a SOM slurry.

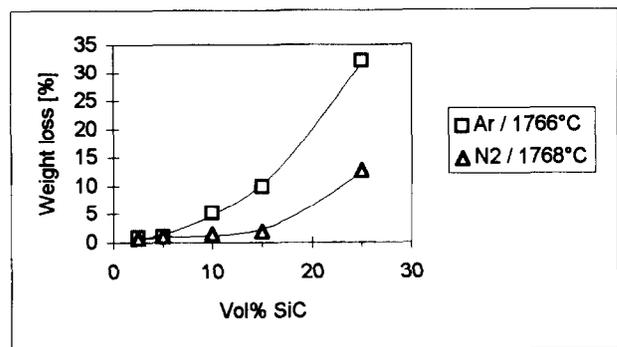


Fig. 19. Weight loss as a function of SiC content for different sintering atmospheres. Samples were prepared from a SOM slurry.

(when hot pressing, these problems are suppressed). The predominant gaseous species that can form are SiO, CO,  $Al_2O_3$  and Al(g). As a consequence, temperature-dependent weight loss is expected to occur and was measured as a function of SiC content. Weight losses in  $N_2$  were found to be negligible up to 10 vol% SiC, slightly increasing at 15 vol% SiC (up to 2 wt% loss, Fig. 18) and strongly increasing at 25 vol% (> 10 wt% loss, Fig. 19). Weight loss in Ar is generally much higher than when sintering in  $N_2$  (Fig. 19) and more than 50 wt% loss (1862°C, 25 vol% SiC, Fig. 20) was found.

X-ray diffraction analysis on a polished sintered specimen of 10 vol% SiC content sintered at 1830°C in  $N_2$  (relative density = 95.5%) confirmed the sole presence of  $Al_2O_3$  and SiC, whereas on the unpolished surface of identical samples, more phases could be detected: AlN,  $\epsilon-SiAl_7O_2N_7$ , and

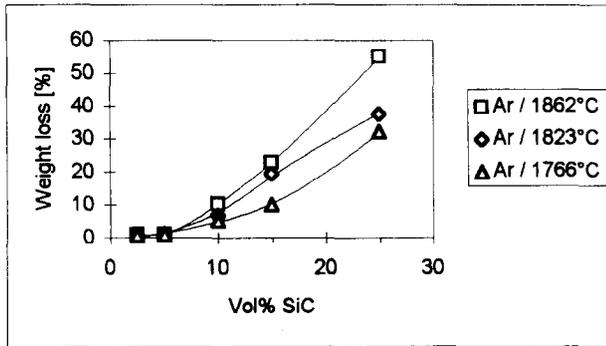


Fig. 20. Weight loss as a function of SiC content and temperature when sintering in Ar. Samples were prepared from a SOM slurry.

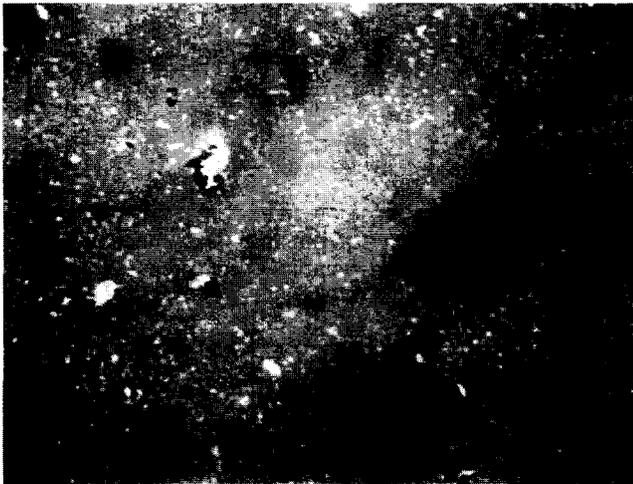


Fig. 21. Optical micrograph of a polished cross-section of a sample containing 5 vol% SiC/Al<sub>2</sub>O<sub>3</sub> prepared by the PAA slurry route. White particles represent SiC. Large areas of Al<sub>2</sub>O<sub>3</sub> with no SiC included are visible. Darkest areas show pores (98% relative density).

Al<sub>11</sub>O<sub>15</sub>N were found in minor traces. This suggests, that sintering in N<sub>2</sub> will lead to a very thin reaction layer surrounding the sample, while the original composition is preserved inside. This does not exclude the existence of additional phases at the grain boundaries.

An important fact to consider for densification is the existence of liquid phases, that might form at higher temperatures.<sup>25-28</sup> As SiC is always covered by a thin layer of SiO<sub>2</sub>, mullite (3 Al<sub>2</sub>O<sub>3</sub>.2 SiO<sub>2</sub>) can form by the reaction with Al<sub>2</sub>O<sub>3</sub>. The melting point of mullite is located between 1828 and 1890°C<sup>25-27</sup> and it thus lies within the temperature region examined for sintering. A second melt can form by an Al<sub>2</sub>O<sub>3</sub>-10 mol% Al<sub>4</sub>C<sub>3</sub> eutectic at 1827°C.<sup>28</sup> Whether the Al<sub>2</sub>O<sub>3</sub>/SiC system provides enough Al<sub>4</sub>C<sub>3</sub> for this melt to exist in significant amount is not known and still has to be investigated by a thorough examination of grain boundaries, which will be done in the future. A look at Fig. 17 shows that a possible discussion of

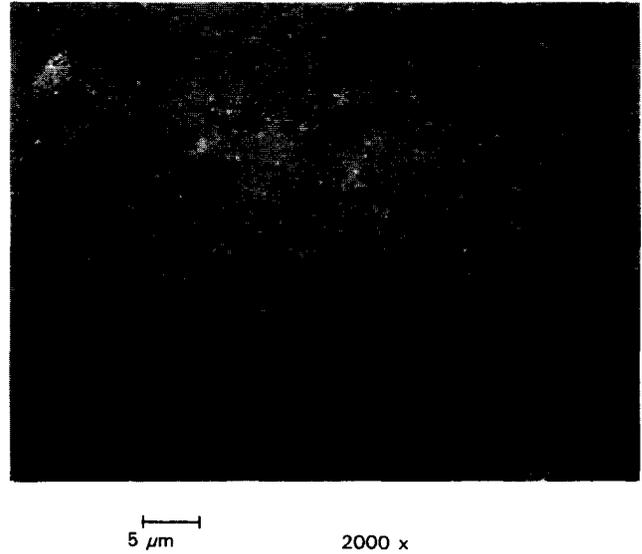


Fig. 22. Optical micrograph of a polished cross-section of a sample containing 5 vol% SiC/Al<sub>2</sub>O<sub>3</sub> prepared by the SOM slurry route. White particles represent SiC<sub>2</sub>, dark, larger areas indicate pores (92% relative density). Homogeneous distribution of the phases is apparent.

appearing liquid phases when sintering at higher temperatures only seems to be important for samples with higher SiC content (10 and 15 vol%), as these samples show peak values of relative densities around 1880°C. For samples with lower SiC content, a different behaviour was found, revealing a slight (pure Al<sub>2</sub>O<sub>3</sub>, 5 vol% SiC) or rather strong (2.5 vol% SiC) decrease in relative density with increasing temperature. The reason for this difference might be the overall presence of a melt in the whole sample which can obviously be realised in samples with higher SiC content. When the SiC content is too low, melts can form locally, but as they do not co-mingle, they cannot affect the densification process. The value of 10 vol% SiC can be compared to concentrations of SiC needed to affect percolation-dependent properties, such as the electrical conductivity (Al<sub>2</sub>O<sub>3</sub> is non-conducting and SiC is semi-conducting). It was found,<sup>7</sup> that a big change of conductivity in samples prepared by hot-pressing occurred at 15 vol% SiC, a value that exceeds the 10 vol% found in this paper, but lies in the same range as the determined value.

Optical microscopy on polished cross-sections of sintered specimens confirms homogeneous distribution of SiC in the Al<sub>2</sub>O<sub>3</sub> matrix (Fig. 22).

## Conclusions

Homogeneous slurries with high solid loadings (47 vol%) and no restriction to the SiC/Al<sub>2</sub>O<sub>3</sub> ratio can be produced, using a small organic molecule

(SOM) as a dispersing agent. Problems in the other developed method of powder handling using polyacrylic acid (PAA) to stabilise the suspension, arise from a specific interaction between the SiC-mod and the polymer, thus limiting the system to 25 vol% SiC content and below. Sample preparation by slip casting into a porous mould leads to green bodies with high densities (up to 62% of theory). Samples of the PAA system containing only 5 vol% of SiC could be densified to 98.2% at 1800°C in N<sub>2</sub>, compared to 93.2% of the comparable SOM sample. The reason for this difference is not understood at the moment. Samples with higher SiC content (10, 15 vol%) in the SOM system can be densified to high values (> 97%), a phenomenon that still has to be examined.

### Acknowledgement

The authors would like to thank Dr M. Aslan and Dr R. Naß of the 'Institut für Neue Materialien (INM)' in Saarbrücken, Germany, for their experimental support and technical advice.

### References

- Smith, S. M. & Singh, J.P., Processing and characterization of SiC-whisker-reinforced alumina-matrix composites. *J. Am. Ceram. Soc.*, **76**(2) (1993) 497-502.
- Hansson, T., Warren, R. & Wasen, J., Fracture toughness anisotropy and toughening mechanisms of a hot-pressed alumina reinforced with silicon carbide whiskers. *J. Am. Ceram. Soc.*, **76**(4) (1993) 841-848.
- De Arellano-Lopez, A. R. & Dominguez-Rodriguez, A., Plastic deformation mechanisms in SiC-whisker-reinforced alumina. *J. Am. Ceram. Soc.*, **76**(6) (1993) 1425-1432.
- Zeng, K., Breder, K. & Rowcliffe, D., Comparison of slow crack growth behavior in alumina and SiC-whisker-reinforced alumina. *J. Am. Ceram. Soc.*, **76**(7) (1993) 1673-1680.
- Chou, Y. S. & Green, D. J., Silicon carbide platelet alumina composites: I, Effect of forming technique on platelet orientation. *J. Am. Ceram. Soc.*, **75**(12) (1992) 3346-3352; II, Mechanical properties. *J. Am. Ceram. Soc.*, **76**(6) (1993) 1452-1458; III, Toughening mechanisms. *J. Am. Ceram. Soc.* **76**(8) (1993) 1985-1992.
- Niihara, K., New design concepts of structural ceramic-ceramic nanocomposites. *J. Ceram. Soc. Jpn.*, **99**(10) (1991) 974-982.
- Sawaguchi, A., Toda, K. & Niihara, K., Mechanical and electrical properties of Al<sub>2</sub>O<sub>3</sub>/SiC nano-composites. *J. Ceram. Soc. Jpn, Int. Ed.*, **99**(6) (1991) 510-513.
- Nakahira, A. & Niihara, K., Sintering behaviors and consolidation process for Al<sub>2</sub>O<sub>3</sub>/SiC nanocomposites. *J. Ceram. Soc. Jpn.*, **100**(4) (1992) 448-453.
- Nakahira, A., Sekino, T., Suzuki, Y. & Niihara, K., High-temperature creep and deformation behaviour of Al<sub>2</sub>O<sub>3</sub>/SiC Nanocomposites. *Ann. Chim. Fr.*, **18**(5-6) (1993) 403-408.
- Piciacchio, A., Lee, S. H. & Messing, G. L., Processing and microstructure development in alumina-silicon carbide intragranular particulate composites. *J. Am. Ceram. Soc.*, **77**(8) (1994) 2157-2164.
- Zhao, J., Stearns, L. C., Harmer, M. P., Chan, H. M. & Miller, G. A., Mechanical behavior of alumina-silicon carbide 'nanocomposites'. *J. Am. Ceram. Soc.*, **76**(2) (1993) 503-510.
- Stearns, L. C., Zhao, J. & Harmer, M. P., Processing and microstructure development in Al<sub>2</sub>O<sub>3</sub>-SiC 'nanocomposites'. *J. Eur. Ceram. Soc.*, **10** (1992) 473-477.
- Wohlfromm, H., Processing and properties of Al<sub>2</sub>O<sub>3</sub>/SiC-nanocomposites. In *Proceedings of the International Conference Ceramic Processing Science and Technology*, 11-14 September 1994, Friedrichshafen (Bodensee), FRG (in print).
- Chaklader, A. C. D., Gupta, S. D., Lin, E. C. Y. & Gutowski, B., Al<sub>2</sub>O<sub>3</sub>-SiC composites from aluminosilicate precursors. *J. Am. Ceram. Soc.*, **75**(8) (1992) 2283-2285.
- Hsueh, C. H., Evans, A. G. & McMeeking, R. M., Influence of multiple heterogeneities on sintering rates. *J. Am. Ceram. Soc.*, **69**(4) (1986) C64-C66.
- Hillert, M., Inhibition of grain growth by second-phase particles. *Acta Metall.*, **36** (12) (1988) 3177-3181.
- Coble, R. L., Sintering crystalline solids. I. Intermediate and final stage diffusion models. *J. Appl. Phys.*, **32** (1961) 787-792.
- Zhao, J. & Harmer, M. P., Sintering kinetics for a model final-stage microstructure: a study of Al<sub>2</sub>O<sub>3</sub>. *Phil. Mag. Lett.*, **63**(1) (1991) 7-14.
- Aslan, M., Dörr, C., Nass, R. & Schmidt, H., Microstructural development and mechanical properties of pressureless sintered Al<sub>2</sub>O<sub>3</sub>/SiC composites. In *Proceedings of the International Conference Ceramic Processing Science and Technology*, 11-14 September 1994, Friedrichshafen (Bodensee), FRG (in print).
- Naß, R., Nonninger, R. & Schmidt, H., Oberflächenchemische Modifizierung von Submikron SiC-Pulver. *DKG Jahrestagung*, Bayreuth, 04-07.1992 (in print).
- Cesarano III, J. & Aksay, I. A., Processing of highly concentrated aqueous  $\alpha$ -alumina suspensions stabilized with polyelectrolytes. *J. Am. Ceram. Soc.*, **71**(12) (1988) 1062-1067.
- Cesarano III, J. & Aksay, I. A., Stability of aqueous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> suspensions with poly(methacrylic acid) polyelectrolyte. *J. Am. Ceram. Soc.*, **71**(4) (1988) 250-255.
- Misra, A. K., Thermochemical analysis of the silicon carbide-alumina reaction with reference to liquid-phase sintering of silicon carbide. *J. Am. Ceram. Soc.*, **74**(2) (1991) 345-51.
- Gadalla, A., Elmasry, M. & Kongkachuichay, P., High-temperature reactions within SiC-Al<sub>2</sub>O<sub>3</sub> composites. *J. Mater. Res.*, **7**(9) (1992) 2585-2592.
- Aramaki, S. & Roy, R., Revised phase diagram for the system Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. *J. Am. Ceram. Soc.*, **45**(5) (1962) 229-242.
- Aksay, I. A. & Pask, I. A., Stable and metastable phases equilibria in the system Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. *J. Am. Ceram. Soc.*, **58** (11-12) (1975) 507-512.
- Klug, F. J., Prochazka, S. & Doremus, R. H., Alumina-silica phase diagram in the mullite region. *J. Am. Ceram. Soc.*, **70** (10) (1987) 750-759.
- Lihmann, J. M., Zambetakis, T. & Daire, M., High-temperature behaviour of the aluminum oxycarbide Al<sub>2</sub>OC in the system Al<sub>2</sub>O<sub>3</sub>-Al<sub>4</sub>C<sub>3</sub> and with addition of aluminum nitride. *J. Am. Ceram. Soc.*, **72** (9) (1989) 1704-1709.