4.1 COATING OF SiC

4.1.1 ACTIVATION TREATMENT

Heat treatment of SiC particles in air at 600°C for 30 min indented for impurity burnout results in oxidation of SiC surfaces. The TG Analysis (Fig 3.1) indicate that this process is initiated at temperatures as low as 300-350°C corresponding to the onset of weight gain. This is attributed to the fine particle size and associated high surface area available for diffusion of molecular oxygen leading to the reaction. \(^{130}\)

\[
\text{SiC} + 2\text{O}_2 \rightarrow \text{SiO}_2 + \text{CO}_2
\]

The formation of amorphous silica on heat treated samples was then confirmed by FTIR as shown in Fig.3.3. The appearance of bands at \(\sim 1170, 1070\) and \(460\) cm\(^{-1}\) are due to amorphous silica resulting from the above reaction\(^{128}\). The XRD patterns of the SiC powder before and after heat treatment did not show changes in SiC confirming that the silica phases are amorphous.

It has been shown earlier by Krull et al\(^{69}\) that the silica rich surface layer in SiC particulates formed as a result of such thermal treatments has considerable influence on the microstructural features of the alumina-SiC composites processed from these powders. Formation of a glassy grain boundary phase arising out of the surface silica lead to discontinuous grain growth thereby lowering strength. It was then suggested to remove the surface silica by HF leaching. Washing thermally activated SiC particles in 10% HF removes this surface silica and has been confirmed
by FTIR (Fig 3.4) which shows complete absence of peaks due to amorphous silica after this treatment. Hence thermal activation followed by HF leaching has been used to activate SiC surfaces by removing both carbon and silica impurities.

4.1.2 PRECIPITATION OF ALUMINA PRECURSOR PHASE

In the present study coating of SiC particles with the alumina precursor phase is made through a controlled precipitation from aluminium nitrate solution. The conditions are set to precipitate the desired boehmite phase and avoid formation of bayerite phase. This is achieved by hydrolysing aluminium nitrate solution of concentration 0.025 M at temperatures T > 90°C until a pH level of 7-7.5 is attained. The chemistry of boehmite precipitation is discussed earlier in detail (Section 1.2.2.a of introduction).

Hydrolysis of aluminium nitrate in aqueous solution is a deprotonation process. In solution the salt dissociate forming Al$^{3+}$ ions followed by formation of the solvated cation Al(H$_2$O)$_6$. This undergoes extensive hydrolysis with hydroxyl ions from the added NH$_4$OH leading to the formation of a complex cation consisting of 13 Al atoms. When T > 90°C this polycation transforms to boehmite gel.

4.1.3 COATING MECHANISM

SiC particles in aqueous solution has the surface active silanol groups according to the equilibrium

$$\text{Si} - \text{OH}_2^+ \Leftrightarrow \text{Si} - \text{OH} + \text{H}^+$$

$$\text{Si} - \text{OH} \Leftrightarrow \text{Si} - \text{O}^- + \text{H}^+$$

Solvated cations of Al$^{3+}$ present in solution as Al(H$_2$O)$_6$ can be adsorbed on the SiC surfaces according to the equilibrium$^{104}$.

$$\text{Si} - \text{O}^- + \text{Al}^{3+} \Leftrightarrow \text{Si} - \text{O} - \text{Al}^{2+}$$
In the presence of a base this adsorbed layer undergoes further hydrolysis and condensation to precipitate boehmite leading to boehmite coated SiC particles. The reaction starts with chemical adsorption of a monolayer of the hydrolysed cations followed by addition of further layers which on subsequent hydrolysis and deprotonation lead to formation of boehmite. A schematic illustration of the coating process based on the above mechanism is presented in Fig. 4.1. The formation of boehmite is confirmed by both XRD and FTIR measurements. The FTIR pattern of SiC-25 wt% alumina powders in the gel state (Fig. 3.5) indicates a broad band at ~600 cm\(^{-1}\) indicating Al-O stretching vibrations of an octahedrally co-ordinated Al as in boehmite \(^{129}\). XRD patterns of the precipitated alumina precursor also confirmed the formation of boehmite. On calcination at 500°C the boehmite transforms to \(\gamma\)-alumina with a change in Al co-ordination and the corresponding FTIR pattern (Fig. 3.6) indicates the absence of band at ~600 cm\(^{-1}\).

BET surface area analysis of the coated powders (Fig. 3.7) shows an increase in surface area with increasing alumina fraction. The increase in surface area is due to the porous nature of the adherent coatings. Adsorption isotherm of uncoated SiC resemble that of a typical non porous solid as characterised by the type II behaviour. With coatings up to 15 wt% alumina the trend is more or less the same. On increase in alumina fraction the adsorption behaviour shift to that of type IV indicating mesoporosity (Fig. 3.8a). On calcination of the powders at 500°C, the surface area values drop by almost 41% for all samples. Adsorption isotherms (Fig. 3.8b) of the coated powders after calcination nearly indicate type II behaviour for
Fig 4.1 Schematic illustration of the coating process
lower alumina fractions and a tendency towards type IV behaviour with higher alumina content. This is attributed to the fact that on calcination the coated alumina precursor phase undergo morphological changes and phase transformations leading to coarsening of the fine particles. The FTIR pattern of the coated powder (Fig. 3.6) calcined at 500°C shows band corresponding to \( \gamma \)-alumina. In \( \gamma \)-alumina the Al co-ordination is a mixture of octahedrally and tetrahedrally co-ordinated Al. The band at 600 cm\(^{-1}\) represent that of octahedrally co-ordinated Al\(^{129}\). The AlO\(_4\) bands are usually around 800cm\(^{-1}\) and in the present case this has probably been overlapped with the \( \nu \)-Si-C band. The t-plot analysis of the isotherms (Figs. 3.9a and 3.9b) also confirmed presence of mesoporosity in samples with 15-25 wt % alumina coatings.

TEM observation of the alumina coated SiC powders (Figs. 3.10 a-d) indicate that the coatings appear as layers of fine precipitates adhering firmly to available SiC surfaces. Thickness of the coating varies from surface to surface though even at SiC-5 wt% alumina composition it is difficult to notice any uncoated SiC particles. The average layer thickness is in the range of 50 to 100nm. Coatings appear to be low dense with an open structure and have high surface area as confirmed by BET measurements. With increasing amounts of alumina the coated SiC particles tend to bridge each other and at SiC-25 wt% alumina composition agglomerates of coated SiC particles are seen.

As observed earlier in the case of alumina coating of silicon nitride powder\(^{97}\) the present process also suggests that the alumina precursor adheres to SiC surfaces during the precipitation stage by nucleation and growth process. This has been confirmed by a centrifugation technique where the coated particles showed no
separation of the fine adherent coatings on fast centrifuging from the SiC surfaces. TEM picture (Fig. 3.11) of the SiC-25 wt% alumina powders, as precipitated, shows individual SiC particles covered with fine particles of boehmite confirming this proposition.

At lower amounts of coating the alumina precursor phase covers entirely the SiC surface and is also found to contain no isolated areas of precipitated alumina alone. However it is possible that the coated particles tend to bridge each other through the alumina phase. This tendency is more pronounced with increasing alumina fractions. Moreover on subsequent drying and calcination the SiC particles coated with > 15 wt% alumina fractions form agglomerates. Hence for incorporation of such particles in the processing of composites the coating alumina phase has been restricted to 15 wt% level.

Zeta Potential measurements as presented in Fig 3.12 indicate that the uncoated SiC particles have an iso electric point (IEP) at pH 3.7 below which it has a

![Graph](image)

**Fig. 4.2 Increase in isoelectric points (IEP) of alumina coated SiC particles**
positive surface charge and above a negative surface charge. The pure alumina particles have an iso electric point at pH 9. The coated SiC particles starting with SiC- 5wt% alumina shows a remarkable difference with that of their uncoated counterparts. The IEP is shifted from 3.7 to over pH 7 for SiC-5 wt% alumina coatings which support the earlier proposition that the entire SiC surface is modified as a result of this coating technique. With increase in alumina concentration the IEP goes closer to that of alumina and reaches its maximum of 8.7 at SiC-25 wt% alumina as explained in Fig. 4.2

The present coating technique is based on the heterogeneous precipitation method where fine SiC particles act as nucleation sites for the coating phase. This is based on the fact that in aqueous solution, as discussed in the mechanism of coating, SiC particles contain hydroxyl groups which react with hydrolysed cations of Al³⁺ leading to formation of boehmite. Hydrolysis of dilute aluminium nitrate solution (0.025 M) in presence of activated SiC powders in suspension leads to boehmite coatings under the conditions of T >90°C and a precipitation pH of 7-7.5. The coatings appear as thick precipitates adhering firmly and covering fully the available SiC surfaces. Coatings are extremely fine and less dense. Calcination of these powders at 500°C lead to transformation of boehmite to γ-alumina rich phase. Such coated powders can be effective dispersoids in processing of alumina-SiC nanocomposites.
4.2 PROCESSING OF COMPOSITES

Thermal analysis of the as received boehmite powder indicate that the $\alpha$-alumina transformation temperature is at 1220°C as characterised by the exothermic peak in DTA (Fig 3.13). The formation of $\gamma$-alumina occurs at 455°C as indicated by the endothermic peak in DTA. The whole transformation is accompanied by around 22% weight loss associated with dehydration at $T < 120$°C and dehydroxylation in the temperature range 200-500°C. On incorporation of $\alpha$-alumina seeds the transformation temperature is lowered by 80°C (DTA plot in Fig. 3.14) making use of epitaxial nucleation benefits $^{21-25}$. DTA pattern of the composite precursor (Fig. 3.15) indicates the $\alpha$-alumina formation temperature to be around 1153°C in presence of SiC particles. There is a broad exothermic peak around 300°C and is assigned to the decomposition of nitrates formed during the precipitation of coating phase from aluminium nitrate solution.

4.2.1 EFFECT OF SEEDING ON PHASE TRANSFORMATION

The effect of seeding on $\alpha$-alumina phase transformation in composite precursor gels was then investigated in detail by varying the amount of seeds and following the $\alpha$-alumina transformation temperature from transition aluminas in DTA. It has been observed that a seed concentration only up to 2% by weight (Fig 3.21) of alumina show a significant reduction in transformation temperatures. This is due to the fact that the nucleation rate at which the metastable transition alumina phase transforms to stable $\alpha$-alumina phase is proportional to the nucleation sites / volume. As seed particles are shown to provide $^{27}$ multiple nucleation sites no further increase in transformation kinetics is expected with a decrease in spacing between
seeded particles within a given volume of matrix. Incorporation of α-alumina seeds provide nuclei for the transformation and according to classical heterogeneous nucleation theory this reduces the activation energy required for the transformation thereby lowering the temperature of α-alumina formation. The choice of α-alumina is based on the prerequisite that the lattice parameter mismatch between the final stable phase and the added seed phase should be within 5%.

The enhanced α-alumina phase transformation in seeded samples were further followed by XRD (Fig 3.16). On calcination of composite precursor gels with 2% α-alumina seed at 1000°C / 2h in N₂ the phase composition is a mixture of δ, θ transition aluminas and α-alumina while an unseeded gel forms a mixture of transition aluminas only at identical conditions.

4.2.2 DENSIFICATION

The densification behaviour (Fig 3.22) of sol gel composite precursor with and without α-alumina seeds on sintering from 1550°C to 1700°C shows that the seeded samples attain higher densities than the unseeded counterparts at a given sintering temperature. Moreover densities greater than 96% TD could not be achieved for samples without seed even on sintering at 1700°C for 90 min. This has been observed earlier also in sol gel derived alumina and is attributed to the finer grain size of alumina matrix obtained as a result of seeding. It is suggested that in presence of seed particles the growth of α-alumina into the transition alumina matrix is controlled due to which an aggregate free structure is formed. In the absence of seed the transformation first requires the formation of α-alumina nuclei which involves higher activation energy than in the absence of seed and the subsequent growth of the α-alumina colony results in an aggregated structure.
Alternatively Roy and Yarbrough explained based on the concept of epitaxial nucleation in line with classical sintering theory. When pores are trapped in the interstices of grains as a result of the vermicular growth it is not easy to eliminate them and hence may coalesce and grow in size as grain growth occurs. On the other hand if pores are associated with high angle grain boundaries they are readily eliminated by vacancy diffusion along grain boundaries. This is reflected on the densification behaviour of seeded and unseeded composites where retention of porosity amounting to 3% is observed in unseeded samples even after sintering at 1700°C for 90 min.

4.2.3 MICROSTRUCTURE DEVELOPMENT

The effect of α-alumina seeding on the microstructure development is explained based on SEM observations of polished and thermally etched specimens. At 1550°C (Fig. 3.25a and Fig 3.31a) both seeded and unseeded samples are seen to possess closed porosity. The average matrix grain size in seeded samples is less than 1 μm with grains having equiaxed morphology. The pores are around 500 nm in size though bigger pores are also seen scattered. However the unseeded samples show elongated grains with an average grain size slightly above 1 μm. The elongated morphology of the unseeded samples stems out from the distinctive vermicular growth arising out of porosity redistribution during formation of α-alumina from transition alumina matrix.

On sintering the samples at 1650°C/1h under 80 bar argon pressure the seeded samples achieved 98% TD and the microstructure (Fig 3.26 and 3.27) shows fine grains with uniform distribution of SiC particles. SiC particles are mostly located at the grain boundaries and a few are also seen within the matrix grains.
Messing et al \textsuperscript{57} demonstrated that entrapment of SiC particles takes place during vermicular growth of $\alpha$-alumina phase into the transition alumina matrix. In the case of seeded precursors this mechanism is non operational as the seeds provide nucleation sites for the crystallisation of $\alpha$-alumina. Hence it is reasonable to have reduced intergranular SiC in the case of seeded samples.

There is a marked difference in the dispersion of SiC particles in the unseeded counterpart. SiC particles are getting accumulated at the triple points (Fig. 3.31 b) and the dispersion is non uniform. SiC particles are hardly seen within the grains. This is in contrary to the reported work earlier \textsuperscript{57} where a model based on the growth of $\alpha$-alumina into the transition alumina was proposed for development of intragranular composites. However it was also mentioned that the coarsening of SiC particles at the grain boundary retard the grain boundary breakaway and decreases the tendency for second phase entrapment. As observed in Figs 3.31b and 3.31c SiC particles have undergone significant clustering and coalescence during grain growth thereby reducing grain boundary breakaway. Most of the SiC particles are swept to the grain boundary triple junctions. On sintering the composite precursors at 1700/90 min the samples attained excellent densification (99.2 \% TD) for the seeded composition and the microstructure (Fig 3.28 and 3.29) shows homogeneous distribution of SiC particles. There is grain growth compared to samples sintered at 1650°C and average matrix grain size is of the order of 4 $\mu$m.

The change in microstructures for the unseeded composites on increasing the sintering temperature from 1550 to 1700°C is noteworthy. The microstructure at 1550°C shows good dispersion of SiC particles and hardly any agglomerates could be observed. There is a significant amount of particle coarsening and agglomeration of SiC particles on increasing the sintering temperature to 1650...
and 1700°C. This suggests a difference in grain boundary mobility of the matrix alumina in presence of seeds during the final stages of sintering. A uniform grain boundary movement assisted by the pinning effects of homogeneously distributed SiC particles result in uniform, fine grained and dense microstructures in seeded samples. In the unseeded counterpart the SiC particles are getting dragged by grain boundaries, the mechanism of which remain unclear as the SiC particles are not capable of diffusion at these temperatures.

In summary seeding in alumina-5vol% SiC composite precursor gels was found to favour α-alumina transformation at lower temperatures, promote densification to values greater than 99.2% TD and prevent agglomeration of SiC particles leading to fine grained, uniform microstructures.

### 4.3 DENSIFICATION AND GRAIN BOUNDARY PINNING

The densification data of monolithic alumina and alumina-5 vol.% SiC nanocomposites as shown in Figure 3.23 shows that the presence of SiC particles severely inhibit densification. The composite sample attain only ~95 % TD compared to >99% for monolithic alumina on sintering at 1550°C. For the same degree of densification in composite samples a sintering temperature of 1700°C is required. However the microstructures of nanocomposite samples have much finer grain sizes compared to alumina though sintering temperature of composite samples were 100°C or more higher for same degree of densification. This suggests that the second phase SiC particles could be pinning grain boundaries\textsuperscript{76,77,78} preventing grain growth in alumina.
Fig. 4.3 shows the AFM micrograph of alumina and composite samples having nearly the same densities of > 99% TD. Figure 4.3a shows the microstructure of alumina with grains having straight grain boundaries. On the other hand alumina-5 vol% SiC composites show irregularly shaped grains and distorted grain boundaries as in Fig 4.3b. The presence of SiC particles along the grain boundaries restrain grain boundary migration and the boundary energy will decrease proportional to the particle dimensions. Consequently larger SiC particles are more effective than the smaller ones in grain growth inhibition of alumina.

Fig. 4.3 AFM pictures of (a) sintered alumina (b) nanocomposite (note the difference in microstructure scale)

4.4 FRACTURE MODE

As shown in Fig 3.30a monolithic alumina has mainly intergranular fracture. Because of thermal expansion anisotropy on cooling residual stresses exist at some alumina/alumina grain boundaries thereby weakening them. A crack would therefore
propagate selecting these weak grain boundaries and hence intergranular fracture is observed. However, transgranular fracture is also seen in the present samples probably due to fine grained microstructure.

Presence of SiC particles in the nanocomposite (Fig. 3.30b) on the other hand, induce pure transgranular fracture due to two reasons.

i) Because of the large thermal expansion mismatch between matrix alumina and SiC inclusions tensile residual stresses are created around the inclusions within a matrix grain during cooling after sintering. The stress field around intragranular particles of a sintered body is always greater than that around particles along the grain boundaries because the internal stresses around intergranular particles can relax more due to grain boundary diffusion. This induces the crack to extend to particles and promote transgranular fracture.

ii) SiC particles along the grain boundaries rivet the alumina/ alumina interfaces strengthening the grain boundaries and reducing grain boundary fracture.

4.5 DEPENDENCE OF CALCINATION CONDITIONS ON DENSIFICATION

Table 4.1 summarises the precursor compositions of alumina–5 vol% SiC calcined at mentioned temperatures and the sintering behaviour. The precursor calcined at 1000°C and having a mixture of transitional alumina phases along with
$\alpha$-alumina (XRD plot in Fig 3.16) gave maximum densification on sintering. The 700°C calcined sample composed of a mixture of $\gamma$-alumina and $\delta$-alumina had less compaction density and the samples cracked further on sintering. Moreover the weight loss on sintering of these samples were maximum (7.31%).

Table 4.1 Phase formation and characteristics of alumina-5 vol% SiC composite precursors on calcination

<table>
<thead>
<tr>
<th>Calcination Temperature °C</th>
<th>Alumina phases</th>
<th>Green density (%TD)</th>
<th>Sintered Density (%TD)</th>
<th>Weight loss on sintering (% Initial)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>$\gamma$-alumina + $\delta$-alumina</td>
<td>46.25</td>
<td>cracked</td>
<td>7.31</td>
</tr>
<tr>
<td>800</td>
<td>Transitional aluminas + traces of $\gamma$ alumina</td>
<td>48.37</td>
<td>97.6</td>
<td>6.55</td>
</tr>
<tr>
<td>900</td>
<td>Transitional aluminas</td>
<td>49.77</td>
<td>97.7</td>
<td>6.18</td>
</tr>
<tr>
<td>1000</td>
<td>Transitional aluminas + $\alpha$-alumina</td>
<td>48.23</td>
<td>99.2</td>
<td>5.15</td>
</tr>
</tbody>
</table>

This is associated with the incomplete dehydroxylation of these samples during calcination resulting in residual OH groups. On heating to high temperatures for sintering, these hydroxyl groups undergo chemical decomposition leading to pore channels or microcracks which later grows to introduce cracks in the sample as has been observed in the present case. On increasing the calcination temperature to 800°C the weight loss is reduced to 6.55 and samples attained 97.6% TD. The samples calcined at 900°C also attained comparable densification but the sintering weight loss was even reduced. The extent of dehydroxylation is increased on account of the increased calcination temperatures and the amount of residual OH groups are
decreased which prevented the formation of cracks in sintered body. Highest density and minimum weight loss was observed for the precursor composition obtained after calcination at 1000°C indicating complete dehydroxylation.

Dilatometer studies carried on these samples (Fig 3.18 a-c) show a two step shrinkage curve with a total linear shrinkage amounting to 22%. The first step corresponds to the transformation of transitional phases to α-alumina which is associated with around 9% linear shrinkage. The shrinkage associated with the densification process starts around temperatures >1300°C and extends to over 1700°C where it can be assumed that the samples have no more open porosity. The onset of first step shrinkage corresponds to the calcination temperature of the precursor and the total shrinkage attained in this step increases with decreasing calcination temperature. As the total shrinkage for all the precursors remain more or less at 22% initial it can be inferred that the shrinkage associated with densification is less for samples calcined at T< 1000°C. This is reflected also on the sintered density levels of these precursors.

FTIR spectroscopy analysis on boehmite derived alumina indicate that there is a change in Al co-ordination with the phase transformations. In boehmite and fully crystallised α-alumina the Al co-ordination is fully octahedral and in transition aluminas the co-ordination is both tetrahedral and octahedral. FTIR pattern of alumina-SiC composite precursor calcined at 1000°C (Fig 3.19) also indicated the existence of Al in both tetrahedral and octahedral co-ordinations. The enhanced sintering characteristics of such precursors are assigned to the compositional mixture containing transition and α- aluminas and the enhanced diffusion rate of the Al
species present at that calcination temperature. Moreover, the change in pore morphology from slit shaped pores in γ-alumina to shallow hexagonal pore in transition aluminas during the topotactic transformation may also contribute to the enhanced densification characteristics of 1000°C calcined precursor.

4.6 INFLUENCE OF MgO ON THE PROCESSING OF NANOCOMPOSITES

It is very well known and accepted that MgO is a very effective dopant for alumina in increasing the densification rate and controlling the grain growth kinetics. MgO decreases the grain boundary mobility by a solid solution pinning thereby reducing pore entrapment within grains. In the present study MgO doping on alumina has yielded the same results of improved microstructural features (Fig 3.37 a and Fig. 3.37b). However the situation is quite different on the use of 1 wt % MgO in the processing of alumina-SiC nanocomposites. There was an increase in sintered density compared to samples without MgO (Fig 3.36). Nevertheless, the mechanism operating is significantly varied compared to MgO doping in alumina. Microstructure analysis as presented in Fig 3.38 (a-c) indicates exaggerated grain growth at temperatures T ≥1550°C. At 1450°C the grain sizes are small but the microstructure shows areas devoid of matrix grains indicating the presence of glassy phases which are leached out during chemical etching. On increasing the temperature the glassy phase completely wets the matrix grains and grain growth starts. Microstructure at 1550°C and 1650°C show long continuous columnar grains with low alumina/alumina grain boundaries. Grain morphology is typical of liquid phase formation in sintering.
In the ternary system of MgO-Alumina-SiO₂ the lowest melting phase is a ternary eutectic of protoenstatite, trydimite and cordierite\textsuperscript{132}. This forms at temperature of 1355°C and is the source of liquid phases in MgO doped alumina-SiC nanocomposite. SiC particles are always associated with a certain degree of silica formed due to oxidation during high temperature heat treatment which create areas rich in silica leading to the formation of the eutectic. Once the liquid is formed it completely wets the grains with increase in temperature leading to discontinuous grain growth.

4.7 COMPARISON OF PROCESSING METHODS

A comparison of the sol gel coated precursors for alumina-SiC nanocomposites is done with composites processed by the conventional solid state mixing route. The properties of the sol gel processed samples are basically based on the intimate mixing of the dispersed phase with that of matrix phase in the sol state and the precursor composition that forms after calcination. Modification of SiC surfaces by introducing alumina coatings has provided the same surface characteristics as a result of which flocculation of the boehmite sol with coated SiC resulted in uniform and homogeneous distribution of SiC particles within gel network preventing segregation of them. This is clearly reflected in the final sintered microstructures (Figs.3.25 to 3.28) where it is hard to find any SiC agglomerates. The TEM picture of sol gel alumina- 5 vol% SiC presented in figures 4. 4a and 4.4b clearly shows the presence of SiC particles both within the grains and also along the grain boundaries. The matrix grains are relatively fine with the average grain sizes around 1-2 μm. The high magnification picture shows an alumina grain with SiC particles inside.
Fig. 4.4a TEM picture of sol gel derived alumina-SiC nanocomposite

Fig. 4.4b TEM picture of nanocomposite showing SiC particles within grains
Relatively smaller particles are entrapped within grains and larger particles remain at the grain boundaries. The curved grain boundaries formed as a result of pinning by SiC particles are characteristic of a nanocomposite microstructure.

The nanocomposites prepared from $\alpha$-alumina /SiC mixtures also showed good densification behaviour on sintering at 1700°C/90 min. Densities greater than 99% were achieved (Fig.3.35b). But the dispersion characteristics of SiC is significantly different from that of sol gel derived samples. The SEM pictures shown in Fig 4.5 a and b compare the nanocomposite derived from tami alumina/ SiC mixture with that of sol gel derived one. The matrix grains have an average size around 2$\mu$m. The SiC particles undergo partial agglomeration and gets segregated at the triple junctions. The smaller SiC particles are seen evenly distributed without getting agglomerated.

![Fig 4.5a SEM picture of sol gel derived alumina-SiC nanocomposites](image)
Fig 4.5b SEM picture of nanocomposite from tamei alumina /SiC mixtures

4.7 COMPARISON OF PROPERTIES BETWEEN ALUMINA AND NANOCOMPOSITE

The improvements in strength and toughness originally obtained by Niihara and co-workers\textsuperscript{44-47} was never been achieved on a reproducible basis in the subsequent works that followed by other groups\textsuperscript{67}. As has been explained in detail in the introduction, apart from the discrepancies on the reported values of strength and toughness, there is a general agreement that nanocomposites possess beneficial effects of grain boundary strengthening resulting in better values for strength, creep resistance and wear properties. Mechanisms based on reduction in processing flaw sizes\textsuperscript{52}, creation of residual stresses on account of the large thermal expansion mismatch between alumina and SiC\textsuperscript{44} and the differences in residual stress relaxation
behaviour are proposed in order to explain the strengthening and toughening effects in nanocomposites.

Fig 4.6 Schematic illustration of the sol gel coated process compared with conventional powder mixing route (a) sol gel coated (b) powder mixing.

In the present work, as given in Table (3.2), a comparison of the mechanical properties of strength, toughness and hardness gave mixed results. There is an improvement of strength by 25% (504 MPa to 630 MPa) for nanocomposite
compared to monolithic alumina but the fracture toughness reduced by 6% (4.32
\text{MPa.m}^{1/2} \text{ to } 4.06 \text{ MPa m}^{1/2}). The hardness value shows an increase of 12 % from
17.2 \text{ GPa for monolithic alumina to 19.3 GPa in nanocomposite. Considering the
general proposition that the type of processing flaw in alumina is either large volume
pores or large columnar grains formed as a result of discontinuous grain\textsuperscript{133,134}
growth the observed strength improvement in nanocomposite can be explained on the
basis that such processing flaws are absent in much lesser extent in nanocomposite.
The common processing flaws observed in nanocomposites are associated with SiC
agglomerates formed during the cold compaction followed by differential shrinkage
during sintering\textsuperscript{50}.

Fig. 4.7 \textit{SEM micrograph of a typical processing flaw in nanocomposites.}

Fig 4.7 shows a representative one with a size of around 5\textmu m which is much less
than long grains of size more than 10 \textmu m observed in alumina and possibly explains
the improvements in strength. The reduction in $K_{IC}$ values for nanocomposite can
also be explained on the basis of different grain morphology. In alumina, presence of
long plate like grains lead to modest toughness increase compared to grains with
irregular morphology in nanocomposite (Figs. 4.3 a and b).