CHAPTER 2

EXPERIMENTAL

2.1 RAW MATERIALS USED

The details of the various materials used in the present investigation are provided below (Table 2.1)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Trademark</th>
<th>Manufacturer</th>
<th>Purity</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-alumina</td>
<td>Tamei-DAR HPA 0.5</td>
<td>Tamei Corporation, Japan Condea, USA</td>
<td>99.99% 99.99%</td>
<td>200 nm 450 nm</td>
</tr>
<tr>
<td>Aluminium Nitrate</td>
<td>Riedel deHaen</td>
<td>Analytical Reagent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boehmite Powder</td>
<td>Disperal</td>
<td>Condea, Germany</td>
<td>11 μm</td>
<td></td>
</tr>
<tr>
<td>α-SiC</td>
<td>FCP 40 NLC</td>
<td>Norton Company, Norway</td>
<td></td>
<td>180 nm</td>
</tr>
<tr>
<td>Hydrofluoric Acid</td>
<td>E-Merck, India</td>
<td>Analytical Reagent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium Hydroxide</td>
<td>Riedel deHaen</td>
<td>Analytical Reagent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>solution</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitric Acid</td>
<td>Riedel deHaen</td>
<td>Analytical Reagent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesium Nitrate</td>
<td>Alfa Aesar, Johnson Mathey, Germany</td>
<td>Analytical Reagent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Orthophosphoric Acid</td>
<td>E-Merck, Germany</td>
<td>Extra Pure</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.2 EXPERIMENTAL PROCEDURE

2.2.1 ACTIVATION OF SiC

100 gram SiC powder is mixed with 100 ml hydrofluoric acid (40% solution) and stirred for 5 min. It was then diluted to 500 ml and the suspension was allowed to settle. The supernatant is decanted off and the powders are then repeatedly washed with distilled water (minimum 5 times) and dried at T < 70°C. Dried powders are characterised by XRD and FTIR.

2.2.2 COATING TECHNIQUE

Activated SiC powder was dispersed in aqueous medium by ultrasonication for 30 min followed by ball milling for 12 h and the suspension was used for coating experiments. For each experiment, 4 gm SiC was dispersed in 1 litre distilled water and mixed with respective amounts of aluminium nitrate solutions of 0.025 M concentration to give 5, 10, 15, 20 and 25 wt % alumina coatings as given in Table 2.2.

Table 2.2 Experimental details for obtaining alumina coated SiC particles

<table>
<thead>
<tr>
<th>Wt. of SiC (g)</th>
<th>Wt. % Alumina</th>
<th>Wt. of alumina (g)</th>
<th>Wt. of Aluminium nitrate (g)</th>
<th>Vol. of water for 0.025 M aluminium nitrate solution (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>5</td>
<td>0.2</td>
<td>1.4711</td>
<td>157</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>0.4</td>
<td>2.9422</td>
<td>314</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>0.6</td>
<td>4.4133</td>
<td>471</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>0.8</td>
<td>5.8844</td>
<td>628</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>1.0</td>
<td>7.3555</td>
<td>784</td>
</tr>
</tbody>
</table>
The mixture was heated to temperatures >90°C and boehmite was precipitated during stirring by drop wise addition of ammonia till pH reached 7.5. Coated particulates were removed from the suspension by centrifugation at 4000 rpm for 10 min, repeatedly washed with ethanol and dried at 75°C for 48 hrs. Dried powders were characterised by TEM. The powders were then calcined at 500°C for 2h at a heating rate of 3°C per minute. Calcined powders were subjected to Multipoint BET surface area analysis, FTIR, TEM, Zeta Potential measurements and XRD.

2.2.3 PREPARATION OF COMPOSITE

a. Preparation of Boehmite Sol

250 gram boehmite powder was dispersed in 2.5 litre deionised water and the pH was brought down to 2.5 by drop wise addition of 10% HNO₃ under constant stirring conditions. The mixture was stirred for 24 hrs and the non dispersible hard agglomerates were removed by sedimentation. It was then stabilised to a sol with constant stirring and pH adjustment. The sol was then estimated for alumina content by first drying (T-60°C) weighed amounts in an alumina crucible followed by heating at 1200°C for 1 h.

b. Preparation of Alumina Seed Suspension

100 gram α-alumina powder was dispersed in deionised water and ultrasonicated for 30 min followed by ball milling for 24 h in a PVC container using high purity alumina balls of diameter 4.5-5.5 mm. The ball milled suspension was diluted to 1 litre and the pH was adjusted to 4.0. It was then kept for a period of 7 days and the particles that settled were removed. The decanted portion was then estimated for seed concentration.
c. *Sol Gel Processing of Composites.*

In a typical experiment for the preparation of 50 gram Alumina-5 vol % SiC, 647.60 g boehmite sol equivalent to 46.970 g alumina was added with 22.32 gm α-alumina (equivalent to 2 wt % seed) seed suspension.

![Flowchart](image.png)

**Fig.2.1 Flowchart showing the preparation of sol gel alumina-SiC composites**
Coated particulates (SiC : alumina ratio 4:1) obtained just after the precipitation from aluminium nitrate solution were dispersed in the sol and the mixture was flocculated to pH 7.5 by drop wise addition of ammonia to obtain a viscous gel which was later centrifuged, washed and dried. The composite gel precursors were calcined at 1000°C for 2h under N₂ atmosphere. Calcined precursor was then ground, attrition milled in ethanol, dried and compacted to bars of dimensions 40 x 6 x 4.5mm. Sintering was then carried out in a gas pressure sintering furnace at temperatures ranging from 1550-1700°C with a soaking period of 1-1.5 h under N₂ or Ar atmosphere at 80 bars. The whole process is presented as a flowchart in Fig. 2.1 and the sintering schedule in Fig 2.2.

![Sintering Schedule Diagram](image)

**Fig. 2.2** Sintering schedule followed for Alumina-SiC nanocomposites

Alternatively the following experiments were also done.

### 2.2.4 DEPENDENCE OF CALCINATION CONDITIONS

Alumina-5 vol % nanocomposite precursors prepared by sol gel processing were calcined at 700, 800, 900 and 1000°C under nitrogen for 2 h. The calcined
powders were attrition milled in ethanol for 3h using zirconia balls at 500 rpm, dried at T~ 75°C. Powders were compacted to bars 40 x 6 x 4.5mm by uniaxially pressing at 25 MPa followed by CIP ing at 500 MPa. They were then sintered at 1650°C for 1h under nitrogen gas pressure (80 bars).

2.2.5 EFFECT OF NUCLEATING SEEDS

α-alumina nucleating seeds were introduced in boehmite sol (0 to 5 wt %) during composite preparation. The effect of seeds on the α-alumina phase transformation temperature was studied using DTA. Alternatively α-alumina seeded samples were sintered in the temperature range 1550 – 1700°C for 1h under argon atmosphere and the effect of seeds on densification and microstructural development were studied.

2.2.6 COMPARISON WITH CONVENTIONAL ROUTES

The effect of alumina coatings on SiC on the processing of alumina-5 vol. % SiC nanocomposites were studied by a comparative study with sol gel, transition alumina and high purity α-alumina powder derived samples. Transition alumina powders were prepared by calcining boehmite at 1000°C for 2 h in air. Preparation of sol gel samples are as described above. The transition alumina and α-alumina derived samples were prepared by attrition milling the mixture of SiC with corresponding amounts of alumina for alumina-5 vol. % SiC composites in ethanol for 3 h at 500 rpm. using TZP balls. Sol gel powders were also attrition milled after calcination. The compacted powders were sintered in the temperature range 1550 – 1700°C.
2.2.7 INFLUENCE OF MgO

The effect of MgO dopant on the densification and grain growth of alumina and alumina-SiC nanocomposite were studied by introducing 1 wt % MgO during the sol gel preparation. Magnesium nitrate salt solution was used as the precursor. Sintering of alumina samples were done at 1550°C for 2 h in air and composite samples were done in the temperature range 1450 to 1700°C in nitrogen at a pressure of 80 bars. The sintered samples were characterised by density, SEM and grain size measurements.

2.3 CHARACTERISATION

a. Thermal Analysis

Thermogravimetric and differential thermal analysis of the precursor gels were carried out (Netzsch Gerätebau GmbH, Germany) at a rate of 10°C/min in N₂ up to 1300°C with alumina as the reference standard. The effect of alumina nucleating seeds on the α-alumina phase transformation temperature was determined from the DTA plots. Thermal analysis of the as received SiC powders were also done for monitoring the oxidation behaviour of such powders.

b. Dilatometric studies

Thermomechanical analysis (Baehr Gerätebau GmbH, Germany) of the composite precursors calcined at 1000°C was done on cylindrical samples of length 6.5 mm in the temperature range 1600 to 1700°C under N₂ atmosphere using the schedule followed for sintering.
c. Fourier Transform Infra Red Spectroscopy

Infrared spectra ( Nicolet, Magna 560, Madison, WI, USA) of the SiC powders and composite precursor powders were measured on pellets prepared by mixing the powders (~300mg) in KBr. Measurements were carried in the wave number range 400-4000 cm$^{-1}$

d. Zeta Potential Analysis

0.1 wt % of the coated powders, pure alumina and SiC powders were dispersed separately in 1 litre of deionised water using NaNO$_3$ as electrolyte. The samples were aged for 24 h and the pH is adjusted on each aliquot batches of 100 ml until values remain unchanged for 20 min. Zeta Potential measurements were then made on a Malvern Zetameter 4, UK.

e. Surface Area Analysis

Multipoint surface area measurements and adsorption isotherms were obtained at 77K using S 2400, Micromeritics, USA system. Specific surface area were analysed by the BET method. The t-plot method has been used to inspect the nature of porosity in coated samples.

f. XRD

XRD measurements of powder samples were recorded on a Philips Diffractometer (PW 1710, Eindhoven, The Netherlands) in the 20 range 15 to 80°.

g. Microscopy (SEM and SPM)

The sintered bars were ground ( George Miller Nürnberg, MPS 2R 300) flat on all four sides by diamond impregnated wheels, first with 151$\mu$m followed by 15 $\mu$m ensuring a minimum of 500$\mu$m each material removal from all sides. The ground
bars were then polished down to 1μm (Struers Pedimax-2) and thermally etched at 1450°C / 0.5h under static Argon or chemically etched with orthophosphoric acid. Polished, etched microstructures were examined on a Scanning Probe Microscopy (SPM Dimension 2000, nanoscope III-a, Digital Instruments, CA; USA) and on scanning electron microscopy (Model 1530 SEM, Leo, Gemini, Cambridge, UK). Grain size Analysis was done by the linear intercept method using the relation

\[ G = \frac{1.5L}{MN} \]

where 1.5 is a geometry dependent proportionality constant, L the total test line length, M the magnification and N the total number of intercepts.

h. Transmission Electron Microscopy

TEM pictures of powders samples were obtained by dispersing (0.5 wt %) powders in acetone followed by controlled ultrasonication. A drop of the suspension was deposited on to a carbon coated TEM grid and dried under vacuum. The grid was observed on a Philips Transmission Electron Microscope (PW 6585 EM 400, Eindhoven, The Netherlands)

TEM pictures (JEOL, 200 FX II, Japan) of the sintered specimens were prepared by cutting 100 μm thick foils, grinding them to 50 μm and finally ion beam milling to electron transparency.

2.3 MECHANICAL TESTING

a. Density

Sintered specimens were ground parallel on all four sides up to 15 μm finish and the density was measured by Archimedes principle using distilled water as the reference medium. The densities were calculated using the values of 3.98 g/cm³ for alumina and 3.21 g/cm³ for SiC.
b. Flexural Strength

The flexural strength of composite samples were measured by four point bend testing. A schematic representation of a typical four point fixture is represented in Fig. 2.3. The samples were ground to bars of dimensions 2 x 2.5 x 30 mm and the tensile face and adjoining sides were polished down to 1μm surface finish. The edges were uniformly chamfered at 45°. Testing was performed on a ATS series 1600 Universal Testing Machine with an inner span of 12mm and outer span of 24mm. The samples were loaded at the rate of 0.5mm/ min. The breaking loads for the samples give the flexural strength using the standard formula for the strength of a beam in four point flexure, as

\[ S = \frac{3PL}{4bd^2} \]

where \( P \) is the break load, \( L \) is the outer span, \( b \) is the specimen width and \( d \) is the specimen thickness.\(^{120}\)

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![Schematic illustration of a four point bending fixture](image-url)
c. Fracture Toughness Measurement

The Fracture toughness of the composites were measured by the Indentation Strength in Bending method. The samples were polished to a 1 micron finish and indent was created by applying a load of 98.1N using a Vickers Indentor (Zwick 3212) on the midpoint of the tensile face prior to undergoing a standard 4-point bending strength. The weakened specimen broke at a lower load, the Rest Load, $\sigma_R$, and the fracture toughness was calculated using the following equation \(^{121}\).

$$K_{IC} = 0.059(EH^{-1})^{0.125}(\sigma_R P_v^{0.33})^{0.75}$$

d. Hardness

Hardness measurements were carried out a room temperature using a Vickers diamond indenter (Zwick 3212) under a load, $F$, of 98.1N and with a loading time of 20s. An average hardness was then calculated from the results of ten indentations using the following equation

$$H = \frac{F}{2a^2}$$

where $a$ is half length of indent.

2.5 GAS PRESSURE SINTERING

Gas pressure sintering is a process developed in the early seventies and is presently receiving considerable attention \(^{122-127}\). A major advantage of this technique is that it does not require the cladding and decladding of specimens generally required for pressure assisted sintering techniques. The method uses a pressurised gas to promote high temperature densification of specimens from their green body form.

Fig. 2.4 represents a common gas pressure sintering process. First step involves sintering the specimen to closed porosity either under vacuum or at
relatively low pressures using a gas with high diffusivity through the material being densified. The pressure is increased (up to 80 bars) to desired levels once the specimen attains closed porosity. When pores become isolated and contain a gas that has low solubility and diffusivity through the ceramic being densified, the pressure within the pore resists pore closure. This is given by

\[ P_{\text{int}} = \frac{2\gamma}{r} + P_{\text{ext}} \]

Where \( P_{\text{int}} \) – Pressure inside the pore
\( \gamma \) – solid-vapour surface energy
\( r \) – pore radius
\( P_{\text{ext}} \) – External gas pressure

If the pores contain a soluble gas that has high diffusivity through the ceramic, reduction in pore sizes occurs as a function of gas solubility and diffusion kinetics resulting in high densities.

Fig 2.4 A typical gas pressure sintering cycle