CHAPTER 2

ANALYTICAL TOOLS AND CHARACTERIZATION TECHNIQUES

2.1 OVERVIEW

The important characterization techniques that are employed in the present investigation are described in this chapter. Thermal properties of boehmite binder, evolution of crystalline phases, particle size distribution, surface modification, surface area and densification behaviour have been studied using many analytical tools. The sintered ceramic density, microstructure and mechanical properties such as hardness, strength and creep are also analyzed.

2.2 ANALYTICAL METHODS

2.2.1 Thermal Analysis

Thermal analysis is an effective tool to analyze the physical and chemical changes in a material, when it is subjected to controlled heating. In ceramics, the thermal analysis is carried out to understand the decomposition and phase transition behaviour of precursor compounds. Thermo gravimetric analysis (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are the most widely used thermal analysis techniques. The TG and DTA techniques are used to characterize the associated weight loss and thermo-chemical changes during (i) binder burnout in a compact (ii) removal of aqueous and organic solvents of a dried compacts, (iii) dehydration and dehydroxylation of the precursors, (iv) the conversion of thermodynamically unstable phases into more stable phases and (v) the formation of new crystalline phases in the system (Pinwill et al 1992, Liu et al 1999 and Hongsheng Zhao et al 2002). Differential scanning calorimetry (DSC) mainly gives
information about glass transition temperature of a ceramic system. The distribution of unburnt binders within the de-bound ceramic bodies has also been studied using DSC (Kim et al 1996). The determination of the activation energy for thermochemical reactions has also been reported using thermal analytical methods (Wright et al 1989).

2.2.2 Dilatometric Analysis

The thermo-mechanical analysis is another type of thermal analytical tool in which, the densification characteristics of the ceramic green compacts are studied with respect to the heating temperatures. The densification is expected to take place in different stages during heating. At elevated temperatures, the compact shrinks rapidly indicating the reduction of porosities that are generated during forming. Once the powder compacts attained sintering further shrinkage is stopped. The technique is more useful for determining the sintering temperatures of the ceramic systems (Messing and Seongtae Kwon 1997). In the present work, this tool has been used for studying the densification behaviour of extruded alumina-boehmite and composite ceramics such as alumina-aluminium titanate and mullite-aluminium titanate.

2.2.3 Phase Analysis

X-ray powder diffraction technique is widely used for studying the evolution and orientation of the crystalline structures of the ceramic phases (Sato 1984 and Adair 1997). Apart from the crystal analysis, the method is also used for determining the crystallite size. The crystallite size is obtained from the equation 2.1 which is known as Scherer equation (Wu et al 2002).

\[
Crystallite \text{ size } (l) \text{ nm} = \frac{K\lambda(\text{nm})}{26\theta_{hkl} \cos \theta_{hkl}}
\]

(2.1)

where 'k' is the shape factor and for spherical particles it is 0.9. Wavelength \( \lambda \) is 1.54 Å.
In the present study, the transformation sequences of boehmite, sol-gel derived aluminium titanate and mullite precursors, reactive phases of alumina-aluminium titanate composites have been analyzed. The x-ray of A16 SG alumina and boehmite, the major raw materials used in the present work is given in Figure 2.1.

![XRD analysis of boehmite and alumina raw materials](image)

**Figure 2.1** XRD analysis of boehmite and alumina raw materials

### 2.2.4 Particle Size Analysis

The particle size and its distribution analysis of ceramic raw materials is an important parameter for any forming technique. Particle size distribution has definite influence on processing parameters such as stability, flow property, particle packing fired density, and mechanical strength. They also have direct impact on the sintering
temperatures and sintered microstructures. The techniques such as sieve analysis, microscopy, sedimentation, optical and angular scattering are commonly used to measure the particle size (Yasuo Arai 1996) and size distribution. The particle size modification of alumina dispersed in boehmite sol is characterised using this technique. The particle size distribution of the nanoparticulate sols has also been determined.

2.3 PHYSICAL CHARACTERIZATION

2.3.1 Density

Accurate density measurements are an important part of characterization of the physical properties of ceramics. In an experiment, the density of as-pressed pellets is calculated from the sample mass and volume. Mass is measured using a digital balance and sample volume is calculated from the external dimensions of the samples, possessing regular geometric shapes. The liquid displacement method, based on Archimedes' principle, is used to determine the density of sintered ceramics (ASTM C373 1969 and Richerson 1982). The bulk density of the sample is calculated from precise measurements of the dry, saturated, and suspended weights. Bulk density is the weight of an object divided by the bulk volume, $V_b$, the volume of solid plus all open and closed pores. According to the Archimedes' theorem, the equation 2.2 gives the bulk density of a solid.

$$\rho_{\text{bulk}} = \frac{W_{\text{dry}} \rho_{\text{liq}}}{W_{\text{sat}} - W_{\text{susp}}}$$

(2.2)

Where

- $\rho_{\text{bulk}}$ = bulk density of the sample
- $W_{\text{dry}}$ = dry weight
- $\rho_{\text{liq}}$ = density of the saturating/suspending liquid
- $W_{\text{sat}}$ = saturated weight
- $W_{\text{susp}}$ = suspended weight.
The volume of open and closed pores can also be calculated using Archimedes' measurements. The volume of open pores \( V_o \) is determined using equation 2.3.

\[
V_o = \frac{W_{\text{sat}} - W_{\text{dry}}}{\rho_{\text{liq}}}
\]  

(2.3)

The volume of closed pores can be calculated only if the theoretical density (TD) of the material is known. The dry weight divided by the theoretical density gives the true volume, \( V_t \). The volume of closed pores, \( V_{cp} \), is given by the equation 2.4.

\[
V_{cp} = V_b - V_o - V_t
\]  

(2.4)

Where \( V_b = (W_{\text{sat}} - W_{\text{supp}}) / \rho_{\text{liq}} \).

2.3.4 Drying Shrinkage

Ceramic objects processed through wet processing and plastic forming have to be dried for removing the excess liquid phase and moisture, which is associated with dimensional shrinkage. The drying shrinkage has direct relevance in near-net shape fabrication processes. The linear dimensional shrinkage is generally determined from the dimensional changes before and after drying (Griffith and Radford 1969). The linear shrinkage is calculated by,

\[
\% \text{ Linear shrinkage} = \frac{\text{Change in dimensions (L)}}{\text{Original dimensions (L)}} \times 100
\]

In the present work, the diametrical linear shrinkage is calculated for alumina shapes that are processed through gel assisted extrusion.

2.4 MICROSTRUCTURE

The engineering properties of ceramics are largely dependent on the microstructure. The important microstructural features are the grain size, shape of the
grains, amount of porosity, pore size and distribution, the structure and the distribution of any second phase materials. Microscopic analysis is normally carried out on polished and etched surface of the sintered products using a scanning electron microscope (Kingery et al 1976). In solid state sintering, significant grain growth can occur during the final stage of sintering. Because important properties such as mechanical strength often have a strong dependence on grain size, it is necessary to accurately characterize the average grain size of dense ceramics. The linear intercept method yields the grain size of a sample from representative micrographs of polished cross sections (Mendelson 1969 and Wurst and Nelson 1972). For this analysis, it is necessary to select micrographs that are having dense microstructure, with no pores. First, horizontal lines are drawn across micrographs at random intervals. Next, the length of each line L is measured. The number of times each line intercepts the grain boundaries, N, is counted. It is important that the line length is converted to the magnification of the micrograph. Now, the average lineal intercept is given by,

\[ \bar{L} = \frac{L}{N} \]

Making the assumption that the grains are uniform (i.e., roughly spherical) in shape, the average grain diameter is \(\frac{3}{2}L\). Lineal analysis can also be used to calculate the relative density of porous ceramics using a slightly more complex analysis,

\[ \bar{L} = \frac{2}{3}d \]

Where \(d\) = diameter of grains or grain size

In ceramics, grain growth is generally divided into two main types: normal and abnormal. In normal grain growth, grain size and shapes fall within a fairly narrow range. Abnormal grain growth is characterized by the rapid growth of few larger grains at the expense of the smaller ones.
2.5 MECHANICAL PROPERTIES

2.5.1 Hardness

Hardness measurement studies offer valuable information about the mechanical behaviour of materials. Hardness is defined as the resistance offered by a given material to external mechanical force endeavouring to scratch, abrade, and indent or in any other way affect its surface (Rice et al 1994). It is measured by introducing plastic deformation associated with the penetration behaviour of a harder indenter (usually diamond) with a known geometry. Indentation techniques are powerful tools to examine the mechanical performance of ceramics, usually using pyramidal indenters (Fairbanks et al 1982). The highly concentrated stress field at the tip of the indenter induces plastic deformation, even in macroscopically brittle materials such as alumina and the analysis of the permanent indent gives a measure of the hardness. The indentation tests can be classified into two categories namely micro indentation (microhardness) and macro indentation (macrohardness). The difference between these two is the applied load. In micro hardness, the amount of the applied load is below 200g. In the case of macro indentation, the load is normally above 200g and gives the overall hardness of the material.

The hardness ($H_v$) of a material is determined by the ratio of the applied load via a geometrically defined indenter to the contact (projected) area of the resultant impression (Fee 1992).

$$H_v \propto \frac{P}{d^2} \quad \text{(2.7)}$$

$$H_v = 1.8544 \frac{P}{d^2} \quad \text{(2.8)}$$

Where

- $H_v$ - Vickers Hardness (GPa)
- $P$ - applied load (kg)
- $d$ - indentation diagonal length (mm)
When a low Vickers test load is applied to a ceramic material, the measured hardness is usually very high. However, with the increase in load, the measured hardness decreases. At still higher indentation loads, hardness load curves tend to flatten out and hardness becomes constant. The problems relating to the measurement and interpretation of the hardness of brittle materials are still awaiting suitable method of analysis and proper assessment to give valid evaluation of the results. Although the mechanism of deformation is not clearly understood, the micro-indentation test is a useful method for studying the nature of plastic flow and its influence on the deformation of the material. Indentation hardness is also often used as a selection parameter for ranking the wear resistance of materials.

### 2.5.2 Fracture Toughness

Defects, cracks or flaws are inevitably present in all the engineering materials. They may occur during fabrication and heat treatment stages of the material. The fracture resistance of a material in the presence of cracks or discontinuities is known as its fracture toughness. The standard method used for measuring the fracture toughness is single edge V-notched method (Gogotsi 2003). Fracture toughness ($K_{IC}$) of the sample is also measured using the indentation technique (Niihara et al 1982, Breval et al 1985 and Evans and Charles 1976). Method proposed by Niihara is as follows:

$$K_{IC} = \sqrt{\frac{H}{a}} \left( \frac{E}{H} \right)^{2/5} \left[ 0.057 \left( \frac{c}{a} \right)^{3/2} \right] \left( \text{MPa m}^{1/2} \right)$$

Where

- $H$ - Vickers' Hardness (MPa)
- $E$ - elastic modulus (MPa)
- $H = 1.854 \frac{P}{(2a)^{2}} \times 9.8 / 10^6 \text{ (MPa)}$

Where

- $P$ - applied load (Kg)
- $c$ - crack halflength (mm)
- $a$ - half of indented diagonal length (mm)
Depending upon the type of cracks developed around the indentation impression, different expressions have been used. However, a widely used equation for the measurement of fracture toughness has been developed by Evans and Charles (1976) and is given in the equation 2.10.

\[
K_{IC} = 0.16 \frac{H_v a^{1/2} (c/a)_{3/2}}
\]

(2.10)

Where,

- \( K_{IC} \) - fracture toughness (MPa.m\(^{1/2} \))
- \( H_v \) - hardness (GPa)
- \( c \) - crack half length (mm)
- \( a \) - half of indented diagonal length (mm)

2.5.3 Strength

The strength characterization data for ceramics are reported in terms of bend strength (Davidge 1986 and Morrell 1995). The load is applied from three or four contact points to bend the sample. The preferable loading rate is usually between 0.5 mm/min and 1.0 mm/min. In three or four point bending, the flexural strength (also called modulus of rupture, MOR) is given by the equations 2.11 and 2.12.

\[
\sigma_{fl(3PT)} = \text{MOR} = \frac{3PL}{2bd^2}
\]

(2.11)

\[
\sigma_{fl(4PT)} = \text{MOR} = \frac{3Pa}{bd^2}
\]

(2.12)

A standard sample configuration, loading positions and stress distribution pattern is shown in the Figure 2.2. In the present work, 3-point bending strength test is used for studying the strength of the extruded and sintered alumina as well as the composites made out of alumina-aluminium titanate and aluminium titanate-mullite composites.
Creep is the time dependent deformation of materials under the influence of external loads at elevated temperatures. Ceramics, in general, are elastically deformed and then catastrophically fractured when stress is applied to them. At elevated temperatures, in addition to the elastic deformation, plastic deformation also occurs. It has been reported that the creep deformation is affected either by diffusion due to defects or by sliding in association with diffusion. The main factors controlling the creep are applied stress, operating temperature, chemical composition and microstructure. Figure 2.3 shows the equipment setup used for the creep experiments in the present work. It consists of a furnace, automatic loading and unloading facility and continuous monitoring and accurate recording of any deformation occurred on the sample. Creep behaviour of ceramics and ceramic matrix composites has been extensively studied and reported. A review reported by Shiushichi Kimura and Yasuda (1988) discussed in detail the different kinds of creep mechanism that are possible in
Figure 2.3  Photograph of creep setup (TUHH - Germany)
oxide ceramics. Ceramics creep is analyzed either by tensile or compressive creep tests at elevated temperature and stress levels (Carroll and Widerhorn 1988). The creep strain is measured as a function of time. In any creep test, the minimum creep rate ($\dot{\varepsilon}$) is measured. Once the creep rate becomes stationary, the minimum creep rate is determined for particular temperature and stress conditions. Norton’s creep equation (Equation 2.13) is used for determining the stress and temperature dependence of a creep deformation. It is given as,

$$\dot{\varepsilon} = A\sigma^n \exp \left[ \frac{-Q}{RT} \right]$$

(2.13)

Where ‘$n$’ is the stress exponent and ‘$A$’ is constant, both dependent on temperature. The value of ‘$n$’ gives information on the possible creep mechanism and for most of the brittle ceramics it is in the range of 1-2. The activation energy is determined from the Arrhenius plot drawn between log of creep rate and inverse temperature. Here, compressive creep test is conducted using constant load creep equipment.