Chapter-2

(Materials and Methods)

Materials and Methods

2.1 Raw Materials

The raw materials used for the preparation of refractory were tabular alumina, reactive alumina, sea water magnesia, alumina rich spinel, zirconia, flake graphite, nano carbon black, resol type resin, aluminum metal, silicon metal, boron carbide and silicon carbide. A detailed description of them is given below:

2.1.1 Tabular Alumina [T60]

The tabular alumina used (procured from ALMATIS, India) is a pure sintered α-alumina material that has been fully densified by rapid sintering without the use of sintering aids at temperatures in excess of 1800°C. Tabular alumina has characteristic large, well developed hexagonal tablet shaped α-alumina crystals of up to 200 µm length.

Chemical Composition [%] All Sizes (0-3mm, -45µ)	
Al_2O_3	99.5
Na_2O	0.40
SiO_2	0.09
Fe Magnetic	0.02
Physical Properties	
Bulk Specific Gravity [g/cm³]	≥3.50
Apparent Porosity [%]	≤ 5
Water Absorption [%]	≤ 1.5

Table 2.1 Tabular Alumina specifications

2.1.2 Alumina-Rich Spinel AR 78

The spinels are distinguished by their chemistries (66, 78 and 90% alumina). The used spinel was provided by ALMATIS, India, contained a 78% alumina and is known as AR 78. The development of spinel has followed two distinct paths as prescribed by these two separate industry needs: magnesia-rich spinel products for use with magnesia-based bodies and alumina-rich spinel for use with alumina bodies. Within spinel containing refractory formulations AR 78 is preferably used for the fines to the medium sized fractions, whereas AR 90 shows most benefit when used in the medium to coarse size grain fractions.

Chemical Composition [%] Particle Size (-45µ)	
Al_2O_3	74.0
MgO	22.5
CaO	0.24
SiO_2	0.10
Na_2O	0.09
Fe_2O_3	0.20
Fe Magnetic	0.02
Physical Properties	
Bulk Specific Gravity [g/cm³]	3.3
Apparent Porosity [%]	1.8
Water Absorption [%]	0.5

Table 2.2 AR78 specifications

2.1.3 Graphite Flakes (FC97)

Crystalline flake graphite (or flake graphite for short) occurs as isolated, flat, plate-like particles with hexagonal edges if unbroken and when broken the edges can be irregular or angular. It was supplied by Marut Enterprises, India.

Chemical Composition [%] Surface area (6.37 m^2 g^{-1})	
Fixed Carbon	98 +/-2
Moisture	<1
Ash	<1
Volatile Matter	<1

Table 2.3 Flake Graphite specifications

2.1.4 Nano Carbon Black (N220)

Nano Carbon black (obtained from Birla Carbon, India) is a material produced by the incomplete combustion of heavy petroleum products. It is a form of paracrystalline carbon that has a high surface area to volume ratio.

Chemical Composition Surface area (116.5 m^2 g^{-1})	
Fixed Carbon	98.03
Density	1.2 gm/cc
Ash	0.39
Volatile Matter	1.42

Table 2.4 N220 specifications

2.1.5 Resol type Phenol-Formaldehyde Resin (ABRON – PR 100SL)

ABRON - PR100 acquired from ABR organics limited, India is solventless resol type phenol formaldehyde resin with very good wettability and high flow. Extended shelf life for ABRON - PR100 (SL) is achieved by terminating the probable chain extending species to the maximum extent. The oxidative stability of ABRON - PR 100 is superior to the novolak resin, as the number of reactive hydroxyl groups in the polymer chain is less compared to the novolak resins. It is an established fact that resol type of phenol formaldehyde resins is used in space & aerospace applications.

ABRON - PR 100 (SL) offers the following distinct advantages over conventional solvent-based phenolic resins:

❑ It has a long shelf life of 2-3 months when stored at cooler conditions.

❑ The total solid content in the resin is 70-75% (w/w polymer).

❑ It is highly compatible with glass, silica, carbon and aramid fibers/fabric, etc.

❑ Void free components/composites are realized by using ABRON - PR 100 (SL)

❑ The cure cycle of ABRON - PR 100 (SL) is the same as that of any ordinary solvent based resol type phenolic resin.

❑ The unique property of ABRON - PR 100 (SL) is that graphitization occurs at temperatures 600°C and above. This graphitization helps to build up the mechanical properties of the composites/components at elevated temperatures. Hence the components/composites of ABRON -

PR 100 (SL) have better properties at 600°C and above as compared to these components/composites realized from other resins.

❑ ABRON - PR 100 (SL) is an import substitute, used in liquid engine rocket nozzles.

❑ ABRON - PR 100 (SL) is characterized by high solid resin content, high char yield, good ablative properties & high gel time.

APPLICATIONS:

ABRON - PR 100 (SL) can be used as a resin matrix for fiber reinforced composites. It is also used in the manufacture of resin bonded magnesia-carbon and alumina–carbon refractory bricks. It is also useful in the manufacture of tap hole masses of blast furnaces.

SPECIFICATIONS OF ABRON – PR100 (SL)

State: Liquid

Appearance: Light brown or amber colored

Specific Gravity: 1.18 – 1.22

Viscosity (300C) CPS: 600 – 1200

Resin solids at 160°C: 75 ± 2 %

Shelf Life (storage):   3 months at 40°C / 1 months at RT 250°C

2.1.6 AR grade materials

Materials Used	Chemical Formula	Purity (%)	Manufacturer
Aluminum metal powder	Al	98.0	Loba chemie, India
Silicon metal powder	Si	98.5	Loba chemie, India
Sea Water Magnesia UBE98S	MgO	98.5	UBE, Japan
Boron Carbide	B_4C	98.0	Bhukhanwala Industries, India
Silicon Carbide	SiC		
Zirconium oxychloride octahydrate	$ZrOCl_2.8H_2O$	99.5	Sigma-Aldrich
Cerium Sulfate tetrahydrate	$Ce(SO_4)_2.4H_2O$	99.9	Sigma-Aldrich

**Table 2.5** Analytical reagents specifications

2.2 Sample Preparation

The particle size distribution has an important role in the properties of any refractory. Incorrect particle size distribution may cause militancy or the excess binder/solvent requirement. The Andreassen equation:

$$y = \left(\frac{d}{D}\right)^n \times 100 \qquad (2.1)$$

as applied to classify alumina grains in four different size distributions, between 0-3 mm. Here, y is the cumulative percentage finer than (CPFT) a size less than d, D is the maximum particle size and n is an empirical parameter, which was set as 0.4 to obtain optimum apparent porosity and bulk density.

The batch size for Al_2O_3-C refractory was 25 kg. The nano carbon black and the liquid resin were first mixed and heated at 70-80 °C. The requisite amounts of tabular alumina aggregates were then mixed in a 50 Kg capacity Z-Kneader mixture machine for 10 minutes. Mixture temperature was maintained at 100°C. Then fines, antioxidants, and powder resin were added to the mixture and mixed for 30 minutes. The mixture was then unloaded into a tray and kept it inside controlled humidity and temperature chamber for curing (for 24 h). The lump formed if any after curing was crushed and screened properly. Then the volatile material was checked for the mixture and was found to be 1.85%. Cylindrical and cubic stainless steel moulds were filled with this mix by vibro-ramming in order attain uniform filling of the material inside the mould. The mould was then cold isostatically pressed (CIP) at 150 MPa pressure. The CIP samples were dried at 200°C for 12 h. The dried samples were then fired in an electrical furnace at 1400°C for 3 h under reducing atmosphere (coke atmosphere) in a sealed corundum sagger. The flow sheet for the sample preparation is shown in the flow sheet (Fig. 2.1).
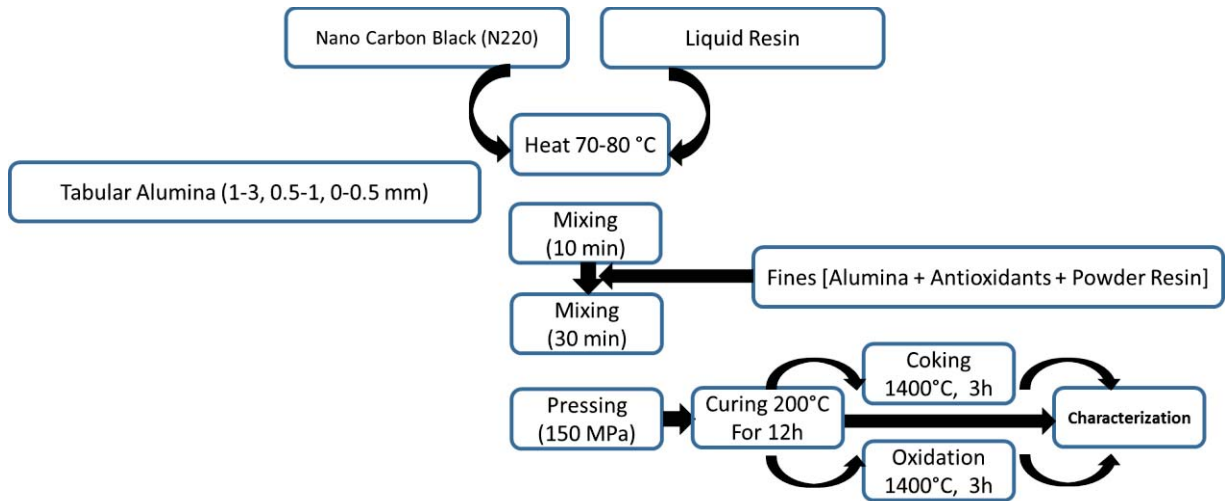
Fig. 2.1 The process flow diagram

2.3 Characterization Techniques

2.3.1 Thermogravimetric-Differential Thermal Analysis (TG-DTA)

TGA is a technique in which the mass of a substance is measured as a function of temperature while the substance is subjected to a controlled rising temperature program. On the other hand, the DTA method consists of measuring the heat changes associated with physical or chemical transformations occurring during the gradual heating of substance. Thermal changes, such as dehydration, crystalline transition, lattice destruction, oxidation, and decomposition, are accompanied by an appreciable rise or fall in temperature and are amenable to DTA investigation. Mutually the TGA and DTA facilitate as TG-DTA equipment and consist of a furnace, a temperature regulator, a specimen block, sensitive weighing machine, thermocouples, and a temperature-recording system.

The thermal properties of the samples were measured using an SETARAM TGA/DT instrument. The melting temperature, crystallization temperature, and heat of fusion of all samples were undertaken at a scan rate of 10 °C min^{-1}. A few milligrams of the test sample and an inert reference sample (Al_2O_3 powder) were placed in two alumina crucibles and put side by side in a heating block. Identical thermocouples were placed in each crucible and connected back to back. The net e.m.f. represents the temperature difference between the test sample and reference sample. The two crucibles were heated at a constant rate, and the temperature difference is plotted either against time or temperature. Any thermal changes occurring in the test sample will cause its temperature to either lag behind or lead the temperature of reference sample corresponding to an endothermic and exothermic peak respectively.
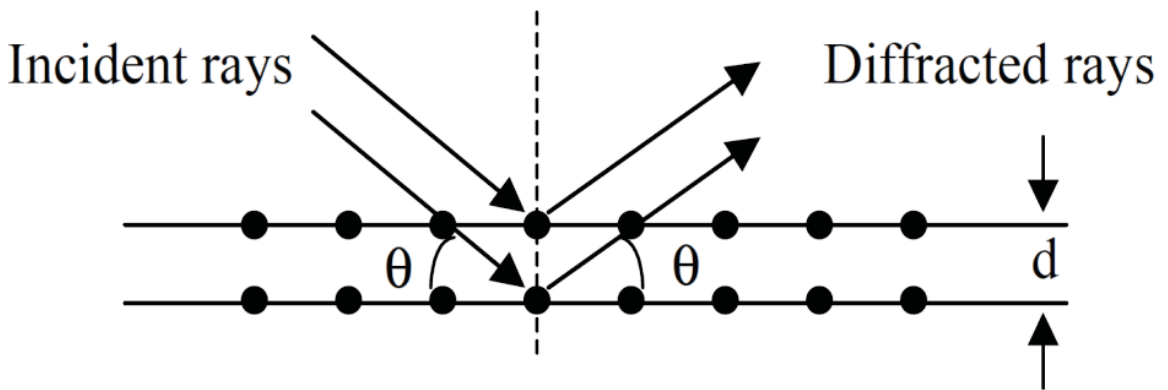
2.3.2 X-ray Diffraction (XRD)

X-ray diffraction utilizes the electromagnetic waves with a wavelength of the order of one angstrom. Because, the lattice constant of the different crystals is the same order of magnitude as the wavelength of the X-rays, which is the first requirement of diffraction. When the X-rays were incident upon a sample, diffraction from different atoms takes place. Diffracted x-rays interfere with each other. In crystals, because the atoms are distributed in a periodic manner, the diffracted waves form sharp interference maxima (peaks) about the symmetry of atoms present in the crystal. The peaks maximum in an X-ray diffraction pattern is directly related to the atomic distances. Therefore, by measuring the distribution of diffraction pattern, one can deduce the crystal structure of material. According to Bragg's law, if diffraction occurs from a

given set of lattice planes where 'd' is the inter-planer distance, the given condition should be followed:

$$2d \sin\theta = n\lambda \qquad (2.2)$$

Where 'θ' is the incident angle, 'λ' is the wavelength of the x-ray, and 'n' is an integer representing the order of the diffraction. This process is shown schematically in Fig. 3.6.

Fig. 2.2 Schematic of diffraction of X-rays by a crystal.

X-ray diffraction experiments were performed using an 18 kW rotating anode (Cu Kα) based Rigaku high-resolution X-ray powder diffractometer operating in the Bragg-Brentano geometry and fitted with a graphite monochromator in the diffracted beam. The generator was operated at 40 kV and 150 mA. The powder samples were placed on a grooved quartz sample holder with the help of a glass slide.

2.3.3 Coefficient of thermal expansion (CTE) using dilatometer

A dilatometer measures the change in dimension of a material when it is heated or cooled. A pushrod dilatometer (V. B. Ceramics, Chennai, India) was used to measure the thermal expansion and glass transition temperature of the

prepared samples. A pushrod dilatometer consists of an intermediary machine which transmits the dimensional change in the sample due to change in the temperature. A linear thermal expansion is defined as the change in length of the sample (ΔL) resulting from a change in the temperature. It is dimensionless and represented by the ratio of change in length of a sample to its original length (L_0). CTE was calculated using the following formula:

$$\alpha_{T_2-T_1} = \frac{\Delta L}{L_0 \ (T_2-T_1)} \qquad\qquad (2.3)$$

where, ΔL and L_0 are the change in the length and initial length of the sample respectively. T_2 and T_1 are the final and initial temperature respectively.

2.3.4 Fourier Transform Infra-Red Spectroscopy (FTIR)

FTIR relies on the fact that the most molecules absorb light in the infrared region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule. The frequency range of IR is measured as wave numbers typically over the range 400 – 4000 cm^{-1}. FTIR spectra were obtained using an FTIR (SHIMADZU-8400S and JASCO-470 plus) in the range of 400-4000 cm^{-1}.

2.3.5 Scanning Electron Microscopy (SEM)

In a Scanning electron microscope (SEM), electrons were used as a source for the characterization of samples. Either by thermionically or via field emission process, the electrons were emitted from a tungsten cathode, which was focused by two successive condenser lenses into a very narrow intense beam. With the help of two pairs of coils, the beam of electrons was focused on the

sample surface. Upon encroaching on the sample, the primary electrons transmit their energy inelastically to the atomic electrons of the crystal

lattice. Several scattering processes took place on the sample surface, some electrons managed to leave the surface to be collected by a detector facing the sample. Basically, these electrons were the secondary electrons. Finally, by using photomultiplier tube (PMT) to amplify the signal and modulating this signal with the intensity of a cathode ray tube (CRT), the image of the sample was produced. The research quality SEMs are generally able to produce images with a resolution of ~50 Å.

The surface morphology of the samples was examined with an FESEM ZEISS SUPRATM 40 instrument operated at 5 kV and INSPECT 50 FEI. All the samples were used in powder forms for the observation in SEM.

2.3.6 Energy Dispersive Spectroscopy (EDS/EDX)

In EDS, high energy electron beam is used as a source to excite core level electron from the inner orbital (e.g. the 1s shell) of atom present in the sample. Due to the release of inner core electron, the formation of the hole takes place in a lower shell of an atom. Therefore, to fill the hole in a lower shell an electron from an outer shell of the atom (e.g. the 2s shell) releases its energy, which consequences in the form of X-ray emission. This X-ray emission is the characteristic of the particular atom present in the sample. Therefore, one could recognize the exact atom present in the sample by analyzing the X-ray spectral lines of the atom. To analyze the X-ray cooled Si(Li) detector with an ultrathin (diamond) X-ray window (lithium drifted silicon detector) is used in

EDS. In most of the cases, EDS systems are attached with SEM and utilize the same electron beam source to excite X-rays from the sample subjected to analysis.

The compositional of samples were investigated by using EDS of Oxford X-ray system integrated with Scanning Electron Microscope (SEM). Software known as INCA controlled the Oxford X-ray system. INCA allows users to acquire an X-ray spectrum from a specified point or area.

2.3.7 Apparent porosity (AP) and Bulk density (BD)

ASTM C914-09 is to be employed using boiling water bath. Specimen were coated with wax for magnesia containing samples.

2.3.8 Flexural strength measurements

Flexural strength is the force that a material can withstand before it breaks or yields. Flexural testing is commonly used to determine the flexural strength and modulus of all types of the materials. It is performed on a universal testing machine (UTM) with a 3 point or 4 points bending fixture. In the present work, flexural strength measurements of all the samples were performed according to ASTM C78/C78M. The specimens were tested in a three-point bending fixture with 20 mm span length between the two supports. The universal testing machine Instron, 3344 (Germany) was used for the measurement.

The load and the corresponding deflection were recorded. The flexural strength was calculated using the following equation:

$$R = \frac{3PL}{2bd^2}$$ (2.4)

where, R is the flexural strength (Kg/cm²), P is the maximum applied load, L is the span length, b, and d are the width and depth of the specimen respectively.

The standard deviation, S of the flexural strength values is calculated using the following formula:

$$S = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})^2}$$ (2.5)

where, N is the number of samples, xi is the value of one sample and $\bar{x}$ is the mean value.

2.3.9 Hot modulus of rupture (HMOR)

Very similar to the CMOR, ASTM C1099 covers the determination of the high-temperature modulus of rupture of refractory brick at 1400°C.

2.3.10 Cold crushing strength (CCS)

The CCS is the capacity of a material to withstand axially directed pushing forces. By definition, the compressive strength of material is that value of uniaxial compressive strength reached when the material fails completely. CCS of samples were measured according to ASTM C1194. For testing of each composition, 12 cubic samples were prepared.

2.3.11 Static slag corrosion test

A static crucible method was used for compositions at 1600°C, 5h. The samples were visually compared and corroded dimensions measured.

2.3.12 Thermal shock resistance

ASTMC-1171 correlates the strength loss or reduction in continuity, or both, of refractory brick subjected to thermal cycling. It is measured by the difference in modulus of rupture (MOR) between uncycled specimens and the specimens subjected to thermal cycling.