"Effect of nano clay and nano zirconia addition on the properties of Alumina Ceramics"

Thesis submitted

By

Suprita Kumari

(109-CR-0609)

In partial fulfilment for the award of the degree of Bachelor of Technology

In

Ceramic Engineering

Department of Ceramic Engineering

National Institute of Technology Rourkela

Rourkela, Odisha 769008

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Under the Guidance of

Dr. Sumit Kumar Pal

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DECLARATION BY THE STUDENT

I, Ms. **Suprita Kumari,** a student of Department of Ceramic Engineering, National Institute of Technology Rourkela bearing Roll No: 109CR0609 hereby certify that my B.Tech Project Report entitled *"Effect of nano clay and nano zirconia addition on the properties of Alumina Ceramics",* under the guidance of Prof. Sumit Kumar Pal at National Institute of Technology Rourkela, Rourkela is being submitted in partial fulfilment of the requirements for the Degree of **Bachelor of Technology** in **Ceramic Engineering.** This is a record of bonafide work carried out by me and the results embodied in the Project Report have not been copied from any source. The results embodied in this Project Report have not been submitted to any other University or Institute for the Award of any other certificate or degree.

Date: 13-05-2013

Suprita Kumari

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3

CERTIFICATE

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This is to certify that the thesis entitled *"Effect of nano clay and nano zirconia addition on the properties of Alumina Ceramics"* is submitted by Suprita Kumari, (Roll NO 109-CR-0609) to this Institute in partial fulfilment of the requirement for the award of the degree of Bachelor of Technology (Ceramic Engineering) in Department of Ceramic Engineering, is a bonafied record of the work carried out under my supervision and guidance. It is further certified that no part of this thesis is submitted for the award of any degree.

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ACKNOWLEDGMENT

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ABSTRACT

In this present work, an attempt has been made to study the effect of two different nano additives on the physical properties of alumina ceramics, after sintering. Two different additives which were selected for the purpose are monoclinic zirconia and nano clay, whose particle sizes are in the range of nanometer (d_{50} ~ 15 – 50 nm). The percentage of these additives were varied from 1%, 2%, 5% and 10% (wt %). Different processing methodologies have been employed to prepare alumina ceramics with different percentage of nano additives. These were uniaxial pressing method, solid casing method and gel casting. Green samples were sintered in pressure less condition at two different temperatures viz. 1550ºC and 1600ºC with a holding time of two hours. Sintered samples were then characterized for apparent porosity, bulk density and cold crushing strength. The effect of nano additives on the physical properties of alumina ceramics after sintering was evaluated.

Chapter 1:

INTRODUCTION

1. INTRODUCTION

Alpha (α) Alumina represents hexagonal crystal form. This form is stable above 1200^0C prior to which the gamma phase of Alumina is stable which is cubic in nature. Alumina has melting point near 2050^0C. For polycrystalline alumina maximum density achieved by traditional ceramics processing, followed by high temperature sintering, is around 3.9 gm/cc. Apart from its high melting point, alumina ceramics are of technical importance due to the following aspects.

1. Alumina has excellent wear resistant properties.

2. It is Inert to a broad range of acid as well as alkali attack.

3. Alumina has a very ideal and near perfect tendency to be casted and shaped.

4. Strength and stiffness values are notably on the higher side.

5. It has excellent tribo-chemical and tribo-mechanical behavior.

6. Alumina has wonderful thermal spalling resistance and thermo-mechaniacl properties

The properties of alumina largely depend on its densification. Generally, sintering is associated with densification by mass transport phenomenon, grain growth at high temperature. To achieve better densification, a lot of research has been conducted on finding the sintering additives and its effect on properties of alumina. Studies have shown that, sintering additives with fine particle size are more helpful towards higher densification of alumina. Therefore, now a day a considerable research are being focused on nano additives addition and its effect on sintering behaviour of alumina. Moreover, the final properties of sintered alumina also depend on the processing techniques and different processing parameters, applied towards fabrication of alumina ceramics.

Among different fabrication techniques three conventional and commercially successful techniques have been applied towards the fabrication of alumina articles in the present work. They are mainly uniaxial pressing, slip casting and gel casting.

Slip casting is an old and traditional process which comprises casting a slip (slurry) of particles such as ceramic particles, metallic particles, etc. can be used as long as they are insoluble in solvent, and in particularly a method suitable for forming a cast article of high quality complex shaped bodies [1]. The common casting methods involve drain casting and solid casting; hollow bodies such as crucibles are prepared by drain casting whereas non hollow bodies are prepared by solid casting. Casting process begins by filling a mould with

ceramic slurry having a pourable consistency. The cast is produced when a physical and/or thermal changes causes the slurry to develop a yield strength. These common casting methods are based on colloidal system in which removal of the liquid is used to consolidate particles suspended in slurry. In slip casting consolidation of particles is accomplished as the liquid flows through a porous medium under a pressure gradient [2]. In the present work, solid casting techniques have been adopted to fabricate alumina ceramics.

Gel casting is an attractive ceramic forming process, where we have the flexibility of casting and forming complex shapes. Gel casting is a near-net-shape forming method of advanced ceramic materials. It is used for making high-quality, complex-shaped ceramic parts. The process involves a slurry prepared from ceramic powder and a water based monomer solution which is poured into a mold, polym erized in-situ to immobilize the particles in a gelled part, removed from the mold while still wet, then dried and fired.

Gel casting has the following advantages

1. Through gelcasting, article with complex geometries can be produced better than with other methods.

2. It is not limited to use with any particular ceramic powder.

3. Highly dense as well as porous bodies can be manufactured.

4. Gelcasting offers no size limitation. Complex shapes with thin sections as small as 0.2 mm can be gelcasted [3].

5. Excellent green machinability and high green strength.

6. Quickly adapted for use with new materials and new applications.

7. The processing additives are all organic and leave no cation impurities behind in the fired part.

8. Rapid forming cycles and the formed parts requires little machining.

9. Low capital equipment cost.

 Generally, approaches to enhancing sintering kinetics or lowering the sintering temperature for alumina ceramics follow two ways. The first is to improve powder processing, that is, to use fine starting powders and to eliminate agglomerates in the green body such as by colloidal routes. The second approach is to use sintering aids or additives. Additives in solid solutions can enhance diffusion and hence sintering by increasing defect populations, while additives forming a liquid phase can facilitate particle rearrangement and solution/reprecipitation [4].

Additives which can be used in alumina for different purposes are MgO, MnO, SrO, TiO2, ZrO2, nanoclay, Y_2O_3 *etc*. As mentioned above MgO prevents abnormal grain growth. Magnesia improves the densification of alumina and addition of magnesia can transfer opaque material into translucent one. Role of zirconia is that it acts as toughening agent. Addition of zirconia or silicon-carbide improves toughness of alumina. Role of clay as sintering aid of alumina was not well documented. It can be assumed, clay may form liquid phase due to presence of alkali ions which will wet the alumina particles thus aiding densification.

Clay is naturally produced by weathering action upon igneous rock which is associated with hydration and desillcation processes by disintegration and decomposition of rock by the action of air, water temperature and pressure. Nanostructure of nanoclay improves the fracture behaviour and presence of nanoparticles in the matrix improves the thermo-mechanical properties of the material like wear resistance and hardness. Some of the key properties of nanoclay are it act as filler, binder with water, provide good modulus and tensile strength[2]. For the manufacturing of high alumina refractory containing mullite composition is achieved by synyhesization of mullite by reacting alumina and clay at high temperature[3]. Mullite, having formula 3Al2O3·2SiO2, is a high melting crystalline alumino-silicate material which is generally used as refractory material As mullite is having good high temperature properties and stability which make it useful for several application [4].

Alumina –Zirconia composites has been extensively used in implant and cutting application due to its high wear resistance, high toughness, high strength and high chemical stability. Addition of zirconia in alumina significantly improves its properties like its strength and thermo-mechanical properties. Addition of ZrO_2 also hinders the grain growth of alumina but the densification rate reduces linearly with increasing the percentage of alumina [8]. Strengthening of alumina by addition of zirconia depends on many factors. Phase transformation of t-ZrO_2 to m-ZrO_2 causes considerable amount of absorption of stress bystress field generated due to crack propagation[8]. Further strengthening is achieved due to generation of microcracks by residual stress around already transformed m-ZrO_2. Zirconia act as toughening agent for the alumina ceramics when sintered in air. Grain coarsening occur at higher temperature by annealing. Particles are dragged by migrating alumina gain boundaries causes tetragonal zirconia to coarsen. Also addition of alumina-zirconia composites are

widely used in biomedical implantation of femoral heads in hip joint replacements etc. Due to its high strength and biocompatibility nature.

Therefore, it can be concluded that the effect of nano clay and nano zirconia addition is alumina and evaluation of properties of alumina after sintering requires special attention in the field of technical ceramics. In the present work, therefore, an attempt had been made to evaluate properties of nano additive containing alumina after sintering.

[1] Tatsuo Natori, Kashiwa; Takashi Shimaguchi, Ibaraki; Akhihide Watanabe, Ibaraki; Toshihiro Yamada, Ibaraki; Method of forming cast article by slip casting, United states patent 4,883,621 (1989).
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[4] Low-Temperature Sintering of Alumina with Liquid-Forming Additives, Liang A. Xue and I-Wei Chen,J. Am. Cerom. Soc., 74 [8] 2011-13 (1991)

CHAPTER 2

OBJECTIVE

2. OBJECTIVE

2.1 Objective

The present work aims towards

(a)   Study of addition of nano clay and mono clinic zirconia on the properties of alumina ceramics after sintering
(b)   Processing of alumina ceramics along with different additives by uniaxial pressing
(c)   Processing of alumina ceramics along with different additives by solid casting method.
(d)   Processing of alumina ceramics along with different additives by gel casting method.
(e)   Study of variation of wt percentage of nano additives on properties of sintered alumina
(f)   Study of the   effect on the nano additive on alumina ceramics on different processing routes
(g)   Evaluation of physical properties of alumina ceramics.

3. Chapter

LITERATURE REVIEW

3. LITERATURE REVIEW

3.1 Sintering

This is the thermal treatment of the ceramic bidies at elevated temperature to achieve high density and strength. By the mass transfer mechanism and diffusion pores are reduced as particles go inside the voids and fills it causing increase in density and this mechanism requires high temperatures to oocur. Driving force for sintering is the reduction of high surface area.

There are mainly two types of sintering:

1. Solid state sintering here densification is achieved by the reduction of surface area of the particles by changing its shape and size with no liquid phase present.
2. Liquid state sintering here around 20% liquid phase is present which accelerates desification by improving mass transfer mechanism and high density can be achieved[2].

3.2 Alumina nanoclay system

Marina Jovanovic Ana Beros[3] reported that synthetic mullite can be prepared by using natural raw materials like Klokoti fireclay and metallurgical electrofiltered alumina made in the Alumina Plant ″Birač″. They prepared four type of clay and alumina mixtures by using raw or benefited clay with nonmilling or milling alumina. Two class of mixtures first raw clay at 1700°C and second benefited clay at 1580°C. These mixtures resulted in the best properties of synthetic mullite. Benefiated clay significantl.y effected the properties thanmilled alumina. Amorphous phase was also found due to large amount of impurities present in clay.

V. Srinivasa Rao, et al [4] reported that clay/alumina – titanate nanocomposites can be prepared with varying proportions of clay and alumina , maintaining the matrix modifier and coupling agent composition constant by melt blending. Maleic anhydride (MA)-grafted polypropylene (PP) and MA-grafted EPR modifier were employed. They studied the

morphology of nanocomposites by X-ray diffraction and high-resolution scanning electron microscopy and they found the combination of intercalated and exfoliated nanocomposites and for the setswith titanate, coupling agent showed better dispersion of reinforcing filler. Nanocomposites obtained showed an increase in storage modulus and tan _ values in presence of couplingagents which causes improvement in load-bearing capacity and stiffness of nanocompositein dynamic mechanical analysis studies.

V. Viswabaskarana, et al [5] reported that sybthetic mulite can be prepared by using clay and alumina as raw materials. They studied the mullitizationbehaviour of three south Indians soils (Neyveli, Panruti and Udayarpalayam clays) and three different alumina sources, (reactive alumina, gibbsite and boehmite). They found that after firing the mixture at 1600C for 4 hrs mullitazation occurred under normal atmospheric conditions. Mixture showing high density (2.71g/cm_3) and high strength (82 MPa). The impure Udayarpalayam clay–reactive alumina mixture shows high strength (87 MPa) having low density low density (2.65 g/cm_3). Microstructural st X-ray diffraction for microsturctural studieswas carried out on sintered specimens to estimate the mullitisation behavior of individual clays. Neyveli clay and reactive alumina mixture gave the maximum mullitisation behaviour. Bohemite mixture showed poor mechanical properties as well as poor physical properties.

V. Viswabaskarana, et al [6] reported that three south Indians soils showed mullitization behaviour when treated with calcined alumina. They found that calcined clay (meta kaolin) composition gives better strength and density than the uncalcined clay composition. They studied the microstructure and found that calcined composition were shoeing a higher aspect ratio of mullite crystals. They found that calcined Neyveli clay and fine reactive alumina composition showed a better mullitisation behaviourcompared to other mixtures.

V. Viswabaskaran , et al [7] reported that clay obtained from Neyveli (South India) and reactive alumina (mean particle size of 0.7_m) were starting materials. The densification of mullite was improved by addition of, magnesia and yttria (1–5 wt.%) which were sinter additives to the mixtures. Boehmite was used as reactive alumina (1–7 wt.%). After firing at three teperatures 1500, 1550 and 1600 ◦C for 3 h, mixtures fired at 1600 ◦C showed better properties.The 3 wt.% MgO addition showed improved density up to 2.91 g cm−3   wa achieved by addition of 3 wt.% MgO and maximum strength of 125MPa. Was achieved by addition of Y2O3 which also helped in the formation of equiaxed mullite,

lacking in increase of the density and strength. The boehmite substitution (5 wt.%) resulted maximum density of 96% theoretical density (3.01 g cm−3) and strength of 120MPa. The addition of boehmite resulted in a blend of small to bigger crystals throughout the structure was observed by Microstructural studies.

3.3 Alumina zirconia system

Kensuke Kageyama, Youhei Harada and Hiroshi Kato[8] reported that addition of Zirconia to pre-sintered alumina powder prevented coarsening of alumina grains in agglomerated structures. Grain coarsening and cracking caused the decrease in flexural strength of samples with agglomerated structures. Agglomerated structures enhanced fracture toughness. In particular, a specimen using 21.1 vol% of pre-sintered alumina-rich powder of 32 to 150 mm exhibited increase in fracture toughness by approximately 30% without sacrificing average flexural strength. A SEM observation of crack paths showed that grain bridging did not occur in samples. The compressive residual stress zone in agglomeratedstructures played an important role in raising fracture toughness. Alumina-zirconia composites with agglomerated structures were prepared using alumina or alumina-zirconia powder to obtain large-sized compressive zones in particulate ceramics without degrading flexural strength. Agglomerated powder was obtained by pre-sintering. Alumina-rich agglomerated structures and a zirconia-rich matrix was formed in samples that were produced using pre-sintered powder.

Tatsuro Horiuchi , et al [9] reported that addition of zirconia increases the surface area of transition alumina at the elevated temperatures. They also found that after addition of zirconia there was huge suppression of phase transformation from theta to alpha alumina. Around 50 m2/g surface area was obtained when alumina zirconia composition was fired at 1200C. They also observed that after calcining at 800C zirconia existed in high dispersion state when XRD UV-VIS test was performed. After XPS measurement they found that zirconia existed in monolayer which cover the surface of alumina and which was the probable cause for the suppression of phase from theta to alpha state and large surface area atthe elvated temperature i.e. at 1200C.

A.H. De Azaa, et al [10] reported that new composition of alumina-zirconia nano-composites results in high crack propagation which results in improved lifetime and reliability of ceramic joints. They studied there slow crack- growth behaviour. They discussed the influence of the processing conditions on the microstructure development, of the zirconia toughened alumina composites and the effect of these microstructures, on its mechanical properties.

Chapter 4

EXPERIMENTAL

4. EXPERIMENTAL

The raw materials used were:

Fine Alumina powder, Nanoclay of composition, $SiO_2 \sim 50\%$, $MgO \sim 5\%$, $Al_2O_3 \sim 20\%$, $Cao \sim 2\%$, $Fe_2O_3 \sim 0.5\%$, LOI~20 and particle size $d_{50} \sim$ 15-50 nm, cubic-nanozirconia

Three fabrication techniques were used for determination of sintering behaviour of alumina with nano-clay and zirconia additives. Techniques employed were uniaxial pressing, solid casting and gel- casting.

Different materials used for different techniques are described in the table below:

Table 4.1 Tabulation of materials used for three processes

Fabrication techniques	Materials used
Pressing	fine alumina powder of surface area 4.214 m2/gm, nano-clay, nano m-zirconia, 2% PVA as binder, stearic acid as lubricant, acetone for cleansing, mortar- pestal, 15mm die.
Solid-casting	fine alumina powder of surface area 4.214 m2/gm, nano-clay, nano m-zirconia, Dispersant used is Darvan C; Solvent used is distilled water and moulds prepared from Plaster of Paris were used for the casting.
Gel-casting	fine alumina powder of surface area 4.214 m2/gm, nanonano m-zirconia, Dispersant used is Darvan C; Solvent used is distilled water and mould used was glass petridish, MAM as monomer, MBAM as cross linker, PEG as surface layer, APS as initiator, TEMED as catalyst and petroleum jelly as lubricant.

MAM-Methacrylamide, MBAM-Methylene Bisacrylamide, PEG-Polyethylene Glycol, APS-Ammonium Persulfate, TEMED-Tetramethyl Ethylene Meth Diamine

Compositions prepared were :

Table 4.2 Tabulation of nomenclature of compositions

Composition name	Composition
100-AL	100% Alumina
99-AL-1NC	99% Alumina 1% Nano-clay
97.5-AL-2.5-NC	97.5% Alumina 2.5% Nano-clay
95-AL-5-NC	95% Alumina 5% Nano-clay
90-AL-10-NC	90% Alumina 10% Nano-clay
95-AL-5-ZR	95% Alumina 5% Zirconia
90-AL-10-ZR	90% Alumina 10% Zirconia

4.1. Uniaxial pressing

For the pressing technique 5 pellets for each compositions described above was prepared. First weighed composition was crushed in mortar-pestal and to the composition 4-5 drops of PVA was added and properly in the mortar-pestal. 2gm of composition was weighed for each pellet. Die was cleaned with acetone and stearic acid was applied on the die for lubrication.Weighed composition was filled in the die properly and setteled and punch was pressed on the powder and kept in the hydraulic press. Pressure was set at 4 ton for 90seconds. After pressing operation pellet was taken out carefully. Pellets were kept for drying at 100^0C for 24 hour and then kept for firing at two temperatures i.e 1550^0C and 1600^0C. Then the final prepared pellets were obtained for further characterization.

Whole process is described below through flowchart:

Weighing and crushing of powder in mortar-pestal → Addition of binder PVA 4-5 drops → 2gm was weighed for each pellet

Die and punch was cleaned through acetone and lllubricated with stearic acid

Die was filled with powder and pressed with punch

Whole arrangemaent is kept in hydraulic press where pressure is set at 4 ton for 90 sec

Pellets were taken out carefully

Dried at 100^0C for 1 hour

Fired at 1550^0C and 1600

Figure 4.1 Flow chart of the overall uniaxial pressing

Figure 4.2 Image of sintered pellets

4.2 Solid casting

4.2.1Preparation of Alumina Slip and Its Casting

The required quantity of distilled water was measured in a beaker. To this water required amount of Darvan c i.e 0.5% of solid loading was added and kept for stirring using magnetic stirrer for 2 minutes. To this solution measured amount of composition was added very slowly i.e very less amount at a time for complete and stable suspension for 12 hours. After this slurry was kept in desicator for de-airing. Then the prepared slurry was used for solid casting.the slurry was poured into cleaned plaster of paris mould slowly and after each 5 minsmould was refilled to get solid mass. Cast was kept for air drying for 1 day. Casted body was taken out of mould carefully and kept for drying at 80^0C for 12 hours. Then the dried body was fired at two temperatures i.e. at 1550^0C and 1600^0C. Then the final sintered samples were kept for further characterization.
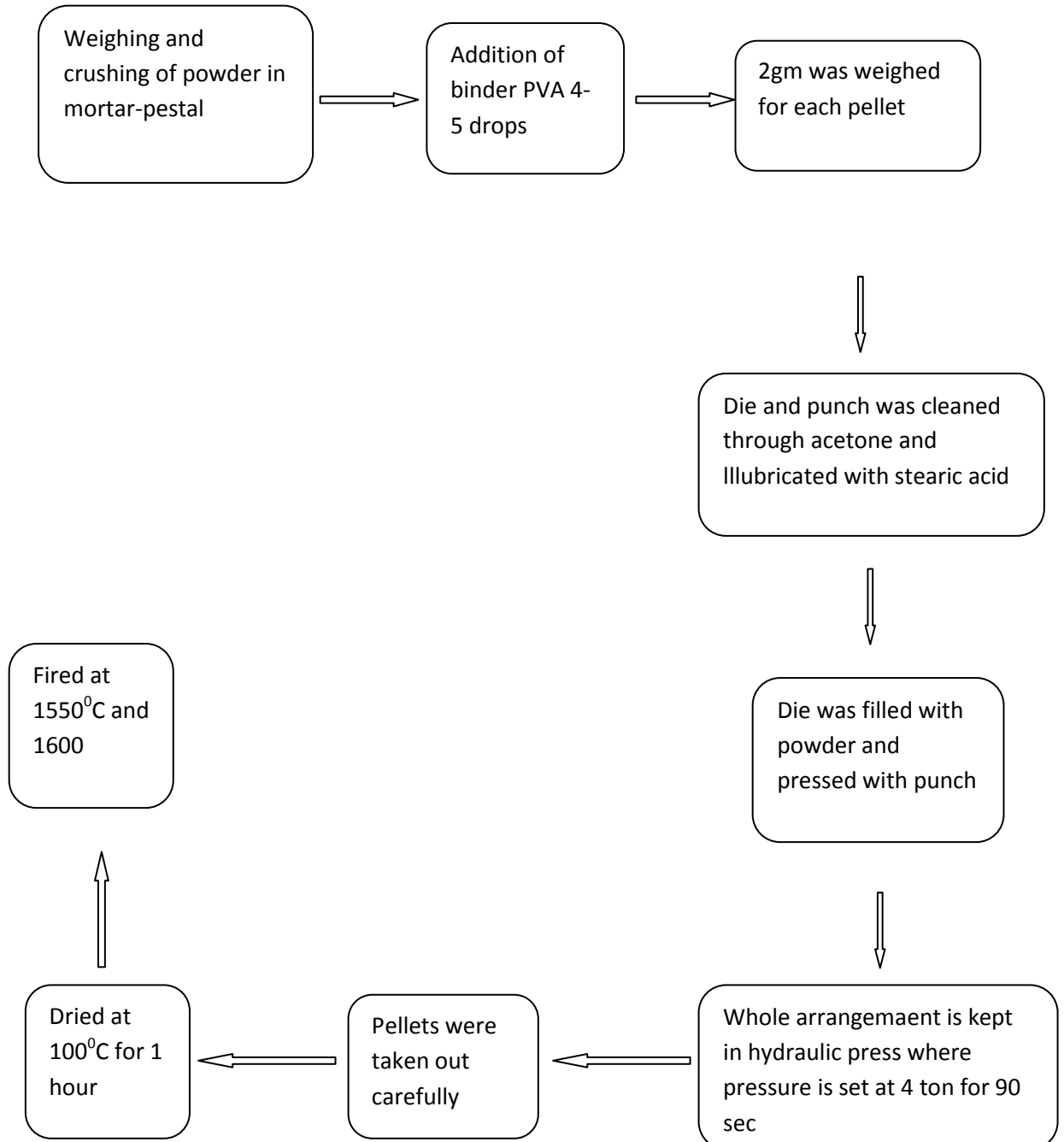
Whole process is described below through flowchart:

```
┌─────────────────────────┐      ┌──────────────────┐      ┌──────────────────┐
│ Required amount of      │      │ Addition of      │      │ Solution stirred │
│ distilled water was     │ ───► │ Darvan-c i.e.    │ ───► │ using magnetic   │
│ measured and kept in a  │      │ 0.5% of solid    │      │ stirrer for 2 mins│
│ beaker                  │      │ loading          │      │                  │
└─────────────────────────┘      └──────────────────┘      └──────────────────┘
                                                                    │
                                                                    ▼
                                                       ┌──────────────────────┐
                                                       │ Addition of weighed  │
                                                       │ composition to the   │
                                                       │ solution very slowly │
                                                       └──────────────────────┘
                                                                    │
                                                                    ▼
                                                       ┌──────────────────────┐
                                                       │ De-airing inside the │
                                                       │ desicator            │
                                                       └──────────────────────┘
                                                                    │
                                                                    ▼
┌──────────────┐                                       ┌──────────────────────┐
│ Fired at     │                                       │ Solid casting in     │
│ 1500⁰C and   │                                       │ plaster of paris     │
│ 1600         │                                       │ mould by filling the │
└──────────────┘                                       │ mould after each 5   │
       ▲                                                └──────────────────────┘
       │                                                            │
┌──────────────┐    ┌──────────────┐    ┌──────────────┐           ▼
│ Dried at     │    │ Casted bodies│    │ Kept for air │
│ 80⁰C for 1   │ ◄──│ were taken   │ ◄──│ drying for   │
│ hour         │    │ out carefully│    │ 1 day        │
└──────────────┘    └──────────────┘    └──────────────┘
```
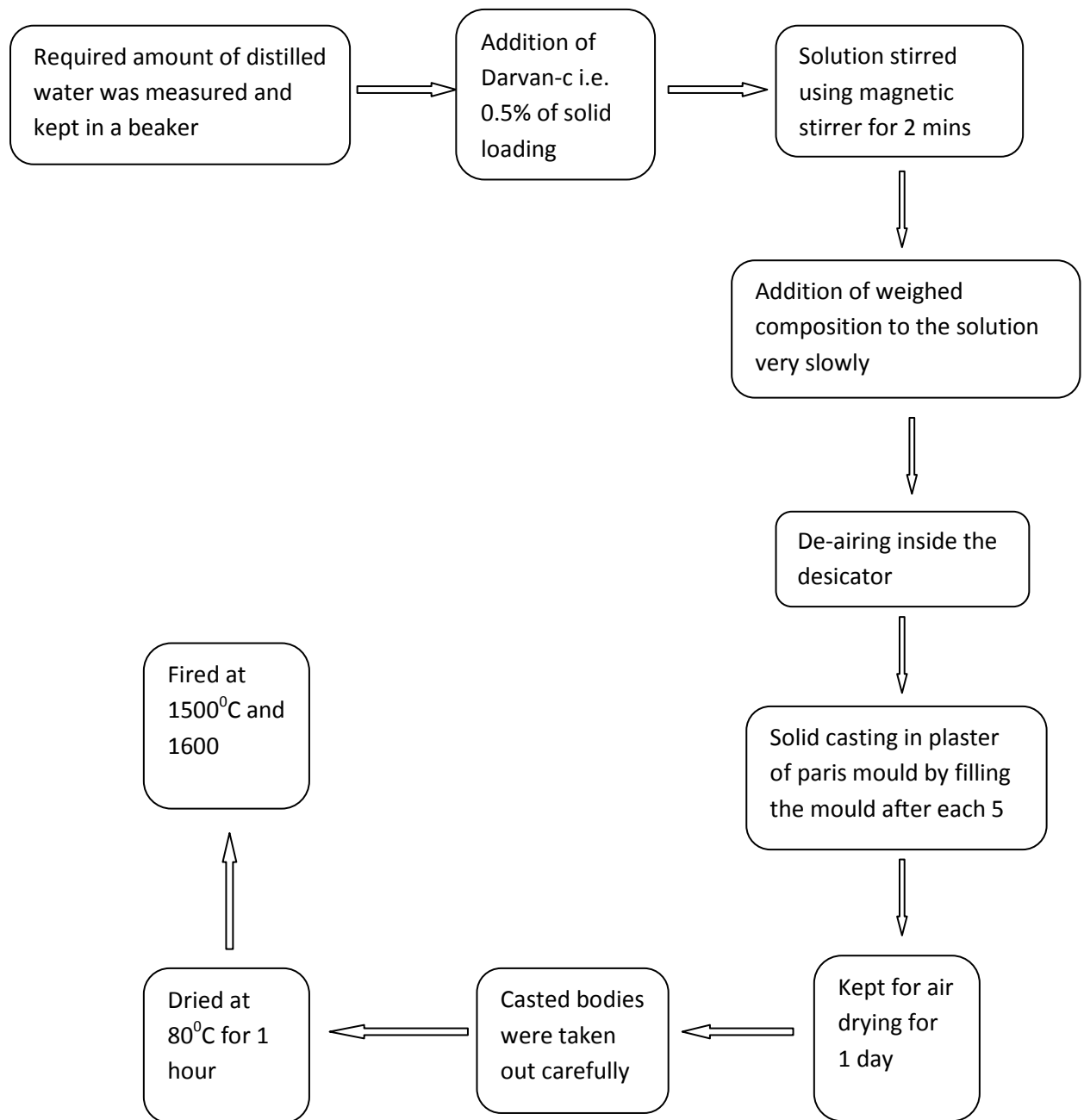
Figure4.3 Flow chart of the overall solid casting

Figure 4.4Image of sintered solid casted bodies

4.3 Gel casting

4.3.1 Preparation of Alumina Slip and Its Casting

The required quantity of distilled water was measured in a beaker. To this water required amount of Darvan c i.e. 0.3% of solid loading was added and kept for stirring using magnetic stirrer for 2 minutes. To this solution measured amount of composition was added very slowly i.e. very less amount at a time for complete and stable suspension for 2 mins. MAM+MBAM added slowly and kept for stirring for 10 hrs, this slurry was kept in desicator for de-airing. Measured amount of PEG was added dropwise and kept for stirring. Petridish was applied was petroleum jelly. To the slurry APS and TEMED was added then. Immediately poured into the mould. Gel- casting in glass petridish mould Cast was kept for air drying for 1 day. Casted body was taken out of mould carefully and kept for drying at 80^0C for 12 hours. Then the dried body was fired at two temperatures i.e. at 1550^0C and 1600^0C. Then the final sintered samples were kept for further characterization.

4.4 De-moulding, Drying, Shaping and Firing of the Casted Bodies

After casting that mould was tapped slowly to remove the casted bodies. After that casted bodies were kept for air drying for 24hrs. Now the sample is transferred to oven for drying which is initially kept at 100 ^{0}C for 24hrs. After the bodies have dried up they are brought into shape by polishing their surfaces using a sand paper. The entire bar shaped samples and cylindrical shaped samples were polished thoroughly. The sample was ready to be fired at 1550 ^{0}C and 1600 ^{0}C with a holding period of 2 hrs in new chamber furnace.

Whole process is described below through flowchart:

```
┌─────────────────┐      ┌─────────────────┐      ┌─────────────────┐
│ Required amount │      │ Addition of     │      │ Solution stirred│
│ of distilled    │ ──▷  │ Darvan-c i.e.   │ ──▷  │ using magnetic  │
│ water was       │      │ 0.5% of solid   │      │ stirrer for 2   │
│ measured and    │      │ loading         │      │ mins            │
│ kept in a beaker│      └─────────────────┘      └─────────────────┘
└─────────────────┘                                        │
                                                           ▽
                                              ┌─────────────────────┐
                                              │ Addition of weighed │
                                              │ composition to the  │
                                              │ solution very slowly│
                                              └─────────────────────┘
                                                           │
                                                           ▽
┌──────────────┐   ┌──────────────┐   ┌──────────────────────┐
│ PEG added    │   │ De-airing    │   │ MAM+MBAM added slowly│
│ dropwise and │◁──│ inside the   │◁──│ and kept for stirring│
│ kept for     │   │ desicator    │   │ for 10 hrs           │
│ stirring     │   └──────────────┘   └──────────────────────┘
└──────────────┘
```

```
                    │
                    ▼
┌──────────────────┐        ┌──────────────────┐        ┌──────────────────┐
│ Petridish was    │        │ To the slurry APS│        │ Immediately poured│
│ applied was      │ ──────▶│ and TEMED was    │ ──────▶│ into the mould   │
│ petroleum jelly  │        │ added            │        │                  │
└──────────────────┘        └──────────────────┘        └──────────────────┘
                                                                   │
                                                                   ▼
┌──────────────────┐                              ┌──────────────────┐
│ Fired at         │                              │ Gel- casting in glass│
│ $1500^0$C and    │                              │ petridish mould  │
│ 1600             │                              │                  │
└──────────────────┘                              └──────────────────┘
         │                                                 │
         ▼                                                 ▼
┌──────────────────┐     ┌──────────────────┐    ┌──────────────────┐
│ Dried at         │     │ Casted bodies    │    │ Kept for air     │
│ $80^0$C for 1    │ ◀───│ were taken       │◀───│ drying for       │
│ hour             │     │ out carefully    │    │ 1 day            │
└──────────────────┘     └──────────────────┘    └──────────────────┘
```
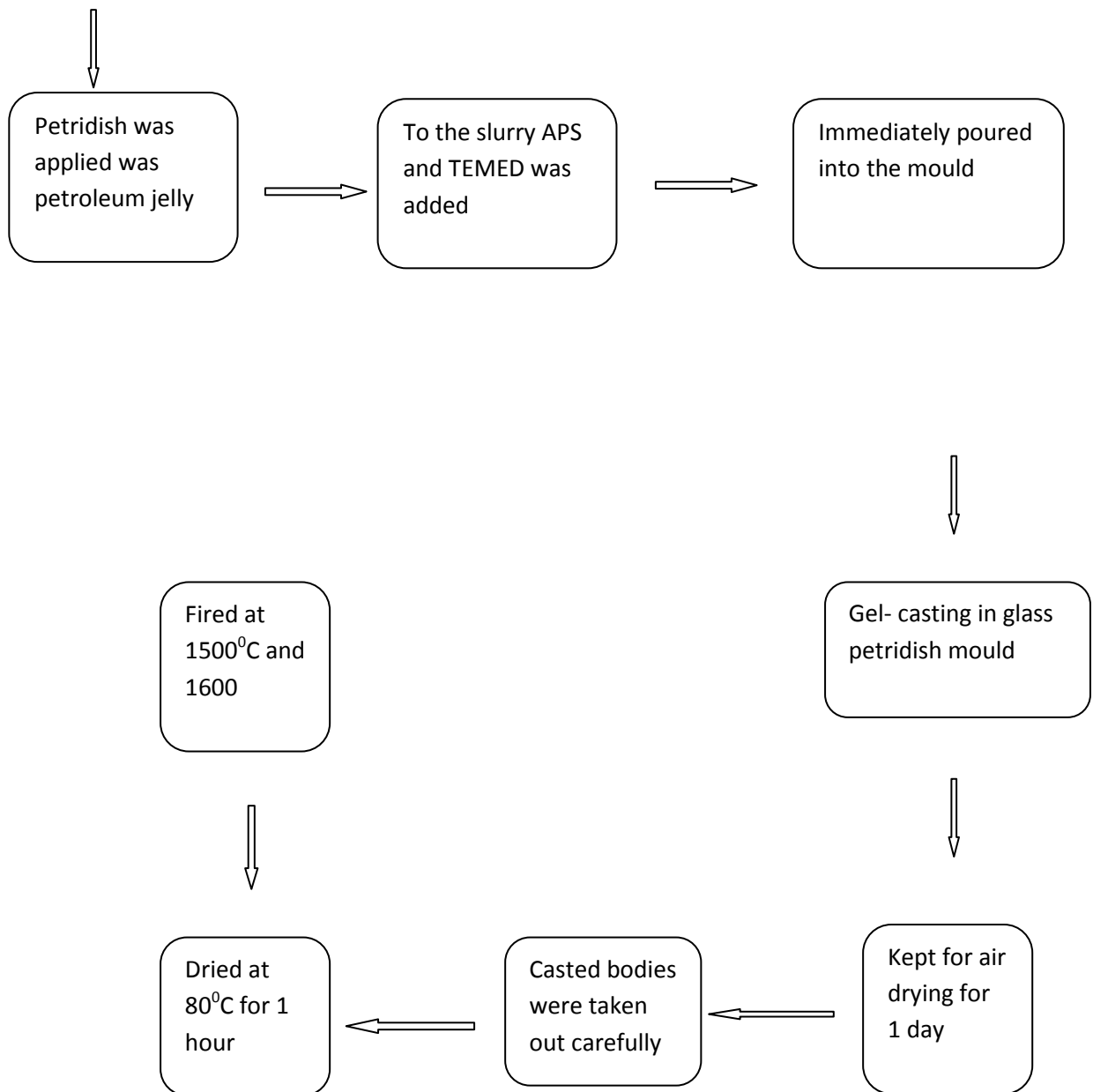
Figure4.5 Flow chart of the overall gel casting

Figure 4.6 Image of sintered gel casted bodies

Chapter:5

CHARACTERIZATION

5. CHARACTERIZATION

5.1 Apparent Porosity

It is a dimensionless quantity which is measured as percentage of volume of open pores to the total volume of the body. This is the property which determines the penetration capacityduring contact of molten metals, slag, dust and fumes. For high temperature application it is desirable to have low AP which prevent the penetration of liquid and thus have high corrosion resistance. It is measured by evacuation method. First of all dry weight of the specimens were taken and noted down. Then those specimens were kept in the desicator to remove all the entraped air bubbles from the open pores for half an hour. Then the suspended weight were taken by immersion of samples in the liquid (here used water) and then specimens were soaked using blotting paper and soaked weight were taken. By using the

formula below AP was calculated:

A.P = [(Soaked Weight – Dry Weight)/(Soaked Weight – Suspended Weight)] x 100

5.2 Bulk Density

It is the quantity which determines the amount of material present in the body. It is expressed as the ratio of the mass of a material to its bulk volume, that is the volume of the given material plus all the pores associated with it. It is very important property for the refractory bodies as an increase of BD increases strength, volume stability, corrosion resistance of the body. It is calculated by using the formula below:

B.D. = [Dry Weight / (Soaked Weight – Suspended Weight)] x density of immersion liquid

5.3 Cold Crushing Strength

CCS is used to determine the compressive strength of the body which tells about the capacity to withstand the load without undergoing deformation. It is very important property of the refractory bodies. It is measured at room temperature so called as cold crushing

strength. For this samples were cut out into cubes and placed inside hydraulic press and load was applied upon the surface of the cube till it gets deformed and the required load is noted down. Then the surface area was calculated. After obtaining these two datas CCS was measured using the following formula :

CCS=Load/Area

Which is in kg/cm^2.

5.4 X-RAY Diffraction

It is a technique used to determine number of phases present, crystallographic structure and mineralogical phases of a natural or fabricated product. X-ray beam is used to obtain the diffraction pattern of the powdered samples. Nano-clay was examined.

5.5 DSC and TG

Differential scanning calorimetric test is used to determine the type of chemical changes occurring over the temperatures i.e. its exothermic or endothermic reaction due to formation of new compounds or due to decomposition of the compound. TG is used to measure the mass gain or loss percentage over the temperature due to formation or decomposition of compounds. Nano-clay was examined.

Chapter: 6

RESULTS AND DISCUSSION

6. RESULTS & DISCUSSION

6.1 XRD ANALYSIS
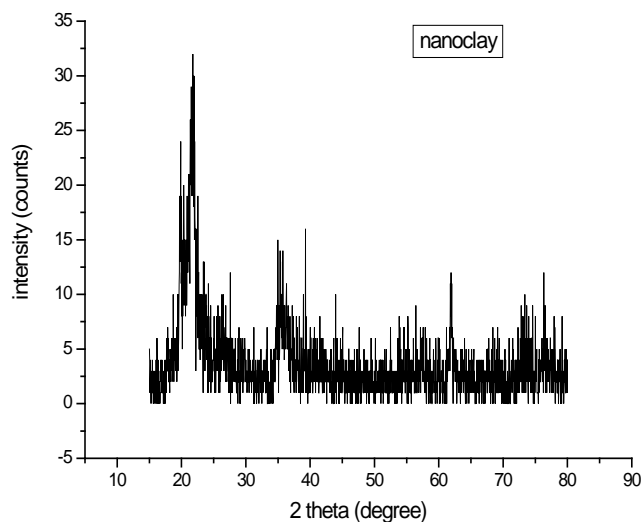
Figure 6.1 X-Ray diffraction pattern of the Nanoclay

In the picture, the XRD pattern of nano clay has been depicted. The highest intensity peak belong to montmorrilonite group of minerals, with crystallite size calculated about 15 nm. After the clay is obtained, it was subjected to DSC analysis and thermo-gravimetric analysis to observe the thermal behaviour of the nano clay. The DSC behavior of the nano clay is shown in Fig 6.2

5`6.2 DSC
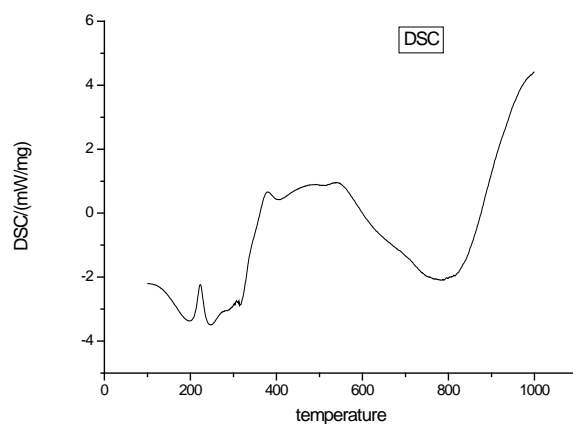
Figure 6.2 DSC plot of nanoclay upto 1000^0C

The differential thermal analysis was carried out up to 1000oC. A small exothermic peak at around 200oC is attributed to los of physically bonded water. The large exothermic dioffuse peak between 400 to 500oC is attributed towards loss of crystalline water in the sample.

6.3 TG
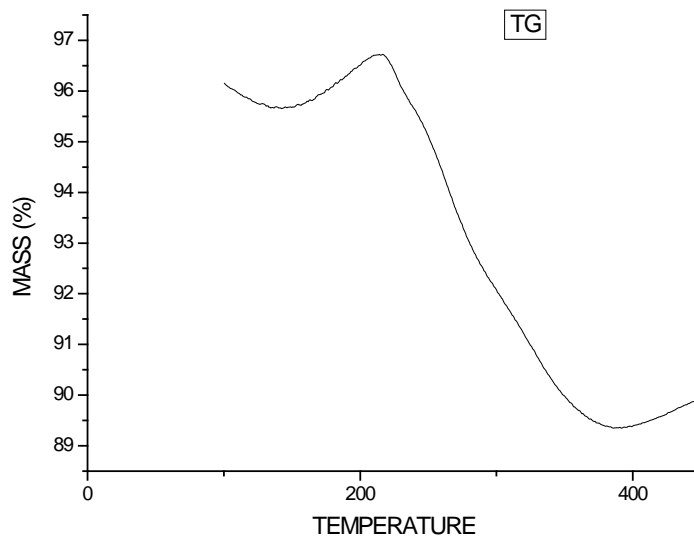
Figure 6.3 TG plot of nanoclay upto 1000^0C

At 200C there is loss in mass then there is sudden rise in mass upto 97% then there is sudden drastic fall upto 400C. Again rise in mass at 550C there is sudden rise in mass at 800C upto 95%,

6.4 Bulk Density

The BD values of all compositions at two temperatures are depicted by the following table:

For pressing technique:

Table 6.1 Tabulation for BD values at two temperatures for solid casting process

Composition	BD at 1550C	BD at 1600C
100-AL	3.495	3.57
99-AL-1NC	3.405	3.461
97.5-AL-2.5NC	3.343	3.421
95-AL-5NC	3.445	3.496
90-AL-10NC	3.275	3.310
95-AL-5ZR	3.574	3.598
90-AL-10ZR	3.686	3.609

For solid casting technique

Table 6.2 Tabulation for BD values at two temperatures for solid casting process

Composition	BD at 1550C	BD at 1600C
100-AL	3.416	3.428
99-AL-1-NC	3.351	3.391
97.5-AL-2.5NC	3.299	3.321
95-AL-5-NC	3.387	3.401
90-AL-10-NC	3.252	3.296
95-AL-5-NC	3.419	3.486
90-AL-10NC	3.425	3.491

For gel casting technique

Table6.3 Tabulation for BD values at two temperatures for gel casting process

Composition	BD at 1550C	BD at 1600C
100-AL	3.476	3.528
99-AL-1-NC	3.413	3.481
97.5-AL-2.5-NC	3.343	3.321
95-AL-5-NC	3.399	3.414
90-AL-10-NC	3.269	3.284
95-AL-5-ZR	3.506	3.529
90-AL-10-ZR	3.457	3.608

For alumina nanoclay system
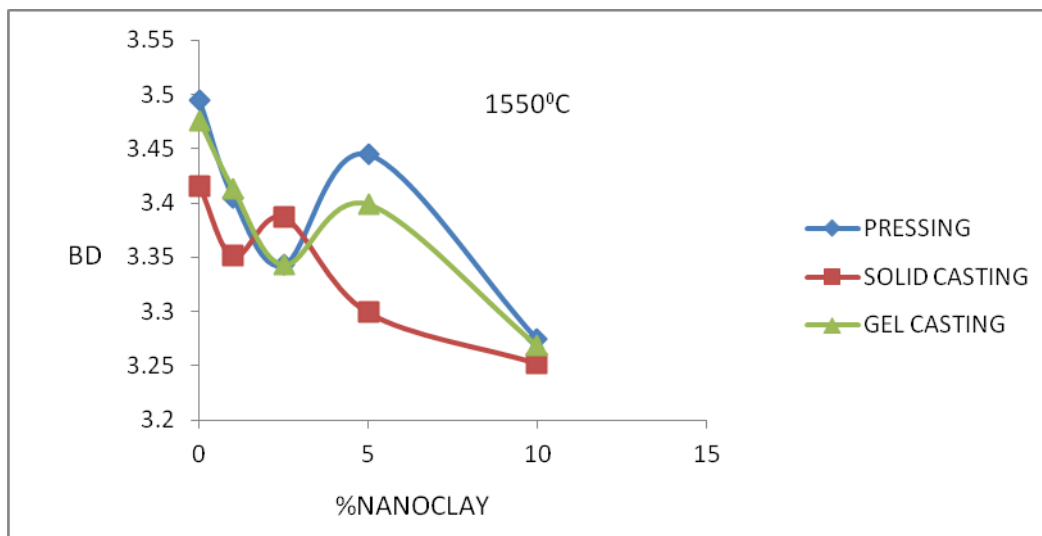
Figure 6.4 BD versus % nanoclay sintered at 1550^0C for three processes

With increasing percentage of nanoclay BD value is decreasing initially in every process. But in between the range of 2.5-5%value is increasing. Among all three processes pressing is showing better BD value having maximum of 3.405 gm/cc. The decrease in bulk denstity can be attributed towards the loss of organic matter from gel casted samples. Further decrease in

bulk density is due to loss of volatile matter from nano clay as there were more incorporation of nano clay in the samples.
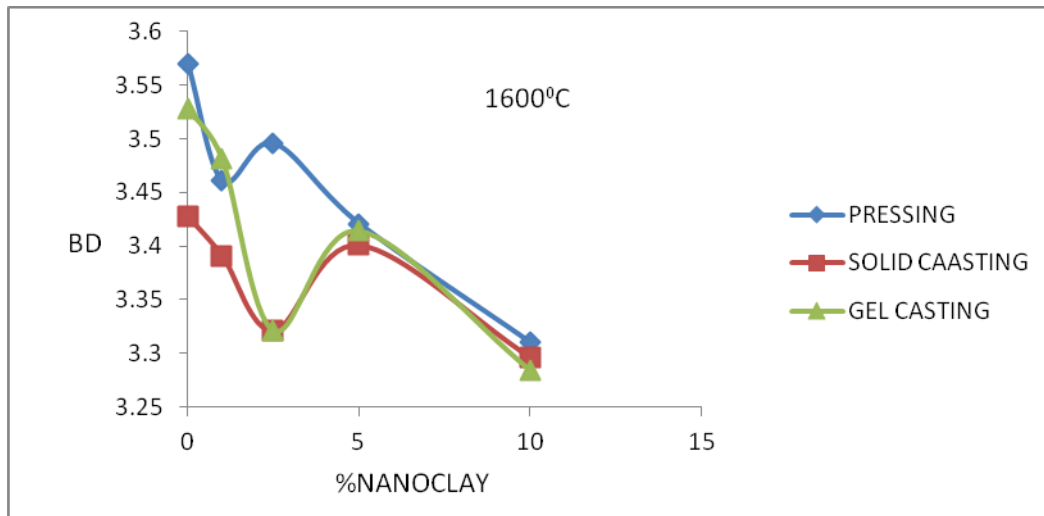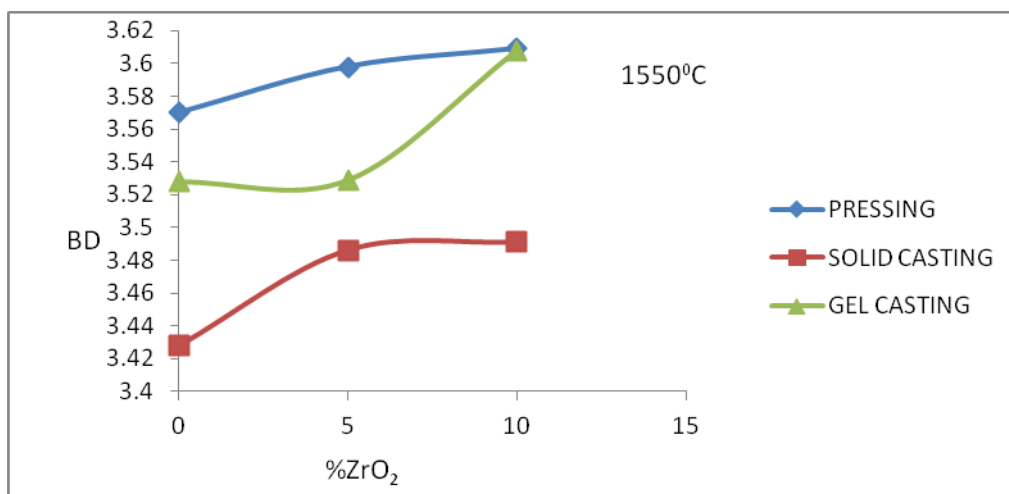

Figure 6.5 BD versus % nanoclay sintered at 1600^0C for three processes

At 1600^0C with increasing of temperature BD is increasing. With increasing percentage of nanoclay BD value is decreasing initially in every process due to loss of volatile matter from nano clay. But in between the range of 2.5-5% value is increasing. Among all three processes pressing is showing better BD value having maximum of 3.461 gm/cc.

For alumina zirconia system

Figure 6.6 BD versus % zirconia sintered at 1550^0C for three processes

With increasing percentage of nanoclay BD value is decreasing initially in every process. But in between the range of 2.5-5%value is increasing. Among all three processes gel casting is showing better BD value having maximum of 3.40.
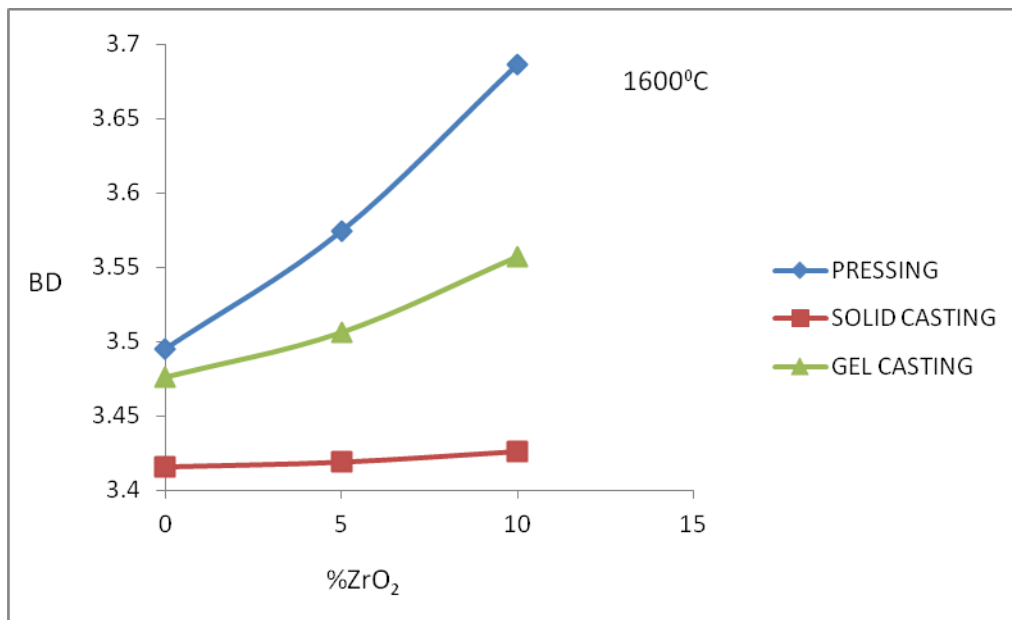

Figure 6.7 BD versus % zirconia sintered at 1600^0C for three processes

At 1600^0C with increasing of temperature BD is increasing. With increasing percentage of nanoclay BD value is decreasing initially in every process. But in between the range of 2.5-5%value is increasing. Among all three processes pressing is showing better BDvalue having maximum of 3.609 gm/cc.

5.5 AP

The CCS values of all compositions at two temperatures are depicted by the following
 table:

For pressing technique:

Table 6.6 Tabulation for AP values at two temperatures for pressing process

Composition	AP at 1550C	AP at 1600C
100-AL	15.13	13.17
99-AL-1-NC	17.25	15.63
97.5-AL-2.5-NC	18.97	17.19
95-AL-5-NC	16.01	14.46
90-AL-10-NC	19.23	18.91
95-AL-5-ZR	15.11	13.13
90-AL-10-ZR	15.02	13.07

For solid casting technique

Table 6.7 Tabulation for AP values at two temperatures for solid casting process

Composition	AP at 1550C	AP at 1600C
100-AL	18.1	14.18
99-AL-1-NC	19.2	16.26
97.5-AL-2.5-NC	19.31	18.01
95-AL-5-NC	18.5	15.25
90-AL-10-NC	21.73	19.18
95-AL-5-ZR	18.02	14.14
90-AL-10-ZR	16.53	14.11

Table 6.8 Tabulation for AP values at two temperatures for gel casting

Composition	AP at 1550C	AP at 1600C
100-AL	13.25	13.14
99-AL-1-NC	14.58	13.63
97.5-AL-2.5-NC	14.44	14.09
95-AL-5-NC	14.81	14.01
90-AL-10-NC	18.63	18.13

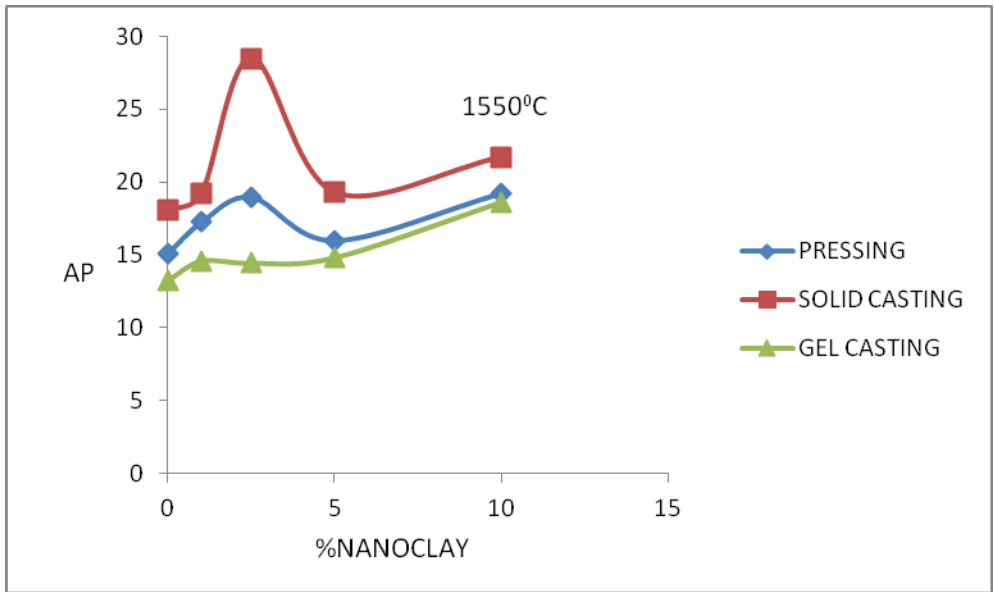|		
95-AL-5-ZR	13.11	13.11
90-AL-10-ZR	13.09	13.08

Figure 6.8 AP versus % nanoclay sintered at 1550^0C for three processes

With increasing percentage of nanoclay AP value is increasing initially in every process. But in between the range of 2.5-5%value is increasing then again rises.
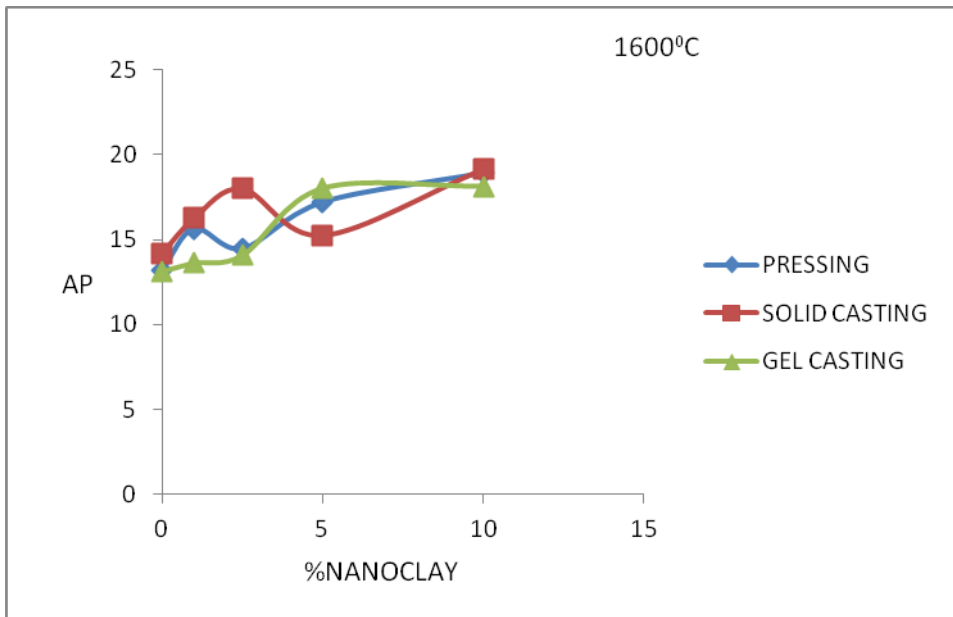

Figure 6.9 AP versus % nanoclay sintered at 1600^0C for three processes

At 1600^0C with increasing of temperature AP is decreasing. With increasing percentage of nanoclay AP value is increasing initially in every process. But in between the range of 2.5-5%value is decreasing then again rises. Among all three processes pressing is showing better AP value having minimum of 15.63%.
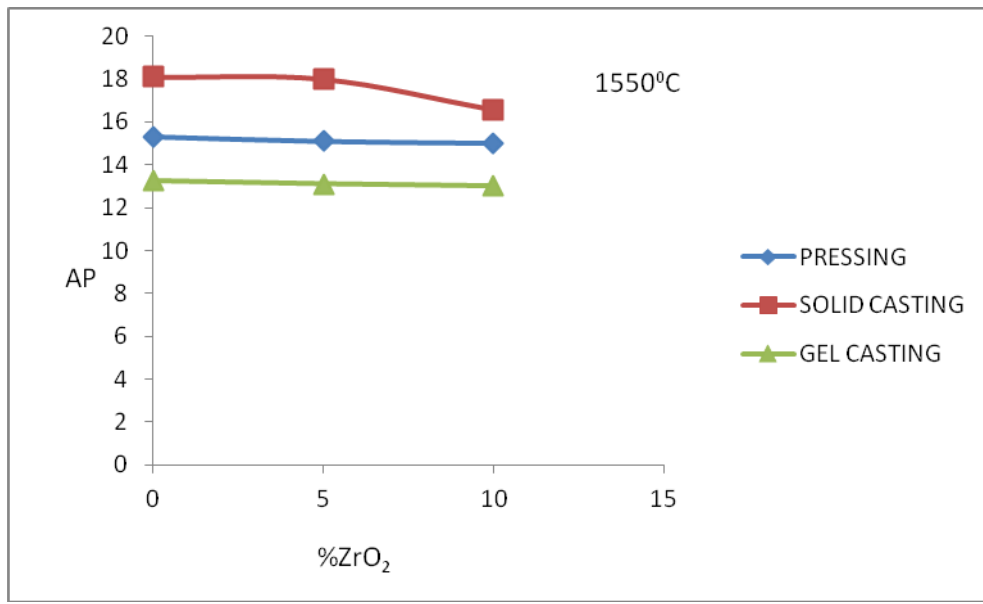
For alumina zirconia system

Figure 6.10 AP versus % zirconia sintered at 1550^0C for three processes

With increasing percentage of zirconia AP value is decreasing in every process. Among all three processes gel casting isshowing better AP value having minimum 15.02%.
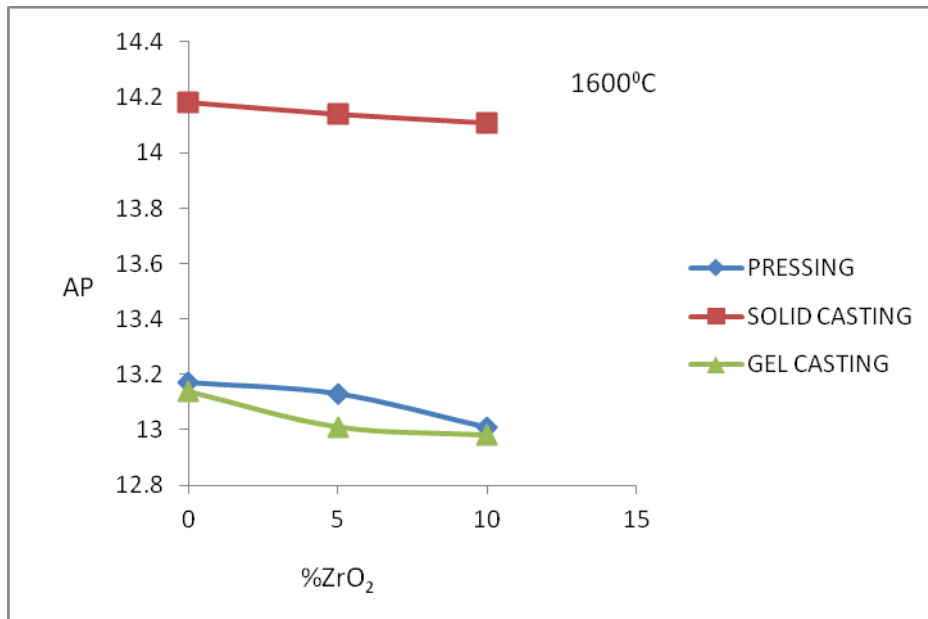
Figure 6.11 AP versus % zirconia sintered at 1600^0C for three processes

At 1600^0C with increasing of temperature AP is decreasing. With increasing percentage of zirconia AP value is decreasing in every process. Among all three processes pressing isshowing better AP value having minimum 13.07%.

6.6 CCS

The CCS values of all compositions at two temperatures are depicted by the following table:

For pressing technique:

Table 6.9 Tabulation for CCS values at two temperatures for pressing process

Composition name	CCS at 1550 ^{0}C	CCS at 1600 ^{0}C
`100-AL	823.13	842.13
99-AL-1-NC	801.67	814.21
97.5-AL-2.5-NC	754.33	743.33
95-AL-5-NC	721.18	721.86
90-AL-10-NC	703.01	711.21
95-AL-5-ZR	828.68	842.13
90-AL-10-ZR	834.14	846.24

For solid casting technique

Table 6.10 Tabulation for CCS values at two temperatures for solid casting process

Composition name	CCS at 1550 ^{0}C	CCS at 1600 ^{0}C
`100-AL	823.13	842.13
99-AL-1-NC	801.67	814.21
97.5-AL-2.5-NC	754.33	743.33
95-AL-5-NC	721.18	721.86
90-AL-10-NC	703.01	711.21
95-AL-5-ZR	828.68	842.13
90-AL-10-ZR	834.14	846.24

For gel casting technique

Table 6.11 Tabulation for CCS values at two temperatures for gel casting process

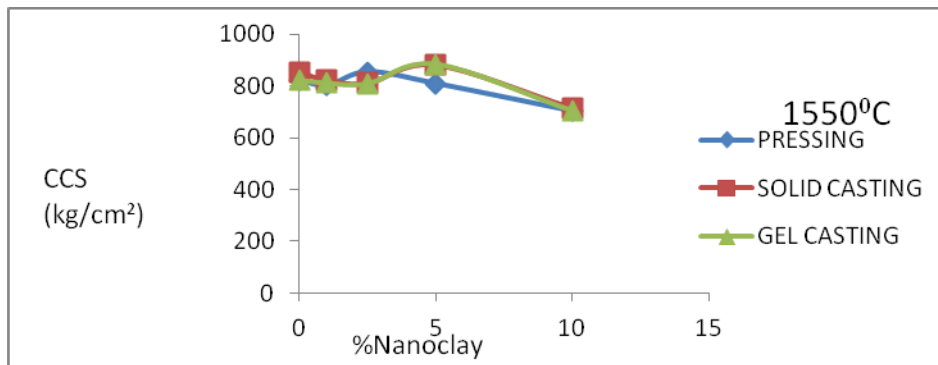| Composition name	CCS at 1550 ^{0}C	CCS at 1600 ^{0}C
`100-AL	823.13	842.13
99-AL-1-NC	801.67	814.21
97.5-AL-2.5-NC	754.33	743.33
95-AL-5-NC	721.18	721.86
90-AL-10-NC	703.01	711.21
95-AL-5-ZR	828.68	842.13
90-AL-10-ZR	834.14	846.24

For alumina-nanoclay system

Figure 6.12 CCS versus % nanoclay sintered at 1550^0C for three processes

With increasing percentage of nanoclay CCS value is decreasing initially in every process. But in between the range of 2.5-5%value is increasing. Among all three processes gel casting is showing better CCS value having maximum of 881.11 kg/cm^2.
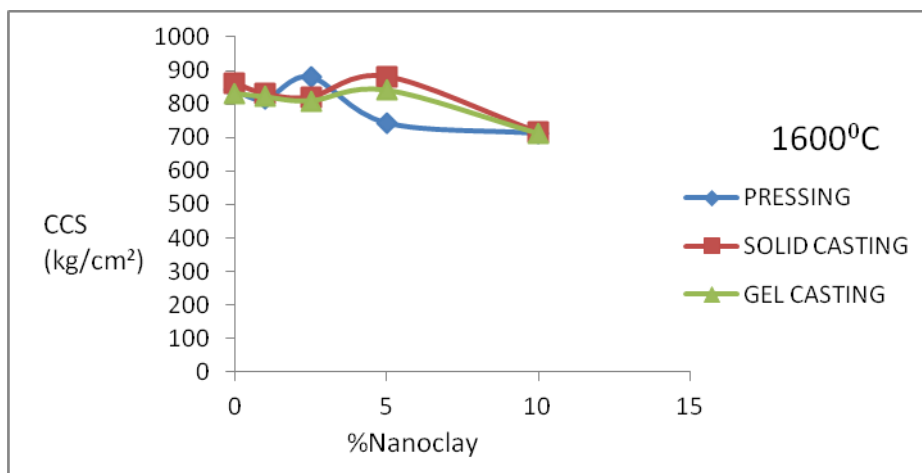

Figure 6.13 CCS versus % nanoclay sintered at 1600^0C for three processes

At 1600^0C with increasing of temperature CCS is increasing. With increasing percentage of nanoclay CCS value is decreasing initially in every process. But in between the range of 2.5-5%value is increasing. Among all three processes gel casting is showing better CCS value having maximum of 881.01 kg/cm^2.
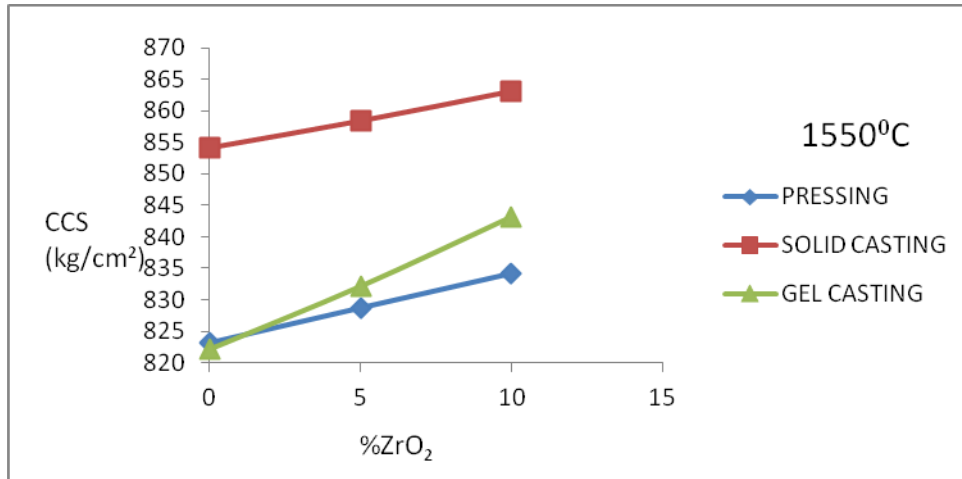
For alumina-zirconia system

Figure 5.14 CCS versus % zurconia sintered at 1550^0C for three processes

At 1550^0C with increasing percentage of zirconia CCS value is increasing in every process. Among all three processes gel casting is showing better CCS value having maximum of 861.61 kg/cm^2.
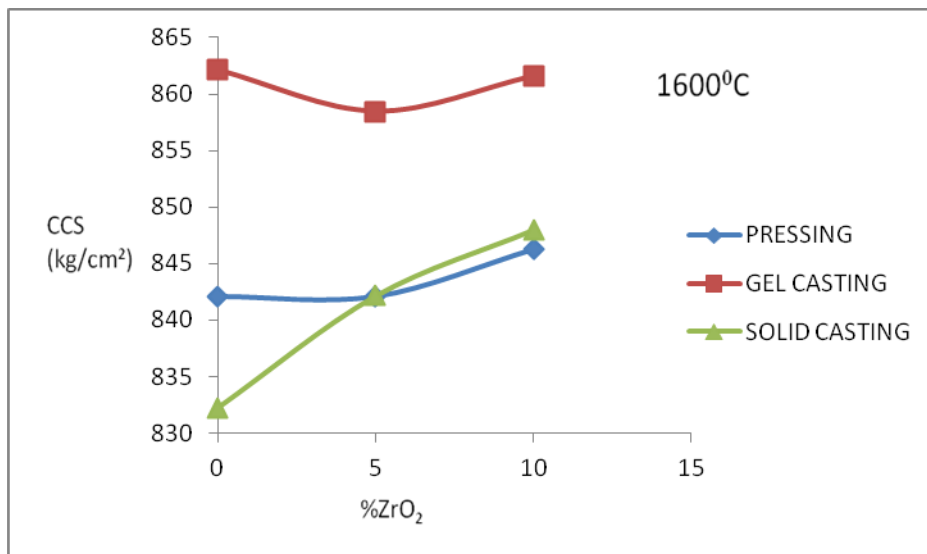

Figure 5.15 CCS versus % zirconia sintered at 1600^0C for three processes

At 1600^{0}C with increasing of temperature CCS is increasing. With increasing percentage of zirconia CCS value is increasing in every process except in pressing where at 5% CCS value is constant and then again increases. Among all three processes gel casting is showing better CCS value having maximum of 861.61 kg/cm^2.

Chapter: 7

CONCLUSION

7. CONCLUSION

Alumina-nanoclay and alumina-zirconia compositions with varying additive percentage were prepared successfully. All the prepared compositions were fired at two temperatures i.e. 1550^0C and 1600^0C and final sintered bodies were prepared using three processes i.e. uniaxial pressing, solid casting and gel casting successfully which were used for further properties measurement. Among all three processes pressing process showed better properties than other two. It was also found that with increasing temperature properties are enhancing. The maximum density obtained was 3.609 gm/cm^3 at 1600^0C pressing process, minimum apparent porosity obtained was 13.07% by again pressing process at 1600^0C and maximum CCS value obtained was 861.61 kg/m^2 by gel casting process. The addition of nano clay in alumina ceramics lead to high porosity which was due to volatile maater loss from the nano clay. Moreover, the glassy phase created due to addition of nano clay may have some non wetting characteristics which prevent further crystallization for nano clay bearing alumina samples

Chapter 8:

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9.REFERENCES

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