

PRODUCTION OF ALUMINA BASED POROUS CERAMICS USING GRAPHITE POWDER AS THE PORE FORMER

A Thesis Submitted
In Partial Fulfillment of the Requirement
For the degree of
BACHELOR OF TECHNOLOGY

By
SHIBA SHAKTI DEHERIA

ROLL 110CR0472



TO THE
DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA
JUNE 2014

CERTIFICATE

This is certified that the work contained in the project entitled “PRODUCTION OF ALUMINA BASED POROUS CERAMICS USING GRAPHITE POWDER AS THE PORE FORMER” by Shiba Shakti Deheria (Roll 110CR0472) in partial fulfillment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering department at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

Dr. (Mrs.) S BHATTACHARYYA
ASSISTANT PROFESSOR
Department of Ceramic Engineering
National Institute of Technology
Rourkela-769008

ACKNOWLEDGEMENT

I express my deep gratitude to my guide, Prof Sunipa Bhattacharyya, Department of Ceramic Engineering, N I T Rourkela, for his valuable advice, time and guidance in the completion of this project work. My heartfelt thanks to all the faculty members for their suggestions during this project work. My sincere acknowledgement to the Research Scholars, M. Tech students and the non-teaching staff for the help and cooperation extended to us. And finally, my hearty thanks to all my friends who have constantly helped me.

Shiba Shakti Deheria
110CR0472

CONTENTS**page no.**

Certificate

2

Acknowledgement

3

Abstract

6**CHAPTER 1: INTRODUCTION****7****CHAPTER 2: LITERATURE REVIEW****11****CHAPTER 3: EXPERIMENTAL WORK****15****CHAPTER 4: RESULTS & DISCUSSIONS****25****CHAPTER 5: CONCLUSIONS****33****REFERENCES**

LIST OF FIGURES:

Figure 3.1 Flowchart for 4vol% PVA binder preparations.	18
Figure 3.2 Diametric Compression Test Showing Loading and Fracture Mode.	23
Figure 4.1 Particle size distribution of calcined alumina.	26
Figure 4.2 Particle size distribution of graphite powder.	26
Figure 4.3 micrograph of pore former graphite powder.	27
Figure 4.4 Variations in volumetric shrinkage of samples fired at three different temperatures.	28
Figure 4.5 Variations in apparent porosity of samples fired at three different temperatures.	29
Figure 4.6 Variations in bulk density of samples fired at three different temperatures.	29
Figure 4.7 Variations in Bi-axial tensile strength of samples fired at three Different temperatures.	30
Figure 4.8 XRD pattern of 1650°C sintered pellets with 0% and 25% pore former.	31
Figure 4.9 micrograph of alumina pellet sintered at 1650°C.	31
Fig- 4.10 micrograph of alumina-25% graphite powder pellet sintered at 1650°C.	32

LIST OF TABLES:

Table 3.1. Batch Calculation done for the Sample Preparation	17
--	----

ABSTRACT

The present work focuses on the production of alumina based porous ceramics and its characterization. Five different alumina samples having graphite wt% between (0 – 25) % were prepared by die pressing. Pellets were fired at different range of temperatures (1450°C –1650°C) with soaking period of 2 hrs. It was found that with increase in the weight percentage (wt %) of graphite, the porosity increases, bi-axial flexural strength decreases. But bi-axial flexural strength increases with the increase in sintering temperature. Bulk density also decreases with increasing in graphite content however the absolute bulk density increases with increasing sintering temperature.

CHAPTER-1: INTRODUCTION

1.1 Introduction.

Porous ceramics is a class of highly reticulated ceramic material that covers a wide range of structures, such as foams, honeycombs, interconnected rods, fibers, or hollow spheres^[1]. Porous ceramics are nowadays being investigated for a variety of applications including molten metal and hot gas filters, light- weight structural components, electrodes, sensors, bioreactors, catalyst carriers, radiant burners and as porous implant in the area of biomaterials due to their specific properties like high surface area, high temperature stability, high permeability, low weight and low thermal conductivity. Some of the example of porous ceramic materials are porous alumina, porous zirconia^[2].

1.2 Typical applications for porous ceramics products include^[3]:

- (i) Thermal and acoustic insulation.
- (ii) Separation/filtration.
- (iii) Impact absorption
- (iv) Catalyst supports.
- (v) Lightweight structures.
- (vi) Porous burners.
- (vi) Energy storage and accumulation.
- (vii) Biomedical devices.
- (viii) Gas sensors.
- (ix) Sonar transducers.

1.3 Types of Porous Ceramics^[4].

All type of porous ceramic comes in two categories:-

Reticulate ceramics:- A reticulate ceramic consists of interconnected voids surrounded by a web of ceramic struts.

Foam ceramics:- Consists of closed and open pores within a continuous ceramic matrix and is usually made by foaming processes applying foaming agents or by powder consolidation using fugitive organic additives as pore formers.

1.4 Alumina Based porous ceramics and its applications ^[4].

Alumina is used for making porous ceramics as most of the alumina-based ceramics possess relatively high strength with improved thermal and chemical resistance. Porous alumina materials are used in various forms, e.g. as porous ceramics for water purification. Applications of porous alumina ceramics have increased in the last decades, especially for environments where high temperatures, excessive wear and corrosive environment are involved. Some applications are filtration of molten metals, high-temperature thermal insulation, filtration of particulates from diesel engine exhaust gases, support for catalytic reactions, and filtration of hot corrosive gases in various industrial operations.

1.5 Pore formers in ceramics.

(i) Graphite Powder^[5].

(ii) Organic Fiber^[6].

(iii) Rice and corn Starch^[6].

(iv) Naphthalene^[4].

(v) Sawdust^[7].

(vi) Calcium chloride^[8], etc

1.6 Graphite powder.

Graphite Powder is used as pore former because it burnt out and forms a void during heat treatment due to removal of graphite^[5]. Graphite powder have the properties like porosity and it also offers considerable long triple phase boundary for catalytic reaction and also provides the channel for gas phase transport^[5].

Pore size control is the key factor in fabrication of porous ceramic body. Particle size and size distribution of the raw materials, processing techniques, types of binder used distribution of binder and sintering affect the final porosity and pore connectivity^[4].

CHAPTER-2: LITERATURE REVIEW

Porous Ceramics and its Applications et al.^[11] :

Porous ceramics are nowadays being produced for a variety of applications like molten metal and hot gas filters, light-weight structural components, thermal insulation, electrodes, sensors, piezo electric & pyroelectric materials, bioreactors, catalyst carriers, radiant burners and as porous implant in the area of biomaterials due to their specific properties like high surface area, high temperature stability, high permeability, low weight and low thermal conductivity.

Lie Fang, Juncheng Liu, Yujun Jhang, Meilin Liu et al.^[6] were investigated the effect of various pore formers on microstructures. They fabricated LCSF porous cathodes by a tape casting process. Basically, they used graphite, carbon black, corn starch and rice starch as pore formers. The microstructures and activity of the LCSF cathodes are found to depend on the morphology, Particle size, shape and nature of the pore former. Based on experiment and performance characterization they found that graphite is most suitable pore former for the fabrication of cathodes for SOFCs by tape casting.

Soumya Surabhi et al.^[4] was prepared alumina based porous ceramic using naphthalene as pore former. She prepared alumina and alumina-naphthalene samples which contain 0%, 20%, 30%, 40% and 50% of naphthalene respectively and sintered them in temp. 1500⁰c, 1550⁰c, 1600⁰c. After characterization she found that porous alumina sample containing higher percentage of naphthalene have the higher porosity and lower strength and vice versa.

Sumin Zhu, Shuqiang Ding, Hong'an Xi, Qin Li, Ruoding Wang et al.^[9] Were adopted a reactive processing method for the preparation of SiC/cordierite composite porous ceramics. SiC particles are bonded to each other by cordierite, which is synthesized from the starting materials of clay, talc and

alumina. Graphite powder is used as the pore former to change the porosity of the specimens. Sintering of the porous ceramics is carried out at 1360°C. After characterization the prepared porous ceramics have a strength value up to 54.6 Mpa at 27.6% porosity. They also found that the SiC/cordierite composite porous ceramics have an excellent resistance to cyclic heat shock treatment due to the unavailability of crack propagation in the porous body.

Ayhan Sarikaya, Faith Dogan et al.^[10] were investigated the effect of various pore formers on the microstructural development of tape-cast porous ceramics and concluded that the thermal and morphological properties of pore formers have a vital effect on the features of resultant microstructures. They found that the pore formers act as templates for the development of porosity by means of pore shape, size and connectivity. Hence porous ceramic can be fabricated without defects by using the requisite pore formers which provide the suitable and adjustable processing parameters.

Graphite powder as pore former et al.^[5]

- (A) Dispersion of graphite powder as the pore formers controls the homogeneous pore structure of the porous ceramic and deeply influence its properties. Shape of pores, pore size, and pore distribution in the porous ceramics are related to the dispersion and characteristics of pore formers.
- (B) Graphite powder can be used as a pore formers because it have higher porosity and offer considerable the long triple phase boundary for catalytic reactions as well as offers channels for the gas phase transport.
- (C) Graphite powder have the unique chemical and physical properties, exhibits good thermal and electrical conductivity, inertness and lubricant ability.

(D) Graphite provides small and uniform pores when it will oxidize. Generally, graphite powder oxidize at temperature between 575⁰c to 775⁰c.

Applications field of Alumina based porous ceramics.^[4]

Field of Bio-Ceramics : Porous alumina ceramic are also extensively used in bio ceramic as it satisfy the basic requirements in bone implant, as a high porosity level for an organization of vascular canals that can ensure the blood supply, compatible mechanical properties with bone structure & a high bioactivity for bone in-growth.

Field of Bone Implants: Porous Alumina is an Ideal Substrate for Bone Substitute, high porosity level is required for the following properties. Porous materials have large surface area, resulting in a high tendency to bio-resorb, which induces high bioactivity. Interconnected pores permit tissue in-growth and thus anchor the prosthesis with the surrounding bone, preventing loosening of implants.

Interconnected porosity acts like an organization of vascular canals which can ensure the blood and nutrition supply for the bone. Alumina is not only bio-inert but also mechanically strong which makes it an ideal substrate for bone substitute. The high porosity is achieved via a sponge technique by which both pore size and density can be changed easily^[4].

CHAPTER-3: EXPERIMENTAL DETAILS

Preparation of green pellets of alumina with graphite

3.1 Raw materials and batch calculation

The specifications of raw materials are given below:

(A) Calcined Alumina from TRL,

(B) Graphite,

(C) PVA from LOBA Chemie,

Batch calculation

Diameter of the die has been used while pressing – 12.0 mm diameter. 20gm of each batch is prepared from which 9 pallets were made for different characterization and testing.

(A) Sample preparation of 100% alumina

For preparing 100% alumina batch, 20gm of calcined alumina is used. From this batch 0.8gm of is taken for pallet preparation.

(B) Sample preparation of 90 % alumina + 10 % graphite

For the preparing batch of 90% alumina + 10 % graphite (weight %),

90% alumina $\frac{90}{100} \times 20 = 18 \text{ gram of alumina.}$

10 % graphite $\frac{10}{100} \times 20 = 2 \text{ gram of graphite}$

(C) Sample preparation of 85 % alumina + 15 % graphite

For the preparing batch of 85% alumina + 15 % graphite (weight %),

Calculation:-

$$85\% \text{ alumina } \frac{85}{100} \times 20 = 17 \text{ gram of alumina.}$$

$$15\% \text{ graphite } \frac{15}{100} \times 20 = 3 \text{ gram of graphite}$$

(D) Sample preparation of 80% alumina + 20% graphite

For the preparing batch of 80% alumina + 20 % graphite (weight %),

Calculation:-

$$80\% \text{ alumina } \frac{80}{100} \times 20 = 16 \text{ gram of alumina.}$$

$$10\% \text{ graphite } \frac{10}{100} \times 20 = 4 \text{ gram of graphite}$$

(E) Sample preparation of 75% alumina + 25% graphite

For the preparing batch of 75% alumina + 25 % graphite (weight %),

Calculation:-

$$75\% \text{ alumina } \frac{75}{100} \times 20 = 15 \text{ gram of alumina.}$$

$$25\% \text{ graphite } \frac{25}{100} \times 20 = 5 \text{ gram of graphite}$$

Table 3.1. Batch Calculation done for the Sample Preparation

<i>Sample specifications</i>	<i>Weight of alumina (gm)</i>	<i>Weight of graphite (gm)</i>
100% alumina	20	–
90% alumina and 10 % graphite	18	2
85% alumina and 15 % graphite	17	3
80% alumina and 20 % graphite	16	4
75% alumina and 25% graphite	15	5

4% PVA binder solution preparation

Polyvinyl alcohol was obtained from LOBA Chemie [chemical formula: $(C_2H_4O)_n$].

The binder solution was prepared following the steps mentioned in the Fig. 3.1

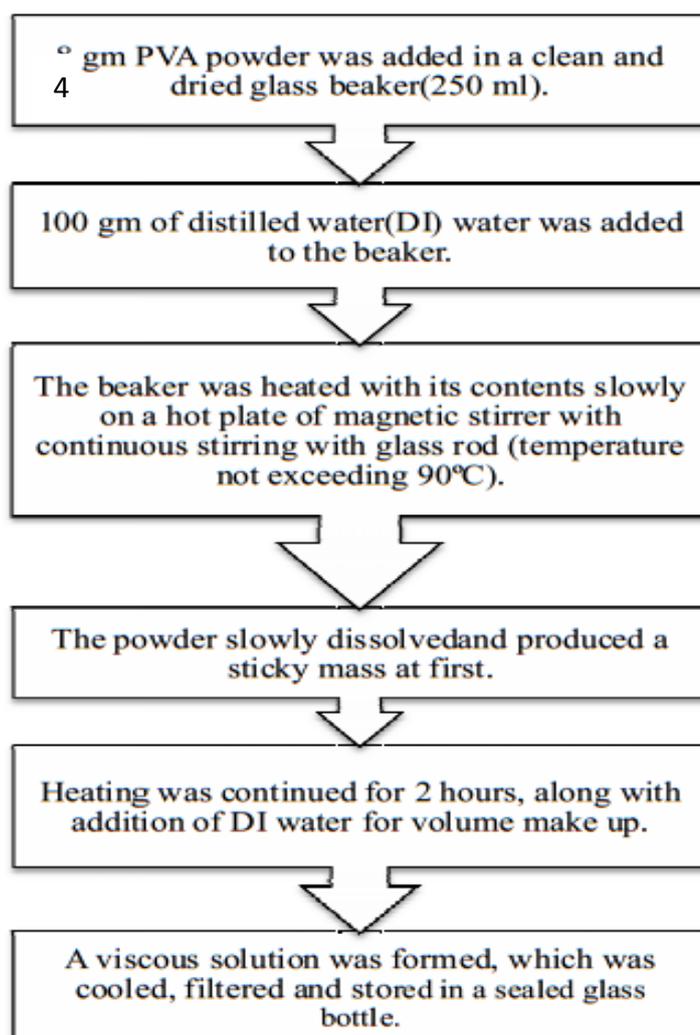


Fig 3.1 Flow chart for 4% PVA solution preparation

Mixing and drying of batch

Calcined alumina and alumina-graphite pellets were prepared using calcined alumina powder and graphite powder. At first, calculated amount of calcined alumina powder was weighed and mixed using pot mill, the batch composition of 20 gram was mixed using ethanol medium in pot mill for 4 hour (this is done for all 4 batch composition except the pure 100% alumina batch.). After mixing the batch is taken out and dried initially at 60°C then 100°C until complete removal of ethanol. Dried batch is thoroughly mixed in an agate mortar pestle with the required amount of PVA (4% PVA solution) The PVA solution was thoroughly blended with alumina by mixing it in agate mortar for 30 minutes. The dry powder was then weighed to the required amount for making the pellets.

Green compaction

Pellets were made by dry pressing in a hydraulic press (Carver Press USA) at a load of 3 tonnes, with dwell time of 60 seconds. Acetone was used for cleaning the die to prevent contamination and sticking and 5% stearic acid solution was used for lubrication.

Drying of green pellets

Green pellets formed by dry pressing were dried in oven (100°C).

3.2. Sintering of green pellets

The pressed pellets were sintered in an electrical resistance heating furnace at 1450°C, 1550°C and 1650°C. At each sintering temperature, the holding times for different batches were 2. An intermediate soaking period of 2 hour at 900°C was provided for graphite burnout. The samples were heated at 2°C/min till 900°C followed by heating at 5°C/min till the final sintering temperature. Following the holding at the final temperature, the furnace was switched off for cooling and the samples were taken after the furnace temperature reached below 100°C.

3.3. Characterization of raw materials and sintered pellets

Chemical analysis of alumina

In the chemical analysis of alumina, titration test is done to determine the amount mixed oxides, silica and alumina content in the calcined alumina.

Particle size analysis

Partical size of alumina and graphite is determined using. Zeta seizer is used to determine PSD (Particle Size Distribution) Vs intensity & volume.

True density determination

True density of the graphite and alumina is done. Finely grounded sample of alumina is taken in pycnometer. The dried weight of empty pycnometer and weight with sample and pycometer is recoded reaming volume of pycnometer is filled with water. And the pycnometer is kept in vacuum for 2 hour. Again weight is taken by filling remaining volume with water.

And true density is calculated by using formula:-

$$\text{true density} = \frac{B - A}{(D - A) - (C - B)} \quad \text{Where,}$$

A=weight of dry and empty pycnometer

B=weight of sample and pycnometer

C=weight of pycnometer + weight of sample + weight of water

D=weight of pycnometer +water

Apparent Porosity, Bulk Density Measurements

The densities of green pellets were determined from the weight and volume. 3 pellets from each type of samples were taken and density was measured. Average of the 3 density measurements were taken into consideration. The following formula was used to measure the density of green pellets: Density = (Mass of pellet)/(Volume of cylindrical pellet)

The apparent porosity, bulk density of sintered pellets was measured. First the dry weight of pellets was measured. Then they were soaked in kerosene kept inside a beaker and were evacuated in a vacuum evacuator till all the air bubbles vanished. After that they were kept inside vacuum for few hours. After removing from vacuum evacuator, the suspended weight and soaked weight of the samples were calculated.

To obtain bulk density (B.D.), the following formula was used:

$$\text{B.D.} = \frac{\text{(dry weight)}}{\text{(soaked weight - suspended weight)}} \quad \text{-----(3.1)}$$

To obtain apparent porosity (A.P.) in %, the formula used is:

$$A.P. = \frac{(\text{soaked weight} - \text{dry weight}) * 100}{(\text{soaked weight} - \text{suspended weight})}$$

----- (3.2)

Shrinkage on firing

The pressed green sample's dimensions is measured using vernier caliper. Diameter and thickness of fired and green sample is measured. The measured dimensions are used to determine the shrinkage using following formula.

$$\% \text{shrinkage} = \frac{\text{intial volume} - \text{final volume}}{\text{initial volume}}$$

Bi-axial Tensile Strength Measurements

The bi-axial tensile strength of the pellets was measured by breaking the samples in a Tinius Olsen Materials Testing Machine (HK10S model). It has a maximum load capacity of 10 KN. The bi-axial tensile strength, S was obtained using the formula:

$$S = \frac{2 * P}{\Pi * D * t} \quad \text{----- (3.4)}$$

Where, P = Maximum

Load D = Diameter of

the pellet t =

Thickness of the

pellet

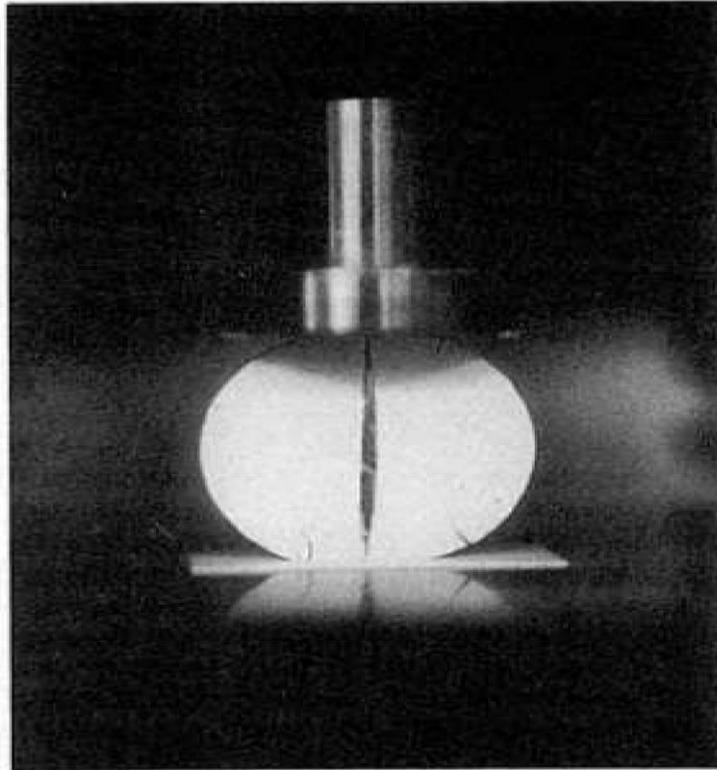


Fig. 3.2. Diametral Compression Test Showing Loading and Fracture Mode^[42]

Scanning Electron Microscopy (SEM)

Scanning Electron Microscope provides topographical and elemental information at magnifications of 10X to 100,000X with unlimited depth of field. A finely focused electron beam scanned across the sample surface generates secondary electrons, backscattered electrons, and characteristic X-rays. These signals are gathered by detectors to form images of the sample displayed on digital screen.. Images and spectra can be printed here, or recorded on CD ROM.

3.3.7 X-ray diffraction

To determine the phase composition of raw material and different batch composition X-ray diffraction analysis is done. The data is plotted and analyzed using X'pert Highscore software.

CHAPTER– 4
RESULTS
AND
DISCUSSIONS

4.1. Raw material analysis:

i. Composition of calcined alumina

Amount of silica found: 2.15 % Amount of Mixed oxide found: 95.92 %

Iron Oxide: 1.78% Amount of Alumina: - 95.92- 1.78 = 94.14 %

ii. Particle size distribution

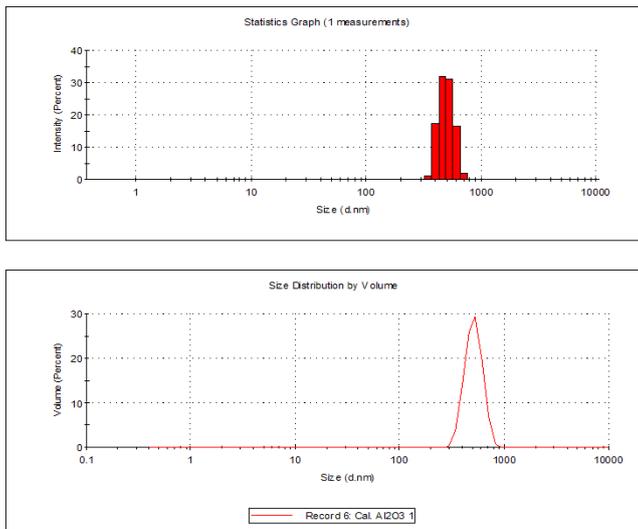


Fig- 4.1 Particle size distribution of calcined alumina

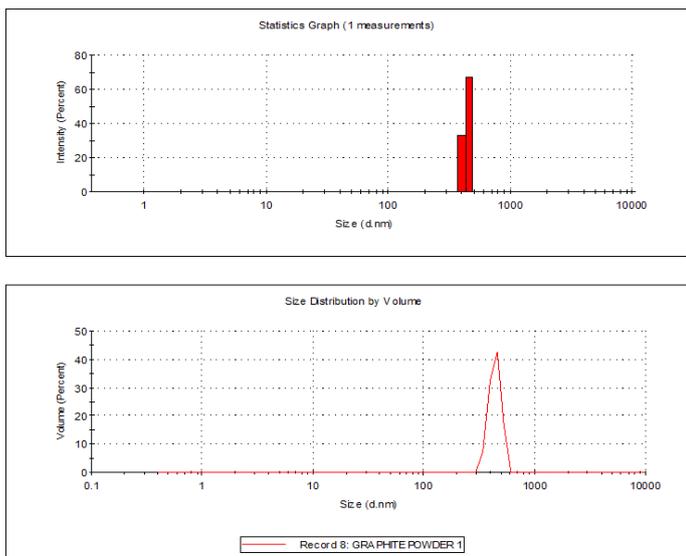


Fig- 4.2 Particle size distribution of graphite powder

Figure- 4.1 and 4.2 showed the differential distribution of particle size of calcined alumina and graphite powder respectively. It shows the relative amount of each size. Both distributions are uni-modal (single peak) but not mono dispersed (all one size).

iii. True density determination by picnometer

True density of alumina - 3.68 gm/cc.

True density of graphite powder - 2.03 gm/cc.

iv. Morphology of pore former

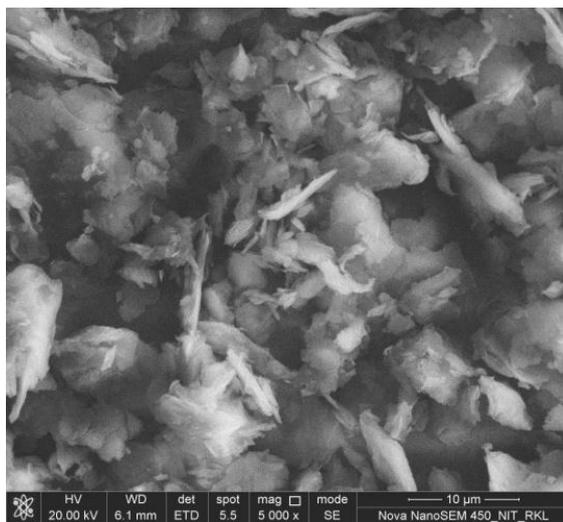


Fig-4.3 micrograph of pore former graphite powder

Fig- 4.3 shows the morphologies of pore formers. Here graphite powder consists of agglomerated platelet-like flakes with a mean length ranging from 5 to 10 μm , and their edges are not clearly distinguishable.

4.2. Characterization of sintered pellets

i. shrinkage:

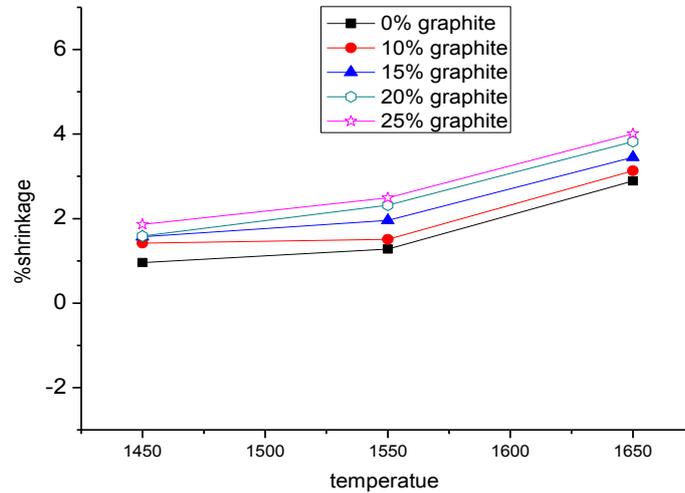


Fig- 4.4 Variations in volumetric shrinkage of samples fired at three different temperatures.

Fig - 4.4 shows the variation of volumetric shrinkage in the sintered alumina and alumina-graphite pellets as a function of sintering temperature for different graphite content. All the plots show similar trend, i.e. volumetric shrinkage increasing with increasing firing temperature. This implies that at higher firing temperature sintering initiates which causes this increase in volumetric shrinkage. On the other hand, it is interesting to note that gradual increase in shrinkage was measured at the same sintering temperature for samples with increasing amount of pore former.

ii. Apparent porosity

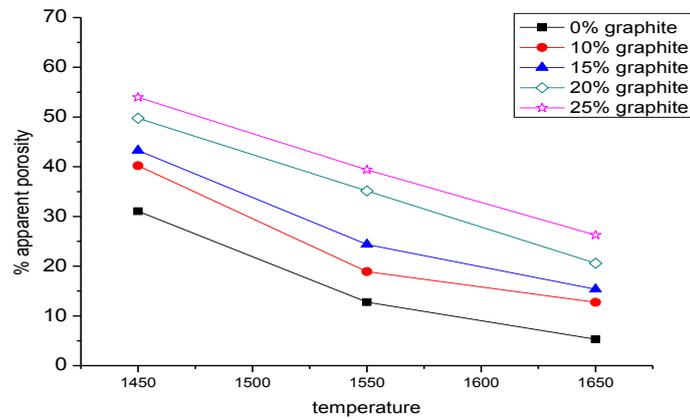


Fig- 4.5 Variations of percent apparent porosity of samples fired at three different temperatures.

Fig 4.5 shows the variation of apparent porosity in the sintered alumina sample and alumina-graphite sample as a function of sintering temperature for different graphite content. All the plots show similar results i.e. porosity decreases with an increase in sintering temperature. This implies that at higher sintering temperature thermally activated material transport into the pores causes reduction in porosity. At a particular temperature with increasing the percent of pore former porosity increases.

iii. Bulk density

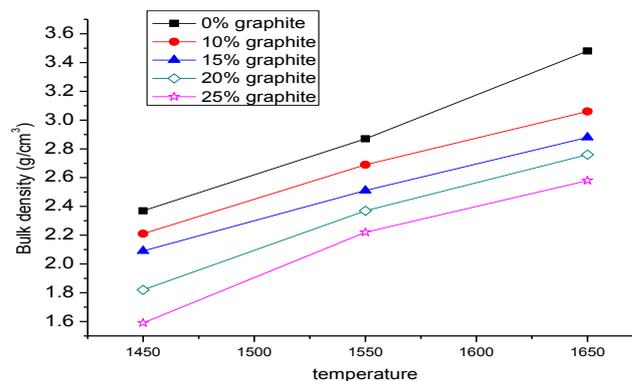


Fig- 4.6 Variations of bulk density of samples fired at three different temperatures.

Fig 4.6 shows the variation of bulk density in the sintered alumina pellets and alumina –graphite pellets as a function of sintering temperature for different graphite content. All the plots show similar nature i.e. bulk density increases with an increase in sintering temperature. However, the absolute value of bulk density decreases with increasing graphite content. This implies that at higher temperature densification occurs that resulting the reduction of porosity and increase in bulk density.

iv. Bi-axial tensile Strength

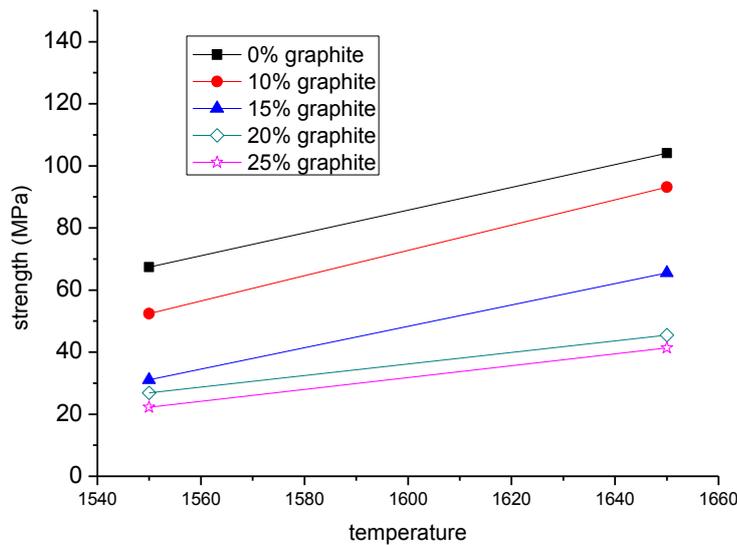


Fig 4.7 Variations in Bi-axial flexural Strength of sintered samples with firing temperature for different amount of pore former.

Fig. 4.7 shows that the bi-axial flexural strength is higher for pure alumina in comparison to alumina –graphite samples, due to higher amount of porosity in the latter samples. Higher porosity implies less load bearing capacity and weak samples. Therefore, the flexural strength decreases with higher graphite content.

v. ***X-Ray Diffraction Analysis.***

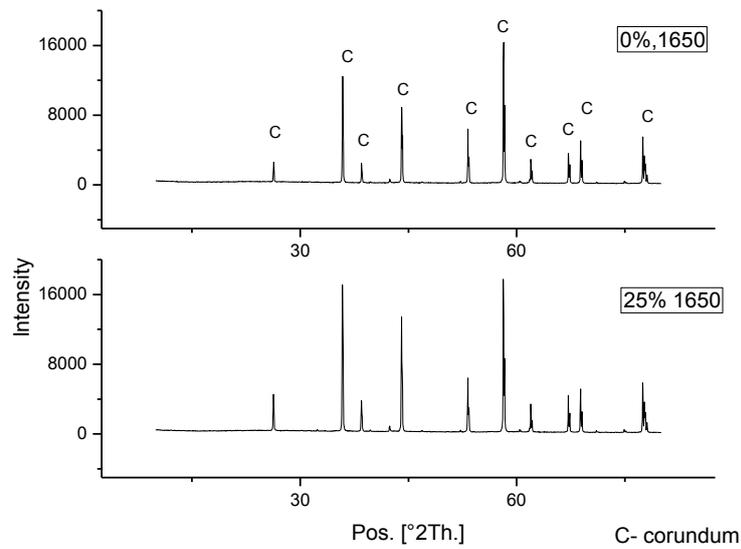


Fig- 4.8 XRD pattern of 1650°C sintered pellets with 0% and 25% pore former

The above pattern shows that after sintering only corundum phase was found no other phase was identified.

vi. ***Field Emissions/ Scanning Electron Microscopy.***

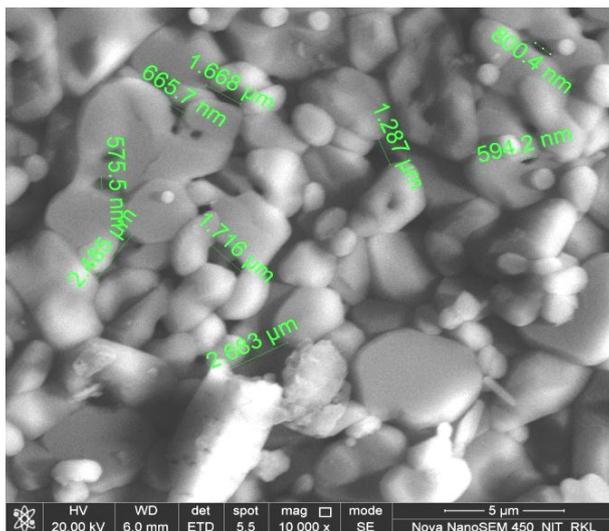


Fig- 4.9 micrograph of alumina pellet sintered at 1650°C

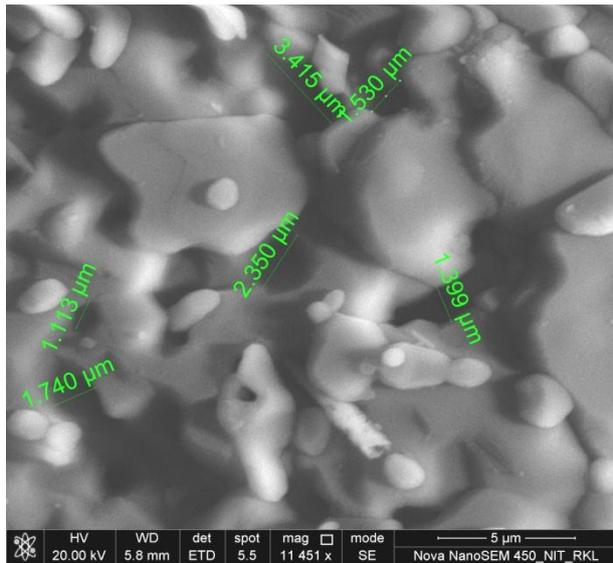


Fig- 4.10 micrograph of alumina-25% graphite powder pellet sintered at 1650°C

From these microstructures it can be said that in absence of pore former porosity is much less and pores which are present are smaller in size. On the other hand in presence of pore former pore size increases, these are not inter granular pore but generated due to the graphite burn out.

CHAPTER-5:
CONCLUSIONS

&

REFERENCES

Conclusions

- i. Graphite powder is a very good pore former which burnt out completely during firing generating pores within ceramic sample.
- ii. With increasing the amount of graphite powder the percent apparent porosity increases and bulk density decreases.
- iii. At 1650°C, 25% graphite containing batch having 30 % porosity, exhibiting flexural strength around 30%.
- iv. Microstructures show that pores formed by the pore former are larger in size and their shapes are different from the inter granular pores.

REFERENCES:-

REFERENCES:-

[1] <http://www.soilmoisture.com/ceramics.html>

[2] <http://www.en.wikipedia.org/wiki/ceramic>

[3] <http://www.rsta.royalsocietypublishing.org/content/364/1838/5.long>

[4] Soumya Surabhi," Production of alumina based porous ceramic using Naphthalene as the pore former," B.tech Thesis," ceramic department," NIT Rourkela," ethesis@nitr," 2012.

[5] Qiang Li and Fei Ma," Study on dispersion of graphite powder as pore former," Department of Chemistry,"East China Normal Universities," Shanghai 200062.Advance Material Research Vol. 412 (2012).

[6] Lifang Nie, Juncheng Liu, Yujun Zhang, Meilin Liu," Effects of pore formers on microstructure and performance of cathode membranes for solid oxide fuel cells," Journal of Power Sources 196(2011) 9975-9979,"

[7] Bachir Chemani , Halima Chemani ," Effect of Adding Sawdust on Mechanical-Physical Properties of Ceramic Bricks to Obtain Lightweight Buliding Material," World Academy of Science, Engineering and Technology 71 2012.

[8] Jan Skalny, Ivan Odler, Julius Hagymassy Jr," Pore Structures of Hydrated Calcium Silicate," Institute of colloid & surface science and department of chemistry," Clarkson College of Technology, Potsdam, New York 13676 USA,"

Journal of Colloid and Interface Science (Impact Factor: 3.17). 03/1971; 35(3):434–440. DOI: 10.1016/0021-9797(71)90143-3.

[9] Sumin Zhu , Shuqiang Ding , Hong'an Xi, Qin Li, Ruoding Wang," Preparation and Characterization of SiC/cordierite Composite Porous Ceramics," Ceramics International 33 (2007) 115–118.

[10] Ayhan Sarikaya, Fatih Dogan," Effect of various pore formers on the microstructural development of tape-cast porous ceramics,"Ceramics Internationals 39 (2013) 403-413.

[11] J. Cao, C. R. Rambo, and H. Sieber," Preparation of Porous Alumina Ceramics by Bio templating of Wood," J. Por. Mat. (2004), Vol. 11, Issue 3, pp 163-172.