

Effect of ZnO addition on the sintering behavior of Al₂O₃

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CERTIFICATE

This is to certify that the thesis entitled, “**Effect of ZnO addition on the sintering behavior of Al₂O₃**” submitted by **Mr. APOORV NEGI** in partial fulfillment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by her 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.

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CERTIFICATE

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ABSTRACT

Densification of alumina has been studied in the present work in presence of Zinc oxide. Zinc oxide as dopant has been added to the extent of 0.5, 1 and 2 weight % to pure alumina and studied for pressure-less sintering. Pellets of without and with ZnO containing compositions were sintered at 1550⁰C 1600⁰C, 1650⁰C and then characterized for densification, phase analysis. A new phase, ZnAl₂O₄, has been observed in the sintered samples indicating reactions between alumina and dopant phase. Results reveal that Zinc oxide is a beneficial sintering additive for alumina on sintering at 1650⁰C, at lower temperatures it has a hindering effect on sintering.

Chapter 1 INTRODUCTION

Chemical Formula: Al_2O_3

Background

Aluminium Oxide (Al_2O_3) or alumina is one of the most versatile of refractory ceramic oxides and finds use in a wide range of applications. It can exist in several crystalline phases which all revert to the most stable hexagonal alpha phase at elevated temperatures. This is the phase of particular interest for structural applications.

Alpha phase alumina is the strongest and stiffest of the oxide ceramics. Its high hardness, excellent dielectric properties, refractoriness and good thermal properties make it the material of choice for a wide range of applications.

High purity alumina is usable in both oxidizing and reducing atmospheres to 1925°C . Weight loss in vacuum ranges from 10^{-7} to 10^{-6} $\text{g}/\text{cm}^2\cdot\text{sec}$ over a temperature range of 1700° to 2000°C . It resists attack by all gases except wet fluorine and is resistant to all common reagents except hydrofluoric acid and phosphoric acid. Elevated temperature attack occurs in the presence of alkali metal vapors particularly at lower purity levels.

It is found in nature as corundum in emery, topaz, amethyst, and emerald and as the precious gemstones ruby and sapphire, but it is from the more abundant ores such as bauxite, cryolite and clays that the material is commercially extracted and purified.

Corundum exists as rhombohedral crystals with hexagonal structure. The unit cell is an acute rhombohedron of side length 5.2\AA and plane angle $\sim 55^\circ$. It is the close packing of the aluminium and oxygen atoms within this structure that leads to its good mechanical and thermal properties.

Properties of Alumina:

Key properties of alumina are

- (a) High wear resistant
- (b) Excellent dielectric properties
- (c) Resistant to strong alkali and acid attack at elevated temperature
- (d) Good thermal conductivity
- (e) Excellent size and shape capability
- (f) High strength and stiffness
- (g) Available in purity range from 90% Al_2O_3 to 99.5% Al_2O_3 for the most demanding high temperature application.

Extraction Routes

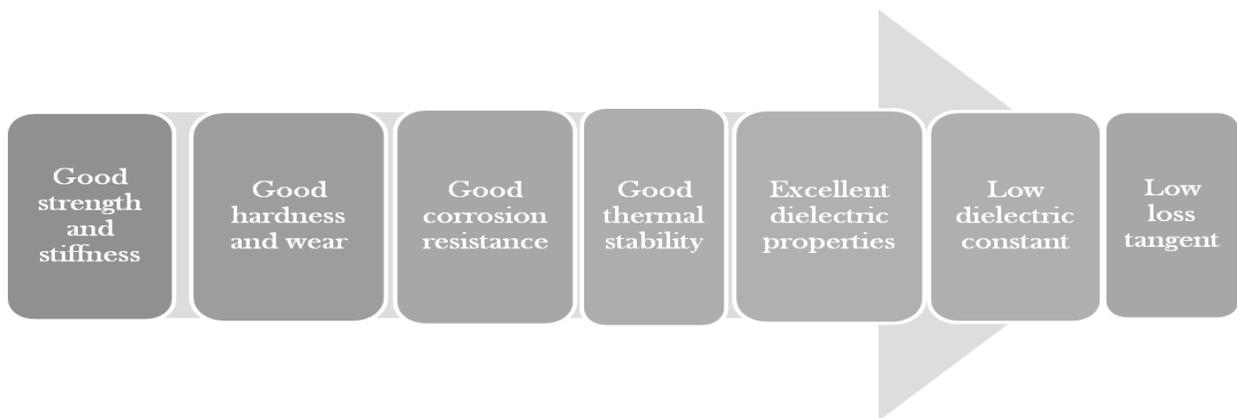
The most common process for the extraction and purification of alumina is the 'Bayer' process. The first step in the process is the mixing of ground bauxite into a solution of sodium hydroxide. By applying steam and pressure in tanks containing the mixture, the bauxite slowly dissolves. The alumina released reacts with the sodium hydroxide to form sodium aluminate. After the contents of the tank have passed through other vessels where the pressure and temperature are reduced and impurities are removed, the solution of sodium aluminate is placed in a special tank where the alumina is precipitated out. The precipitate is removed from the tank, washed, and heated in a kiln to drive off any water present. The residue is a commercially pure alumina.

Other extraction processes are used including pyrogenic treatment of bauxite with soda, and the extraction of aluminium hydroxide from meta kaolin via either the chloride or sulphate.

The yield of alumina from these processes can approach 90%.

For advanced ceramics uses, the alumina manufactured by these processes requires further purification. This is often achieved by recrystallisation from ammonium alum.

Typical Alumina characteristics include:



- Good strength and stiffness
- Good hardness and wear resistance
- Good corrosion resistance
- Good thermal stability
- Excellent dielectric properties (from DC to GHz frequencies)
- Low dielectric constant
- Low loss tangent

Crystal Structure

The most available form of crystalline alumina i.e. α -aluminium oxide is known as corundum. Corundum has a trigonal Bravais lattice. Each unit cell contains six formula units of aluminium oxide. The oxygen ions nearly form a hexagonal close-packed (HCP) structure with aluminium ions filling two-thirds of the octahedral interstices.

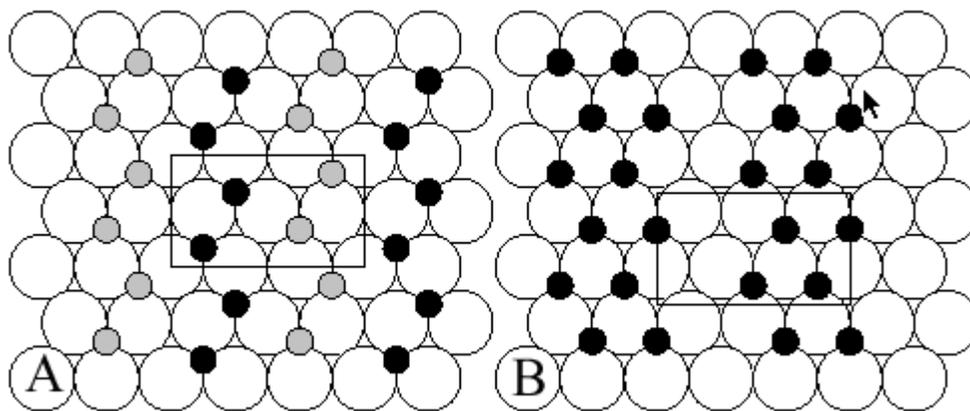


Fig Schematic drawing of the first two layers in alumina structure. Octahedral Al ions are black, tetrahedral are grey

Applications:

With such a range of composition and properties, alumina ceramics find a wide range of applications. Some of the major application areas can be grouped as

High Temperature and Aggressive Environments

Its high free energy of formation makes alumina chemically stable and refractory, and hence it finds uses in containment of aggressive and high temperature environments.

Wear and Corrosion Resistance

The high hardness of alumina imparts wear and abrasion resistance and hence it is used in diverse applications such as wear resistant linings for pipes and vessels, pump and faucet seals, thread and wire guides etc.

Biomedical

High purity alumina are also used as orthopaedic implants particularly in hip replacement surgery.

Metal Cutting Tools

The high “hot” hardness of alumina have led to applications as tool tips for metal cutting (though in this instance alumina matrix composites with even higher properties are more common) and abrasives.

Milling Media

Alumina is used as milling media in a wide range of particle size reduction processes.

Microwave Components

The high dielectric constant coupled with low dielectric loss particularly at high frequencies leads to a number of microwave applications including windows for high power devices and waveguides.

Electrical Insulation

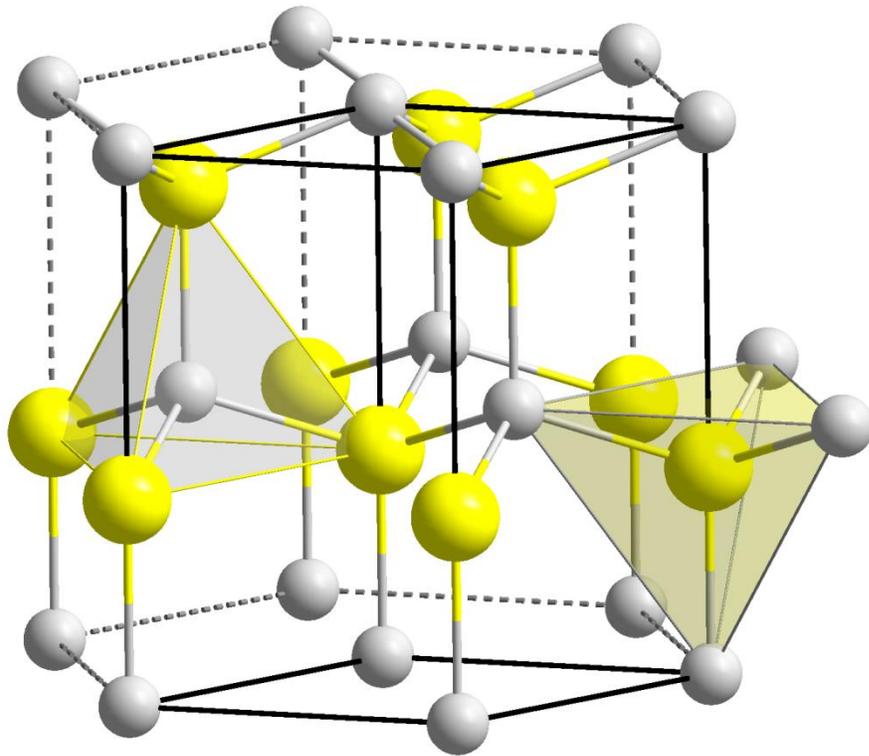
The high volume resistivity and dielectric strength make alumina an excellent electrical insulator which leads to applications in electronics as substrates and connectors, and in lower duty applications such as insulators for automotive spark plugs

Zinc Oxide

Zinc oxide is an inorganic compound with the formula ZnO. It usually appears as a white powder, nearly insoluble in water. The powder is widely used as an additive into numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g., car tires), lubricants,^[1] paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, first aid tapes, etc. ZnO is present in the Earth's crust as the mineral zincite; however, most ZnO used commercially is produced synthetically.

In materials science, ZnO is often called a II-VI semiconductor because zinc and oxygen belong to the 2nd and 6th groups of the periodic table, respectively. This semiconductor has several favorable properties: good transparency, high electron mobility, wide band gap, strong room-

temperature luminescence, etc. Those properties are already used in emerging applications for transparent electrodes in liquid crystal displays and in energy-saving or heat-protecting windows. Here in this work we are using zinc oxide as an additives for the sintering of alumina at different elevated temperature.



Wurtzite Structure

CHAPTER 2 LITERATURE REVIEW

What is sintering?

Thermal treatment that bonds particles together into a solid, coherent structure by means of mass transport mechanisms occurring largely at the atomic level.

Mass movements which occur during sintering consist of the reduction of total porosity by diffusion followed by material transport, mostly density of a collection of grains increases as material flows into voids, causing a decrease in overall size.

The initial powder (green body) has a large surface area relative to its volume, this surface area relative to its volume, this surface area provides the driving force in sintering, which is the reduction of free surface energy resulting from the surface area of the particles.

Different types of sintering:

Sintering basically is of two types.....

(a) Solid state sintering

(b) Liquid assisted sintering

There are different stages of sintering in both types of sintering are described below:

1. Initial stage of sintering:

- (a) Initially there is formation of local point of fusion without shrinkage of compact.
- (b) After some time as temp increases there is a neck formation at the contact point, with the resulting concave curvature at the neck.

2. Intermediate stage of sintering:

- (a) There is formation of necks, and neck growth
- (b) Pores forming arrays of interconnected cylindrical channels.
- (c) Particles centers approaching are another, with the resulting compact shrinkage.

3. Final stage of sintering

- (a) Isolation of pores i.e. relative density exceeding-93%..
- (b) Elimination of porosity
- (c) Grain growth

Mechanism of solid state sintering:

Polycrystalline material sinter by diffusional transport of matters whereas amorphous materials sinter by viscous flow, in polycrystalline materials matter transport takes place along definite paths that define the mechanism of sintering, matter transport takes place along definite

paths that define the mechanism of sintering ,matter is transported from the regions of higher chemical potential to region of lower chemical potential ,there are six different mechanism of sintering in polycrystalline materials.

- (a) Surface diffusion
- (b) Lattice diffusion
- (c) Vapour transport
- (d) Grain boundary diffusion
- (e) Lattice diffusion
- (f) Plastic flow

Surface diffusion, lattice diffusion and vapour diffusion are the only mechanism which leads to the actual densification but all causes the neck to grow and so influences the rate of densification.

While the amorphous materials viscous flow leads to neck growth as well as the densification.

Explanation of solid state sintering:

To enhance the slow in diffusion the one are enhanced or encouraged through the following method.

- (a) Chemical doping
- (b) Atmospheric control
- (c) An appropriate time per temperature cycle

Sintering of Al₂O₃ with aid of MgO:

MgO is added into the Al₂O₃ with a very small amount 0.25 wt% of Al₂O₃ content, this allow the achievement of fine,grained material at full density microstructure studies revealed that MgO eliminates the discontinuous grain growth of Al₂O₃ grains, The grain boundary do not break away from the pores ,which prevents the inclusion of pores trapped inside new large grains, with slow/long diffusion path densification.

The mechanism by which MgO slowdown grain boundary movements in alumina could be the follows.

- (a) The majority of MgO doped into Al₂O₃ resides at the grain boundaries, because the dissolution of MgO in Al₂O₃ is small or 300 ppm,This is due to the relatively large difference in ionic radius radius,0.72 Å for Mg²⁺ and 0.53 Å for Al³⁺ .
- (b) Any fast migration of the grain boundary would have to incorporate Mg²⁺ ions into the Al₂O₃ lattice, will the resulting increase in internal energy, unless a new compound spinel forms.

EFFECT OF ZnO ON THE ALUMINA SINTERING

In our experiment, different amount of ZnO is used as sintering aid as .5%, 1% and 2 wt% to find the sintering effect with respect to 0% batch of pure reactive alumina at different elevated temperature 1500 C, 1600 C and 1650 C.

It has been found that ZnO forms a spinel known as zinc alumina, $ZnAl_2O_4$. The chemical reaction between ZnO and alumina is occurred prior to densification of the powder compact and was accompanied by fairly large expansion. The mixing also plays a significant role the densification rate during reaction sintering and microstructure uniformity of the initial powder compacts.

CHAPTER 3~~PROBLEM STATEMENT:

- 1) To study the effect of ZnO at the three different percentage of additive at three different temperature

We have three batches which contains different wt% of ZnO as additive in alumina containing 0.5 wt%,1 wt% and 2wt%, one batch of 50 gm of 100% pure alumina or 0% ZnO is made which helps to find the difference between the above batches after sintering at different temperatures, 1550⁰C,1600⁰C and 1650⁰C, The soaking time at pick temperature in each process is 2 hours.

- 2) Determination of Shrinkage, Apparent Porosity, Bulk Density and observing the variation.
- 3) Studying the phases by XRD.
- 4) Studying the surface morphology by SEM.

CHAPTER 4 EXPERIMENTAL WORK

4.1 The raw materials used are

- Alumina powder- A 17 NE from ALMATIS GERMAN
- Zinc oxide powder

First of all 4 batches of 50 grams each were made in which different percentage of ZnO(0.5%, 1%, 2%) were added into 3 batches of Alumina such that the whole batch forms a combine weight of 50gm.

4.2 Compaction into pellets:

After weighing and addition of the dopant, 3ml of 2% PVA solution was added as binder. After mixing it for 5 min, the material is sieved 3 times by 500 μ m sized sieve so that we can get proper mixing.

Now sub-batches of 2.2 gm from each batch are separated to form pellets with a die pressed by Hydraulic Press (**carver press USA**) at pressure 1.5 ton on 1.2 mm area with a holding time of 60 sec. Stearic acid is used as lubricant.

4.3 Drying of pellets

After preparing the pellets, they were dried for 24 hrs at 110⁰C.

After drying dimensions were measured for each pellet using Vernier Calliper.

4.4 Sintering of pellets:

Now, from each batch 3 pellets are taken and sintered at 1550⁰C, 1600⁰C and 1650⁰C with soaking time of 2 hrs.

After sintering, shrinkage is calculated.

4.5 Bulk Density and Porosity of sintered pellets:

The bulk density and apparent porosity of the sintered pellets were determined by Archimedes principle using water. Dry Weight is measured and then the pellets were kept in distil water and then vaccuming is done in place of boiling for about 45 min-1 hr. After that suspended weight is measured using apparatus in which pellet is suspended in water and weight is measured. After taking suspended weight, soaked weight is taken. Hence the dry weight , soaked weight and suspended weight were measured. The bulk density and apparent porosity were calculated by the formulas:

Bulk Density = dry weight / (soaked weight – suspended weight)

Apparent porosity= (soaked weight-dry weight) / (soaked weight – suspended weight)

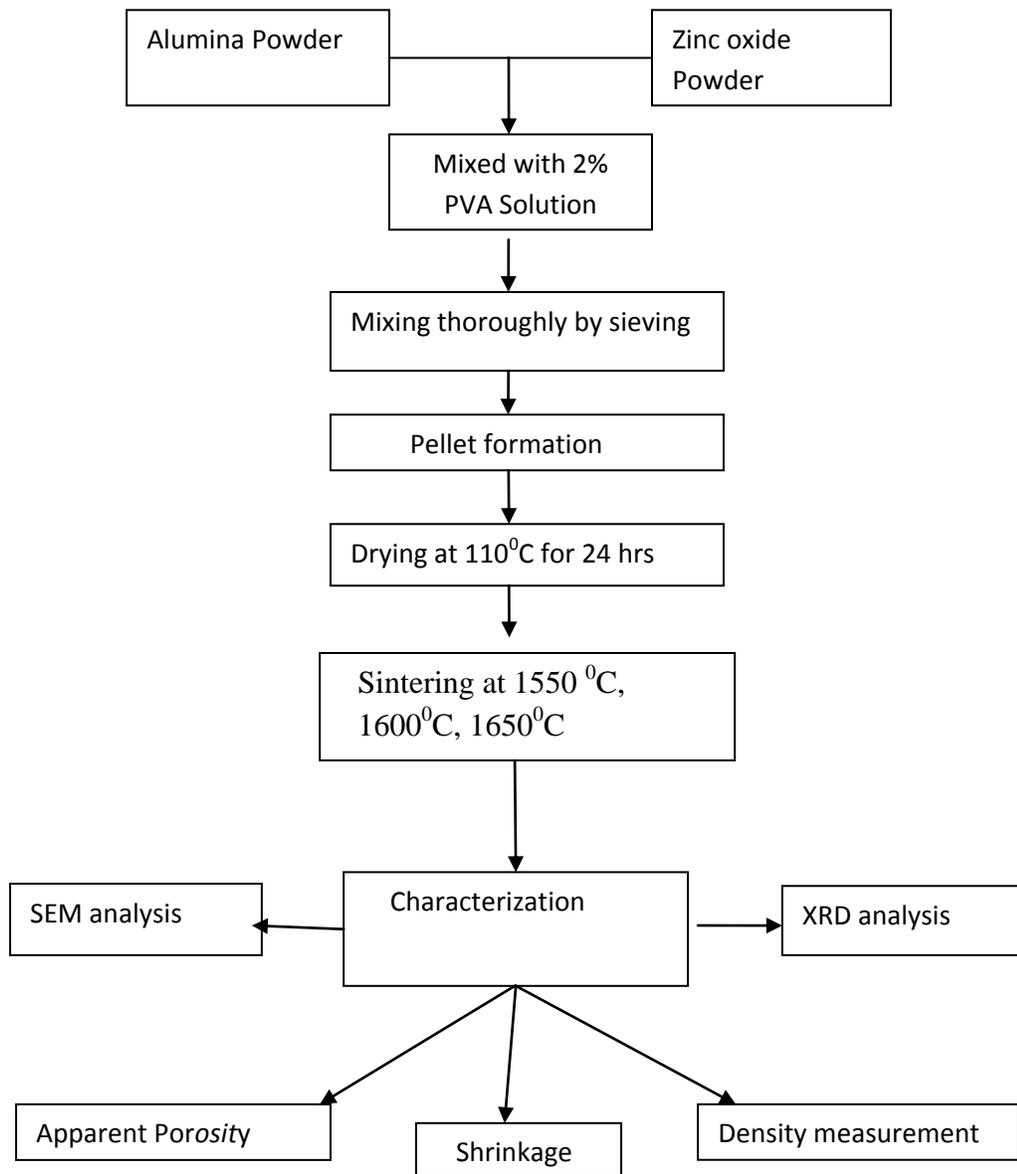
4.6 Phases in sintered powder:

The sintered pellets were powdered of 2% composition at 1550⁰C and 1650⁰C along with 0% at 1550⁰C were subjected to phase analysis by X-ray diffraction (PW1830 diffractometer ,Phillips,Netherland).

This is done to know the different phases present in the calcined powder.The angle range was 10⁰-50⁰ .

4.7 Microstructural analysis by SEM

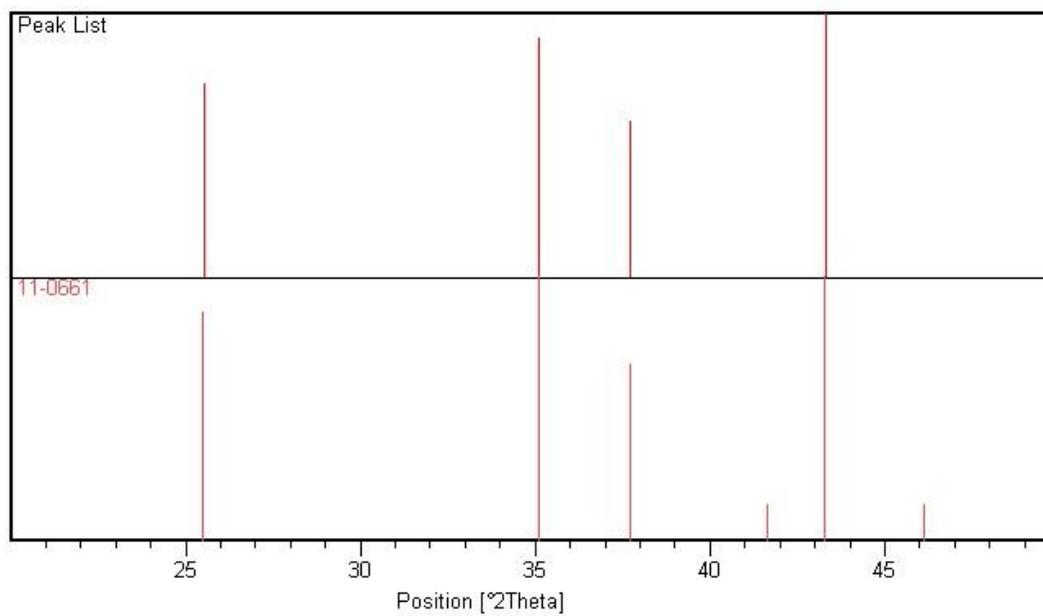
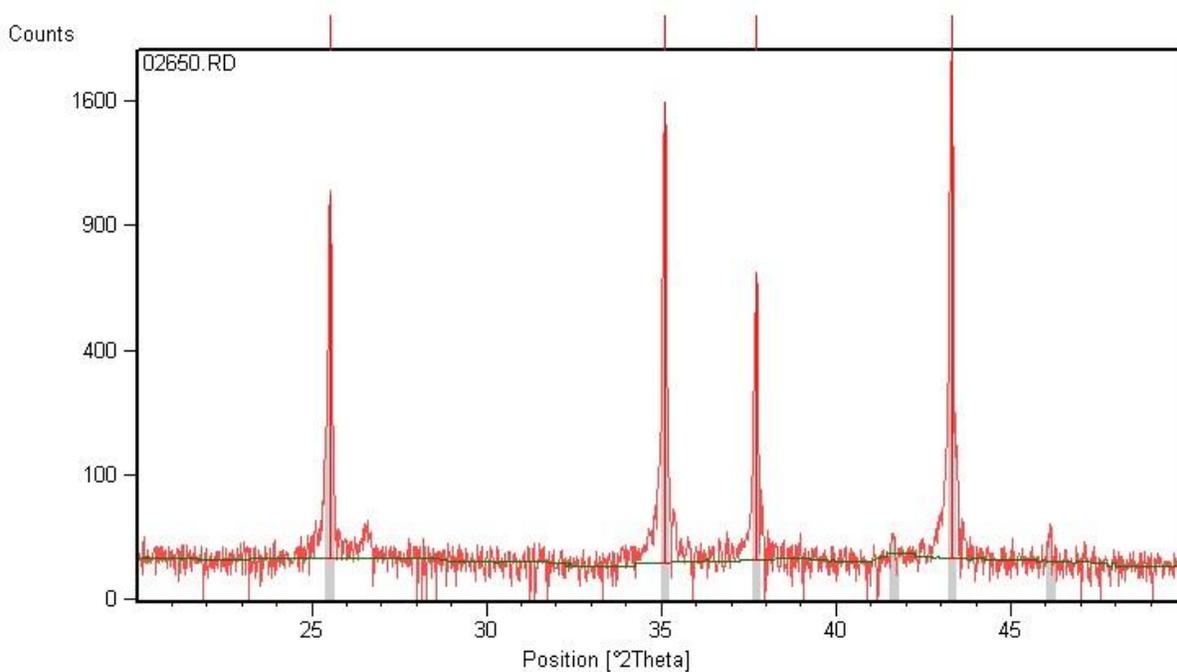
The sintered pellets were taken for SEM analysis. The pellets were sputtered by platinum in a sputtering unit. Then they were loaded for analysis. This analysis helps us to know the complete microstructure of the sintered sample



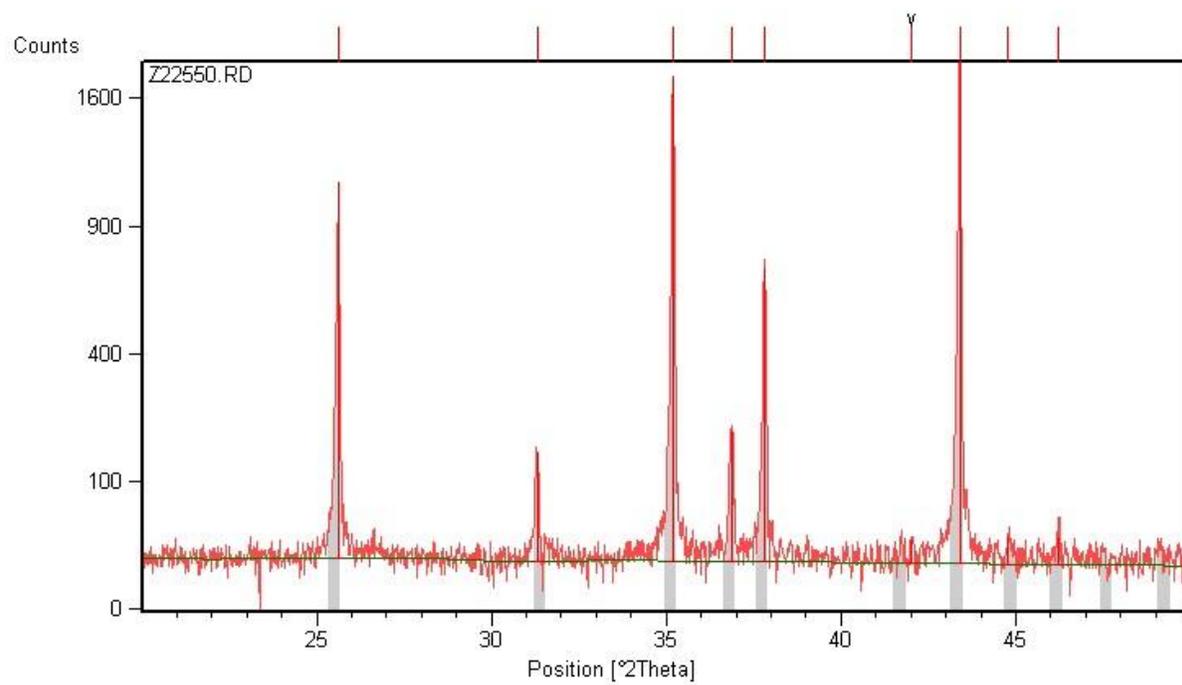
Flow chart of the whole procedure

RESULTS AND DISCUSSION

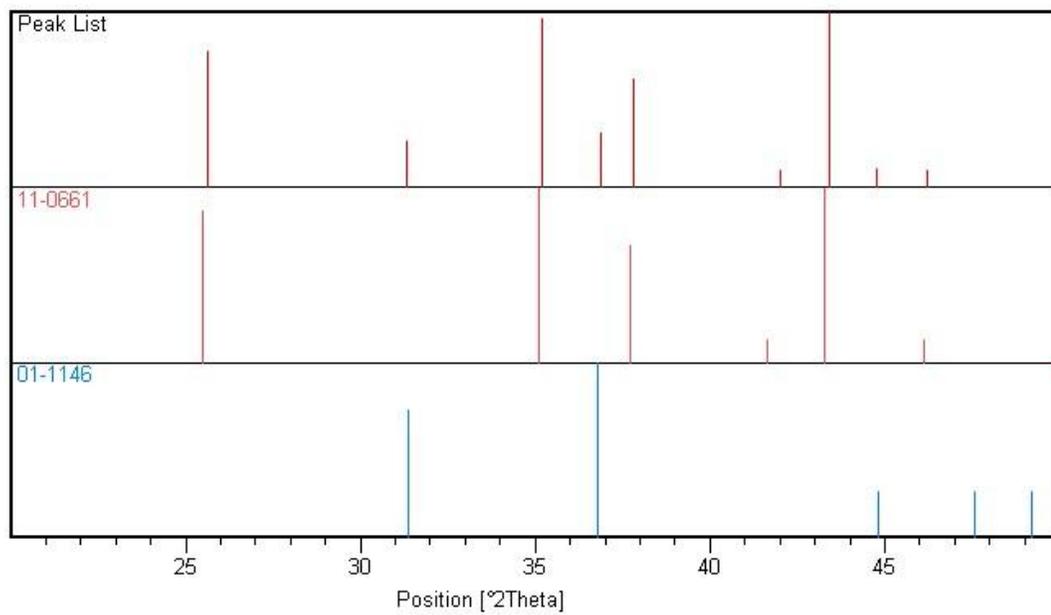
5.1 XRD Analysis



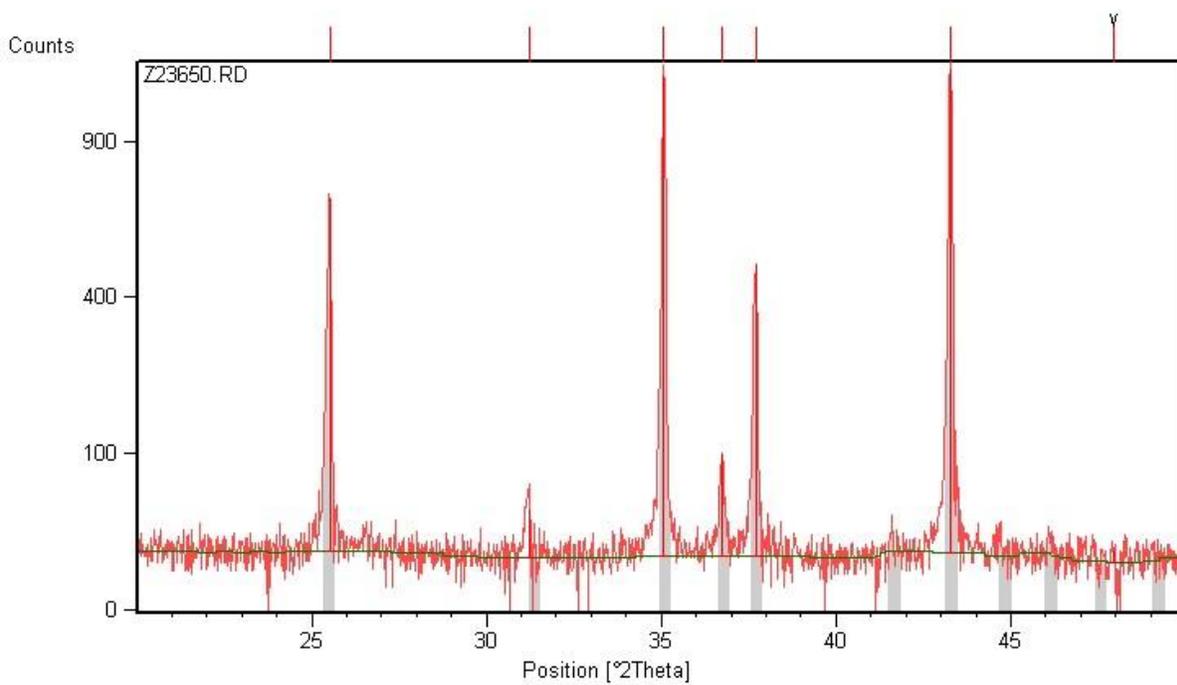
1550°C-2%



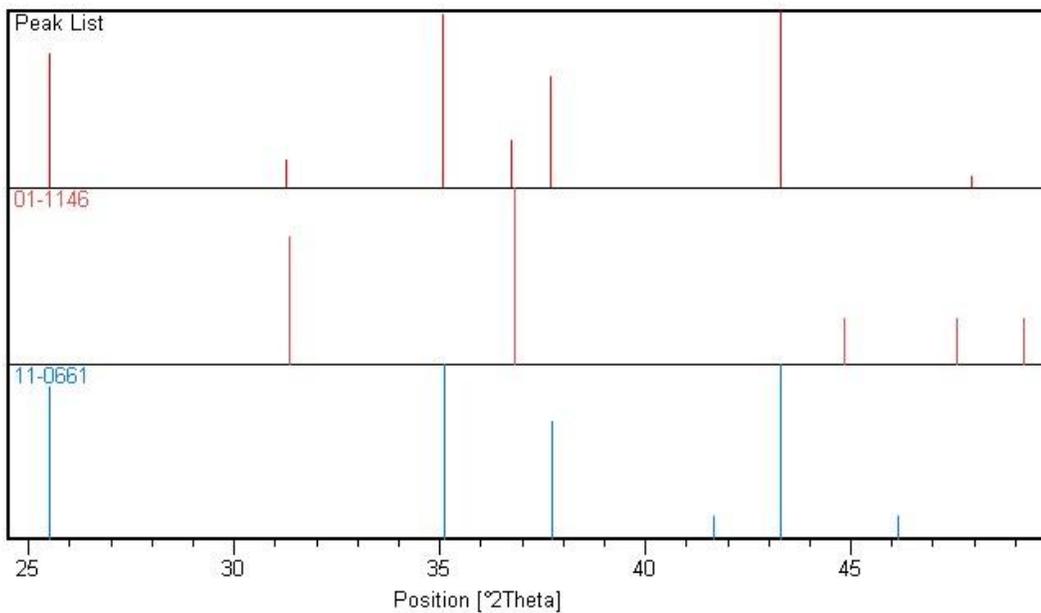
1550°C-2%



1650 C 2%



1650°C 2%



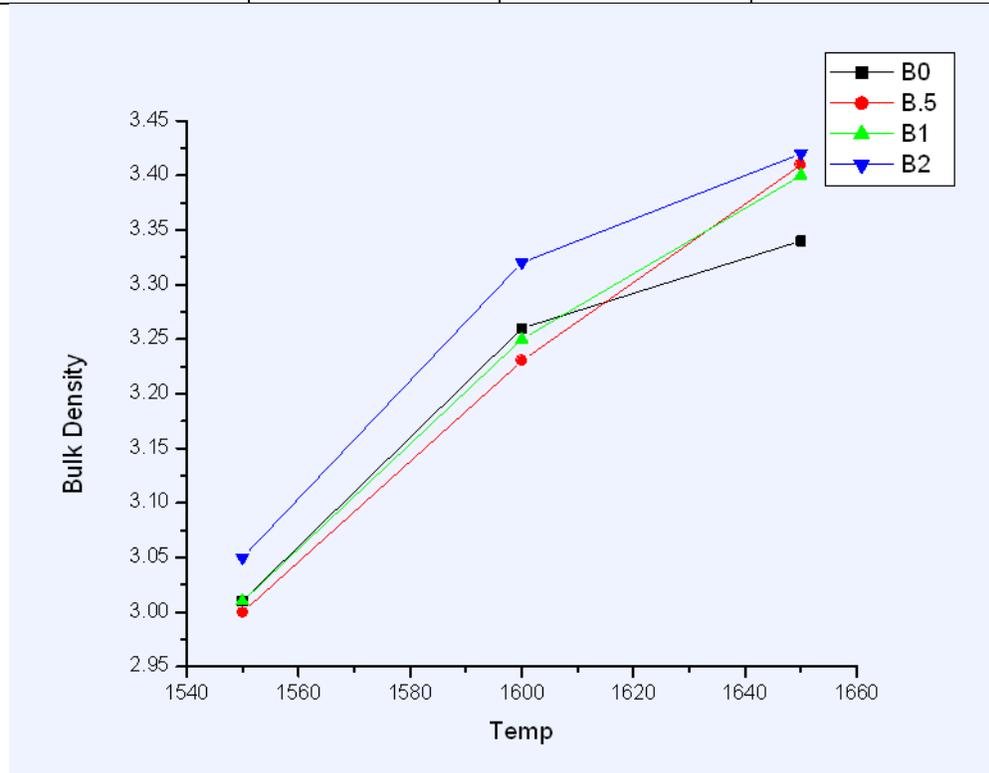
- JCPDF no 11-0861 corresponds to alumina phase
- JCPDF no 01-1146 corresponds to $ZnAl_2O_4$ phase.

From the XRD results we find that all the peaks correspond to either alumina or Zinc aluminate. This indicates a reaction between alumina and zinc oxide and the phase formation as $ZnAl_2O_4$.

5.3 Bulk Density and Apparent Porosity of sintered pellets:

Bulk Density

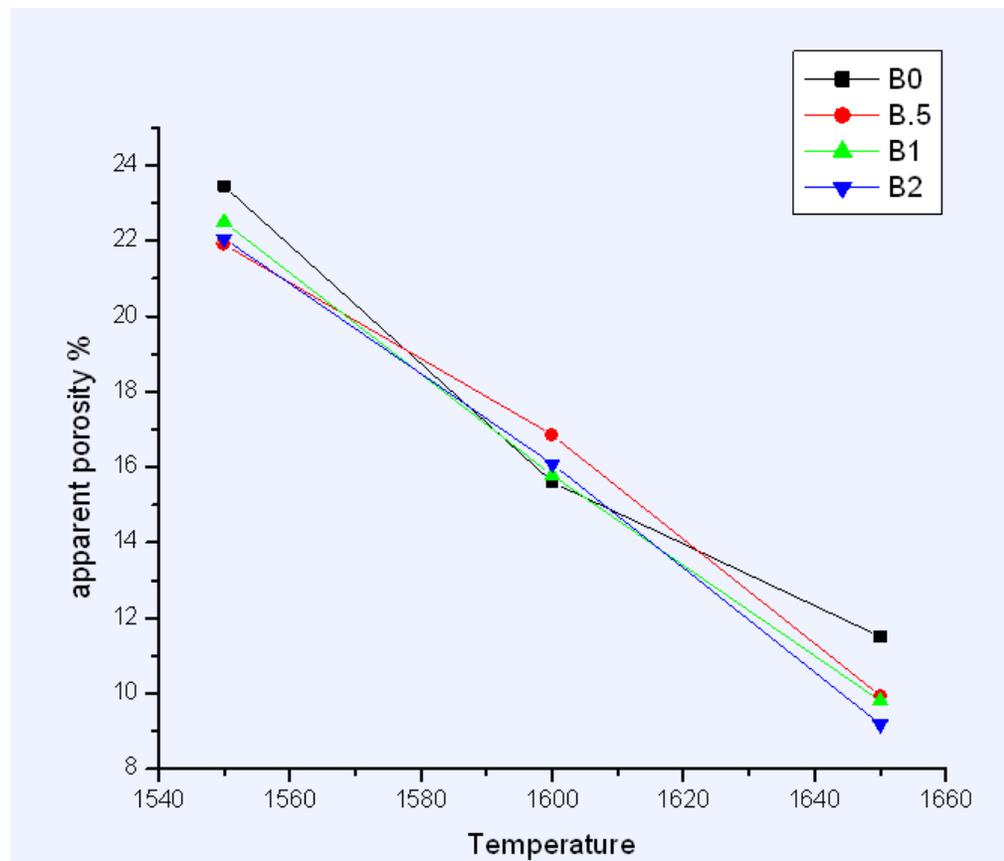
Temperature($^{\circ}C$)	0%	0.5%	1%	2%
1550	3.01	3.00	3.01	3.05
1600	3.26	3.23	3.25	3.32
1650	3.34	3.41	3.40	3.42



Beneficial effect of ZnO on densification was found for all the temperatures at 2 wt% additive but at lower amount there is a negative effect on densification for 1550⁰C and 1600⁰C. For 1650⁰C, density increases for any amount of ZnO addition. But all these beneficial effects were found to be marginally better than that of the without additive containing compositions.

Apparent Porosity

Temperature(⁰ C)	0%	0.5%	1%	2%
1550	23.45	21.91	22.49	22.06
1600	15.61	16.85	15.79	16.09
1650	11.51	9.95	9.81	9.19

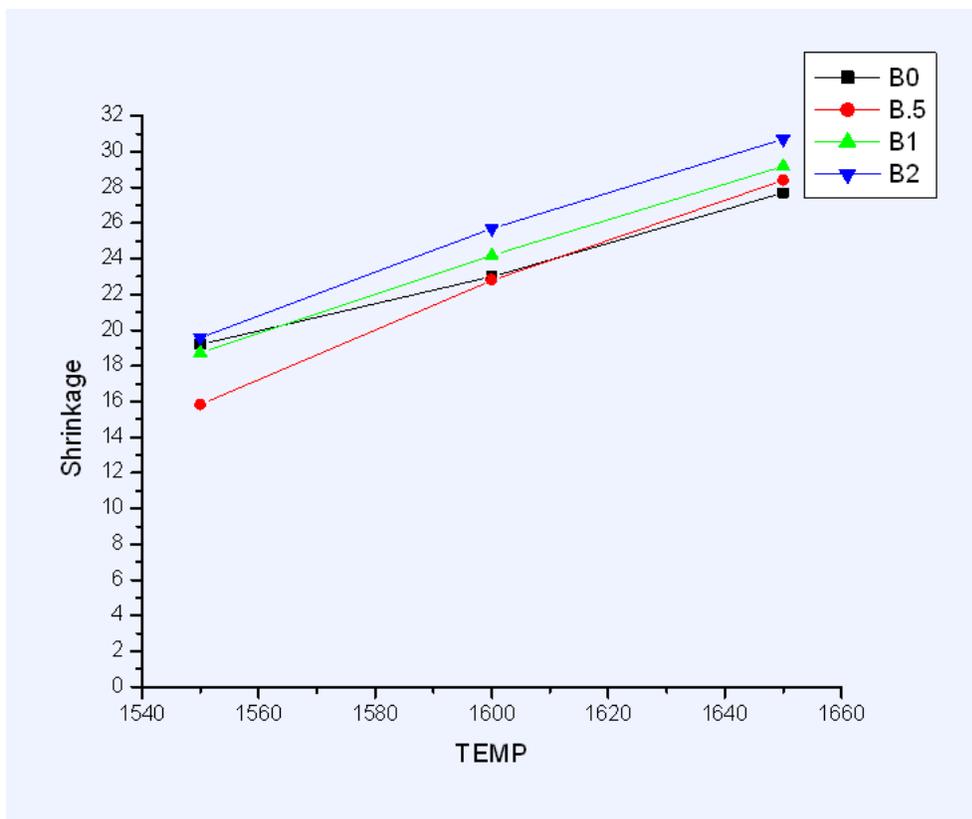


From the plot we

get that the porosity decreases as we increase the temperature as well as with the increase in the dopant concentration.

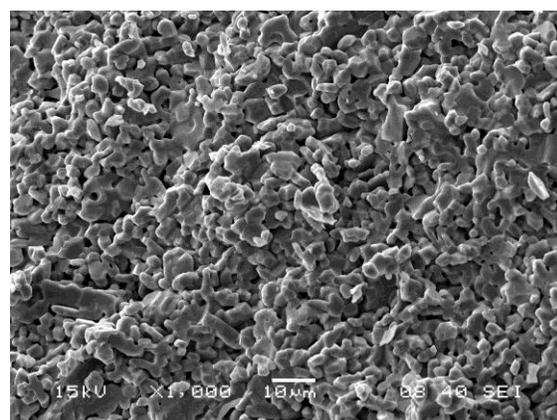
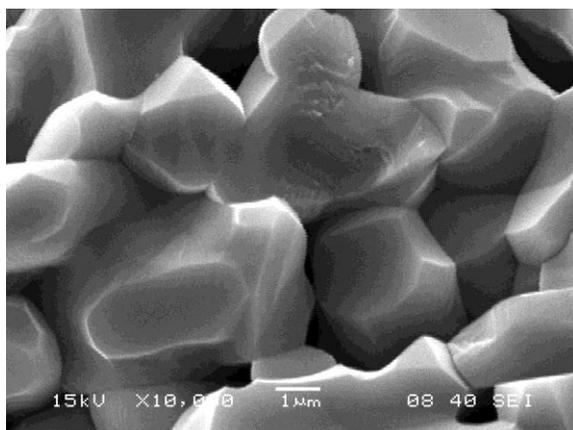
.Shrinkage

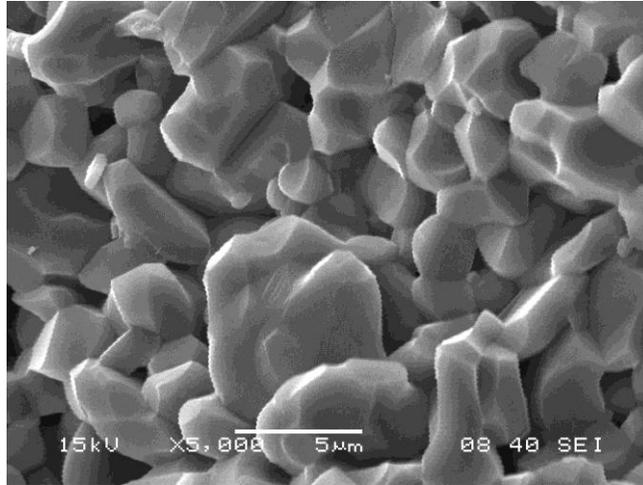
Temperature(°C)	0%	0.5%	1%	2%
1550	19.19	15.82	18.73	19.58
1600	23.01	22.8	24.2	25.7
1650	27.69	28.4	29.19	30.7



From the graph we found that shrinkage increases with increase in temperature as well as with increase in the dopant concentration.

SEM analysis





0% Zinc oxide sintered at 1650°C

SEM study of pure alumina showed that there are variation in the grain size and also the grains are not highly compacted. Porosity is commonly observed.

CHAPTER 6~~ CONCLUSION

It may be concluded that

Reaction between alumina and zinc oxide is occurring at high temperature forming ZnAl_2O_4 phase.

Bulk density, apparent porosity and shrinkage values indicate that zinc oxide is effective as dopant only after 1650°C . Amount of ZnO has nearly no effect on the density values. **Bulk density at 1650°C has increased from 3.34 g/cc to 3.42 g/cc.**

REFERENCES

1. Hernandezbattez, A; Gonzalez, R; Viesca, J; Fernandez, J; Diazfernandez, J; MacHado, A; Chou, R; Riba, J (2008). "CuO, ZrO₂ and ZnO nanoparticles as antiwear additive in oil lubricants". *Wear* **265**: 422.doi:10.1016/j.wear.2007.11.013
- 2.J.S Reed , Introduction to the Principles of Ceramic Processing, 2nd Ed., John Wiley & Sons. 1995.
- 3.W.D Kingery ,Bowen and D.R.Uhlmann, Introduction to Ceramics, 2nd Ed. John Wiley & Sons, Singapore,1991.
4. M.N Rahaman , Ceramic Processing, CRC Presss, Taylor & Frcnis Group, FL, 2007