STUDY OF THE MICROSTRUCTURE OF DOLOMITE DOPED ALUMINA

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

BACHELOR OF TECHNOLOGY

By

SHRAVAN KUMAR KANTHA

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National Institute of Technology Rourkela
Rourkela, Odisha-769008

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Under The Guidance Of

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Rourkela, Odisha-769008

Certificate

This is to certify that the project entitled, **"*Study of the Microstructure of dolomite Doped Alumina*"** submitted by ***Shravan Kumar Kantha***is an authentic work carried out by him under my supervision and guidance for the partial fulfillment of the requirements for the award of ***Bachelor of Technology Degree***in ***Ceramic Engineering***at ***National Institute of Technology, Rourkela.***

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.

Date: -11/06/2011

Rourkela

Dr.Shantanu Behera

Department of Ceramic Engineering

NIT Rourkela

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Abstract

In this work, the microstructure, density and phases produced by adding dolomite to Alumina were determined. Variable concentrations of dolomite such as 1, 2, 3 and 5mol% of dolomite were used as an additive in the reactive sintering of Alumina. The Calcined powders were mixed according to the batch calculations and were pressed to form pellets. The pellets were then sintered at different temperatures.

The characterization and the determination of phases were done by XRD analysis. Scanning Electron Microscope helped to describe the grain morphology and pores distribution. The Dilatometer tests gave an idea about the shrinkage. As the concentration of dolomite was increased the formation of spinel ($MgAl_2O_4$) and Calcium Hexaluminate ($CaAl_{12}O_{19}$) became significant. The formation of more spinel ($MgAl_2O_4$) and Calcium Hexaluminate ($CaAl_{12}O_{19}$) began segregating the pores to the grain boundaries. However, the Bulk Density began decreasing on increasing the amount of dolomite due to the evolution of large amount of Carbon Dioxide (CO_2) which enhanced the pore formation. The shrinkage began at lower temperatures upon increasing the dolomite concentrations.

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Chapter 1

INTRODUCTION AND OBJECTIVE

1.1 Introduction

Alumina or Aluminium Oxide is an amphoteric oxide having the chemical formula Al_2O_3. Aluminium metal is produced from alumina. It is also used as an abrasive material due to its hardness (19 GPA) and as a refractory material due to its high melting point (2072^oC). The world experiences changes every day and any significant change which brings about a revolution is known as an Invention. Alumina used as a refractory material undergoes changes every time so that a better refractory can be formed. Aluminium oxide is normally an electrical insulator but has relatively very high thermal conductivity of 30 $Wm^{-1}K^{-1}$ [1] for any ceramic material. Alumina has vast uses in refractory industry. Alumina-spinel castables developed for ladle refractories resulted in major improvements in durability compared to traditional products.[2]

Considerable work hasbeen done on the doping of magnesia in alumina. The objective of this literature is to study the microstructure of dolomite doped alumina. The alumina-spinel castable which was normally used on secondary steelmaking ladles sidewall has been eventually replaced by an alumina-magnesia type. [3]The reason being fine spinel formed “in situ” by the reaction of $MgO\text{-}Al_2O_3$ in the matrix of alumina-magnesia castables tends to increase the resistance to corrosion and penetration of slag as compared to alumina-spinel castables. [3]

Dolomite is a mixed carbonate mineral consisting of calcium magnesium carbonate $CaMg(CO_3)_2$. Dolomite is a sedimentary rock-forming mineral that is found in massive beds several hundred feet in thickness. They can be found all over the world and are very common in sedimentary rock sequences. These rocks are called appropriately enough dolomite or dolomitic limestone. Disputes have risen about how these dolomite beds were formed and this debate has been called the "dolomite Problem". Dolomite does not form on the surface of the earth but massive layers of dolomite can be found in ancient rocks. They are generally deposited as calcite or aragonite rich limestones, but during a process call diagenesis the calcite and/or aragonite is

altered to dolomite. The process is not metamorphism. Magnesium rich ground waters that have a significant amount of salinity are probably crucial and warm, tropical near ocean environments are probably the best source of dolomite formation.

Dolomite in addition to the sedimentary beds is also found in metamorphic marbles, hydrothermal veins and replacement deposits. Except in its pink, curved crystal habit dolomite is hard to distinguish from its second cousin, calcite**.** But calcite is far more common and effervesces easily when acid is applied to it. But this is not the case with dolomite which only weakly bubbles with acid and only when the acid is warm or the dolomite is powdered. [4]

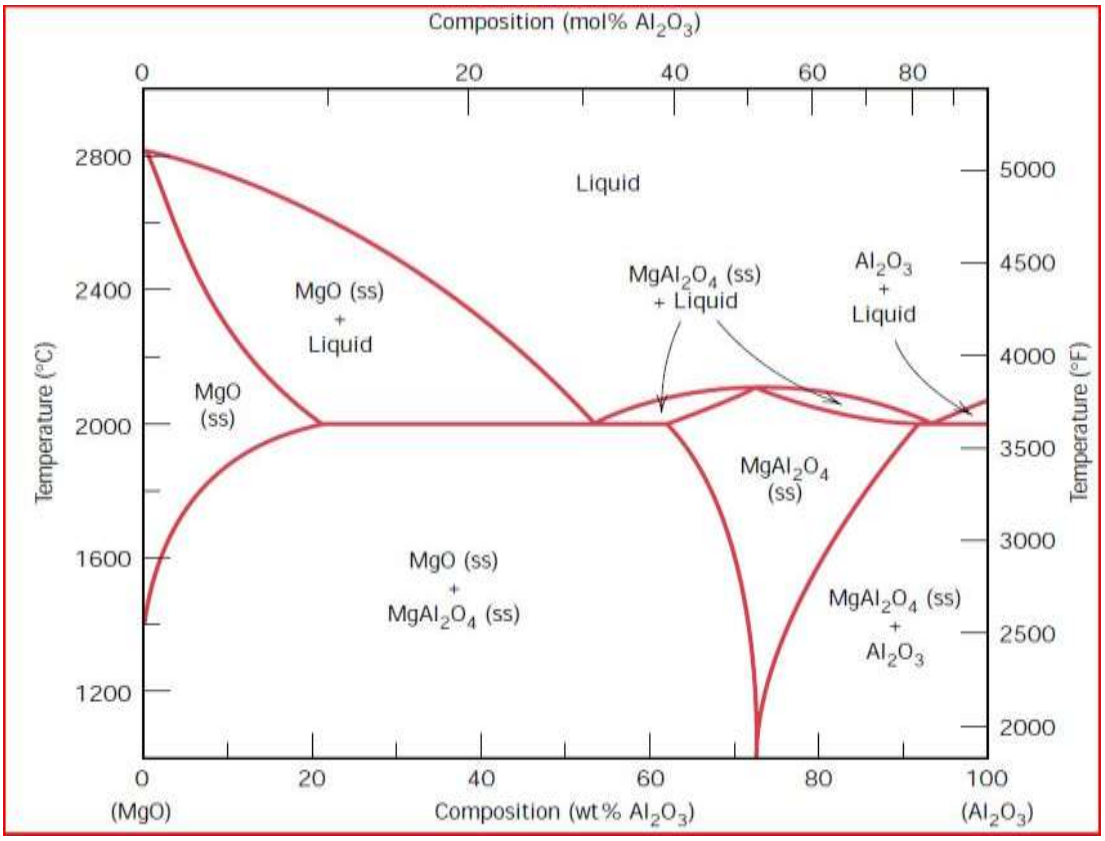


Fig 1.1: Magnesiumoxide – Aluminum oxidephase diagram [5]

Fig 1.1 shows the $MgO-Al_2O_3$ phase diagram. There are two eutectics as shown in the figure which are both at 2000°C. One eutectic is between spinel ($MgAl_2O_4$) and Magnesia and the other is between spinel ($MgAl_2O_4$) and Alumina. From the figure it is quite clear that there is no solid of only Alumina separately whereas Magnesia starts to form a solid solution at 1400°C. Alumina and Magnesia combine to form a solid solution of spinel ($MgAl_2O_4$) when the amount of Alumina just exceeds 70wt%. spinel starts to melt around 2000°C.

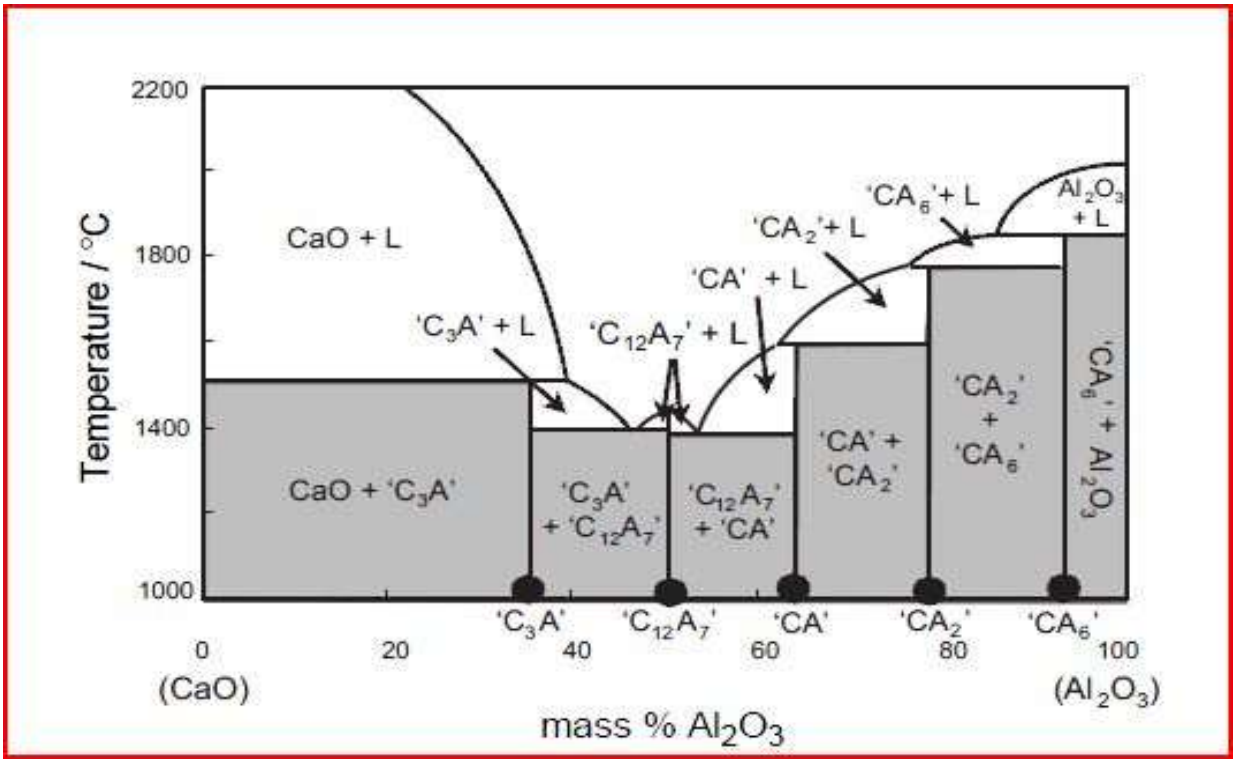


Fig1.2: Calcia-Alumina Phase Diagram[6]

Fig 1.2 shows the $CaO-Al_2O_3$ phase diagram. It is seen that Calcium Hexaluminate phase incongruently melts at around 1800°C. CA_6 and Alumina forms a peritectic at this temperature. From the above figure it is quite evident that CA_6 is most high melting phase formed when Alumina and Calcia are mixed together.

1.2 Objective

1. To prepare dolomite doped alumina green pellets and sinter them till desired density is obtained.
2. To study the phases formed in different dolomite doped concentrations (1, 2, 3 and 5 mol%) in alumina.
3. To find whether spinel ($MgAl_20_4$) and Calcium Hexaluminate ($CaAl_{12}O_{19}$) are formed or not which are very high melting phases.

Chapter 2

Literature Review

2.1 Abnormal Grain Growth of Alumina

According to Il-JoonBae et al. [7] Abnormal Grain Growth of alumina is an extrinsic property. It is controlled by the impurities that are present or remain during the powder synthesis, processing and sintering. Magnesia doping is very effective for controlling Abnormal Grain Growth and in achieving higher densities in alumina regardless of initial particle size, purity, or sintering conditions.

2.2 Bonite Refractory

According to Gunter Buchel et al. [8]Bonite refers to the mineralogical phase of Calcium Hexaluminate (CA_6). It is a new dense synthetic refractory material. It has high hot modulus of rupture and high refractoriness under load. The thermal shock resistance of bonite is also very high. It has a low thermal conductivity and low wettability. It is even highly resistant to alkali penetrations. Hence, bonite refractories have brought about a revolution in the refractory world.

2.3 Magnesia Doping In Alumina

According to L. Radonjic et al. [9]the doping of magnesia increases the densification rate of alumina during sintering. However it does not have any effect on the grain growth rate. The doping of magnesia in seeded alumina decreases the particle size during phase transformation and grain size during sintering. Upon adding magnesia to boehmite sol, no abnormal grain growth was observed. Increasing the magnesia content led to the reduction in the grain size of alumina.

2.4 Thermal Decomposition of Natural dolomite

S. Gunasekaran et al. [10]studied thermal decomposition behavior of dolomiteby thermogravimetric measurements. The DTA curve showed two peaks at 777.8^{o}C and 834^{o}C. These two endothermic peaks were the result of the decarbonation of calcite and magnesite.

2.5 Effect of Liquid Phase And Magnesia On The Grain Growth Of Alumina

According to Tien–Yen Chan et al. [11] when the liquid phase was abundant enough to penetrate into the grain boundaries and junctions of alumina, the alumina phase will develop faceted grains even with the doping of magnesia. But when the concentration of magnesia was high enough to form spinel ($MgAl_2O_4$) the evolution of elongated grains was avoided by the pinning of the grain boundaries.

2.6 Spinelin Refractory Castables

M.A.L.Braulio et al. [12]suggested that Refractory castables containing spinel ($MgAl_2O_4$) are widely used as steel ladle linings because they are highly corrosion resistant to basic slag.

Chapter 3

Experimental Procedure

3.1 Batch Calculation

1 mol of dolomite = 184gms

1 mol of Alumina = 102gms

(1 mol% of dolomite in 99 mol% of Alumina)

1 mol% of dolomite = 1.84gms

99 mol% of Alumina = 100.98gms

100 mol% of Batch = 102.82gms

(2 mol% of dolomite in 98 mol% of Alumina)

2 mol% of dolomite = 3.68gms

98 mol% of Alumina = 99.96gms

100 mol% of Batch = 103.64gms

(3 mol% of dolomite in 97 mol% of Alumina)

3 mol% of dolomite = 5.52gms

97 mol% of Alumina = 98.94gms

100 mol% of Batch = 104.46gms

(5 mol% of dolomite in 95 mol% of Alumina)

5 mol% of dolomite = 9.2gms

95 mol% of Alumina = 96.9gms

100 mol% of Batch = 106.1gms

3.2 Flow Chart of Procedure

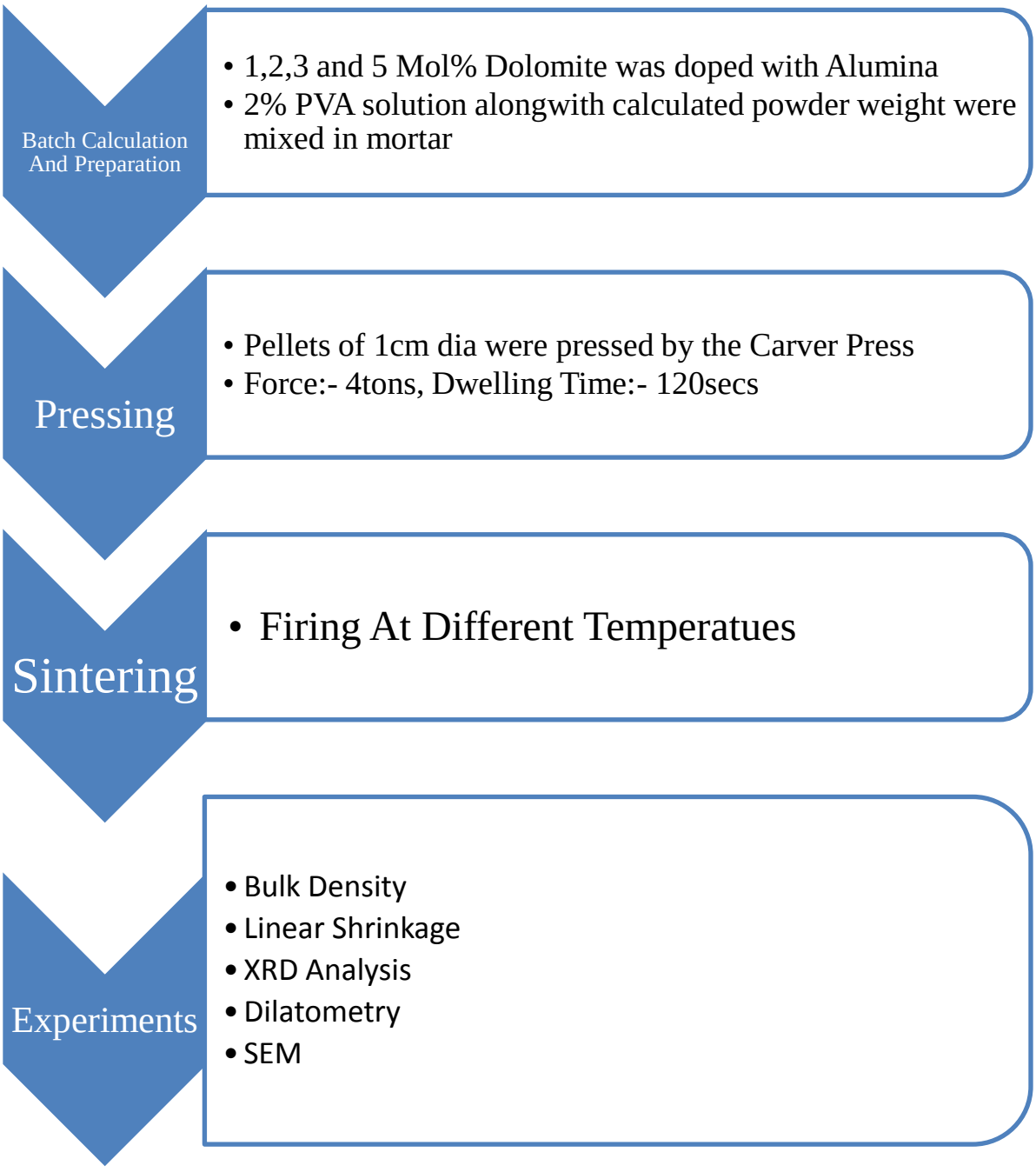


Fig 3.1 Flow Chart of the Procedure.

3.3 Batch Preparation

The correct amount of ESP (Electrostatically Precipitated) dolomite powder and Calcined Alumina powder according to batch calculations were taken in mortar and 2% PVA solution was mixed with it. It was then properly mixed and crushed with the pistil and left to be dried under the Sodium Vapour Lamp.

3.4 Pelletization

The dried powders were then placed in a 1cm die and pressed into pellets using the Carver Press. The force used was 4 US Tons and the dwelling time was 120secs. Care must be taken to clean the die with acetone. It must also be lubricated using stearic acidfor proper Pelletization.

3.5 Sintering

The green pellets were then dried and fried in the desired temperature range for the desired time. The firing was done in Chamber Furnace. The pellets were fried at $1400^{o}C$ and $1600^{o}C$ for soaking time of 6 hours.

3.6 Bulk Density

The dry weight, soaked weight and the suspended weights were measured using the physical balance. Using this data the bulk densities of different samples were measured. The bulk density is given by the under stated formula.

$$\text{Bulk Density} = \frac{\text{Dry Weight}}{\text{Soaked Weight} - \text{Suspended Weight}} \times \text{Density Of The Liquid}$$

3.7 Linear Shrinkage

The diameter of the green pellets was measured and after firing the diameter of the fired pellets was measured again. The difference was expressed in percentage and hence the linear shrinkage was calculated.

3.8 XRD Analysis

The XRD of the different sintered dolomite doped alumina was done with the help of Philips X-Ray diffractometer (PW 1730, Holland) with nickel filtered Cu Kα radiation (λ = 1.5406 A°) at 30 kV and 20mA having a scan range(°2 θ) of 20-80° at a scan speed (°2 θ/sec) of 0.04.

3.9 SEM Characterization

SEM samples were fractured. SEM analysis was carried out on the fractured surface in JEOL-JSM 6480LV at applied generator voltage of 15 KV.

3.10 Dilatometry

The powders were again pressedinto bars of rectangular shape. The small rectangular bricks were then taken for dilatometer tests. The dilatometric curves were obtained by plotting the temperature in X-axis and the change in length by original length in the Y-axis.

Chapter 4

Results & Discussions

4.1 Bulk Densities at Different Temperatures

The samples were fired at 1400^{o}C and 1600^{o}C for 6 hours. Then the change in bulk densities was observed for different concentrations of dolomite at different temperatures.

Table 4.1.1: Bulk Density of Different Concentrations ofdolomite in Alumina fired at 1400^{o}C

MOL% of dolomite	Dry Weight (gm)	Suspended Weight (gm)	Soaked Weight (gm)	Bulk Density (gm/cc)
1	0.983	0.717	1.006	3.4
2	0.956	0.685	0.978	3.26
3	0.753	0.532	0.789	2.93
5	0.793	0.532	0.814	2.81

Sintering Profile for above Data is 2 hours of soaking at 1000^{o}C and 6 hours at 1400^{o}C.

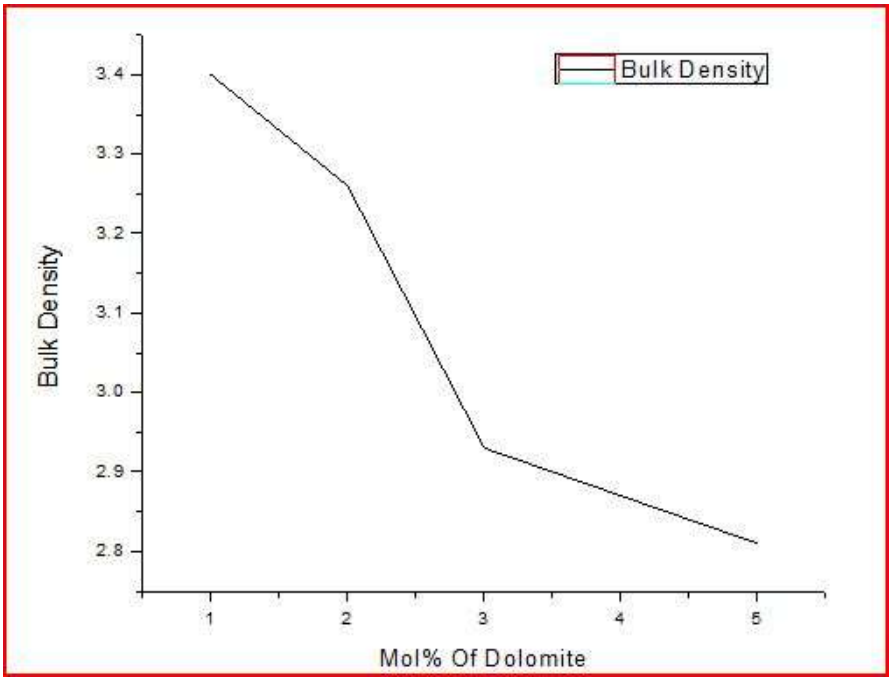


Fig 4.1.1 Bulk Density vs. Mol% of dolomite Sintered At 1400^{o}C

Table 4.1.2 Bulk Density Measurement of Different Concentrations of dolomite fired at 1600^{o}C

Mol% of dolomite	Dry Weight (gm)	Suspended Weight (gm)	Soaked Weight (gm)	Bulk Density (gm/cc)
1	0.947	0.728	0.978	3.79
2	0.940	0.717	0.973	3.67
3	0.853	0.638	0.915	3.08
5	0.676	0.483	0.715	2.91

Sintering Profile of the above data is soaking time of 1hour at 500^{o}C, 2hours at 1000^{o}C and 6 hours at 1600^{o}C.

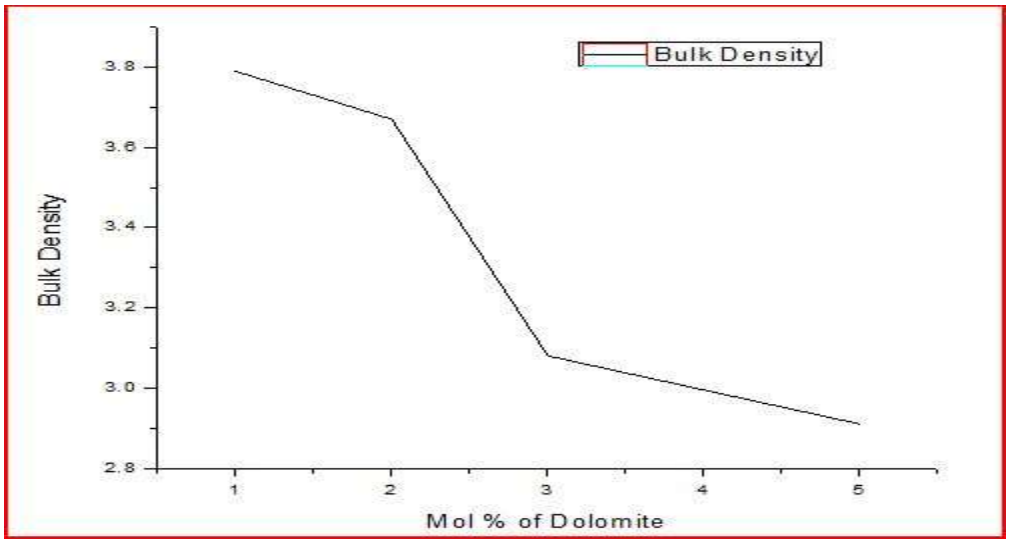


Fig 4.1.2: Bulk Density vs. Mol% of dolomite Sintered At 1600^{o}C

Hence looking at the above data and figures it is was evident that upon increasing the sintering temperature from 1400^{o}C to 1600^{o}C the bulk density of the sample increases. But upon increasing the dopant concentration the bulk density has an inverse effect. It decreases with the increase in dopant concentrations. The soaking at 1000^{o}C was done for the evolution of CO_2.

4.2 XRD Analysis

4.2.1 XRD Diffraction Pattern of 1mol% of dolomite in Alumina

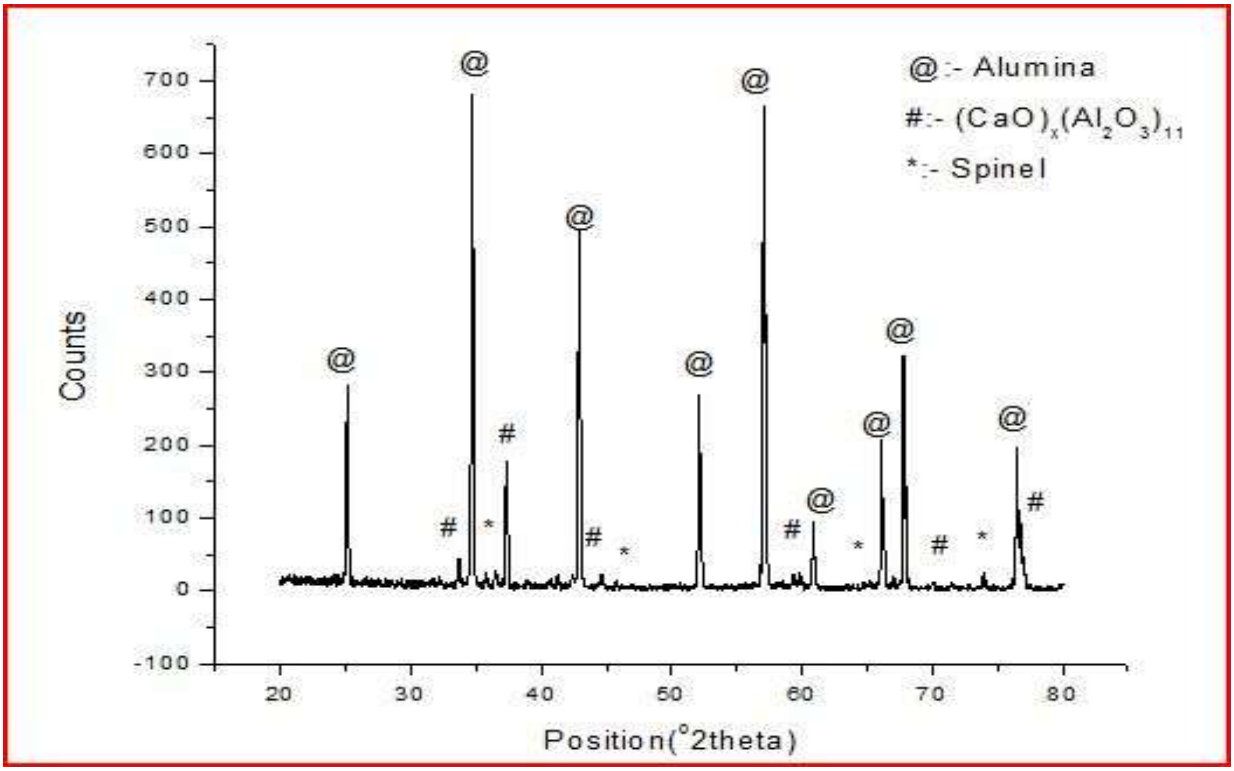


Fig 4.2.1:- XRD Diffraction Pattern of 1mol% of dolomite in Alumina

Fig 4.2.1 shows the peaks and which peak indicates which phase present in the pellet. The above figure and the below stated data indicate that alumina along with spinel and alumina rich Calcia phase $\{(CaO)_x(Al_2O_3)_{11}\}$ is present in the sample.

Table 4.2.1:- Pattern List of 1mol% of dolomite Doped Alumina

Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
11-0661	64	Aluminum Oxide	-0.357	0.605	Al_2O_3
41-0358	10	Calcium Aluminum Oxide	0.032	0.087	$(CaO)_x(Al_2O_3)_{11}$
75-1798	6	spinel, syn	-0.049	0.037	$MgAl_2O_4$

4.2.2 XRD Diffraction Pattern of 2mol% of dolomite in Alumina

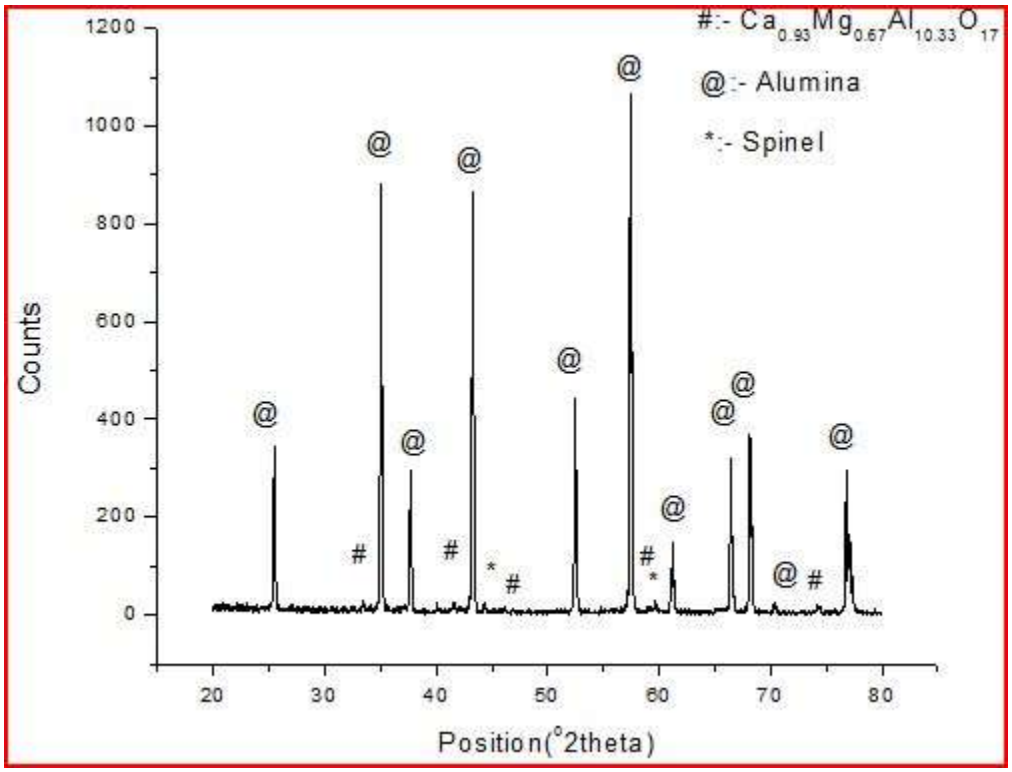


Fig 4.2.2:- XRD Diffraction Pattern of 2mol% of dolomite in Alumina

Fig 4.2.2 shows the peaks and which peak indicates which phase present in the pellet. The above figure and the below stated data indicate that alumina along with spinel and alumina rich Calcia phase ($Ca_{0.93}Mg_{0.67}Al_{10.33}O_{17}$) is present in the sample.

Table 4.2.2:- Pattern List of 2mol% of dolomite Doped Alumina

Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
11-0661	68	Aluminum Oxide	0.000	0.580	Al_2O_3
84-0217	10	Calcium Magnesium Aluminum Oxide	0.000	0.769	$Ca_{0.93}Mg_{0.67}Al_{10.33}O_{17}$
77-0436	3	Spinel	0.000	0.014	$MgAl_2O_4$

4.2.3 XRD Diffraction Pattern of 3mol% of dolomite in Alumina

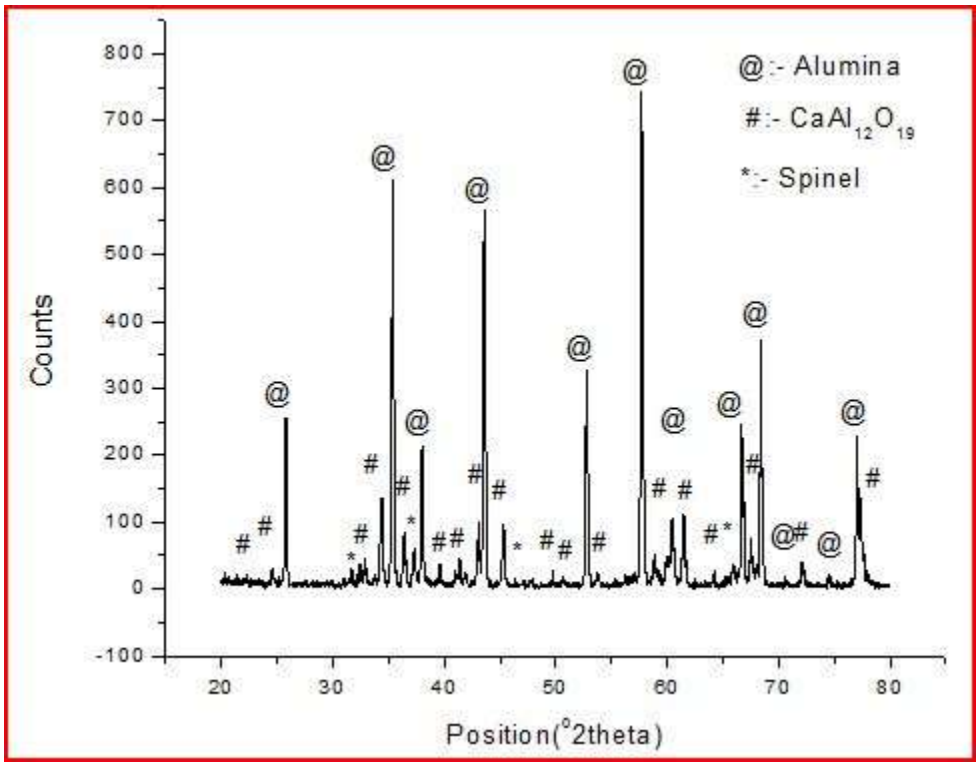


Fig 4.2.3:- XRD Diffraction Pattern of 3mol% of dolomite in Alumina

Fig 4.2.3 shows the peaks and which peak indicates which phase present in the pellet. The above figure and the below stated data indicate that alumina along with spinel and alumina rich Calcia phase ($CaAl_{12}O_{19}$) is present in the sample.

Table 4.2.3:- Pattern List of 3mol% of dolomite Doped Alumina

Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
46-1212	68	Corundum, syn	0.175	0.877	Al_2O_3
84-1613	57	Calcium Aluminum Oxide	0.150	0.143	$CaAl_{12}O_{19}$
73-1959	44	Magnesium Aluminum Oxide	0.253	0.076	$MgAl_2O_4$

4.2.4 XRD Diffraction Pattern of 5mol% of dolomite in Alumina

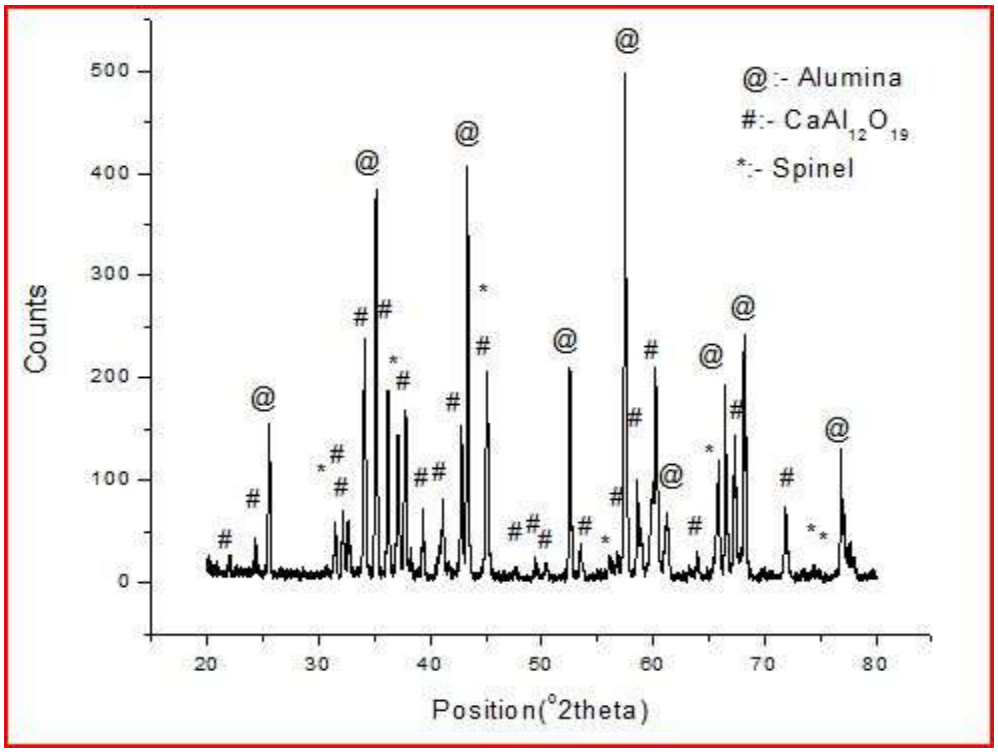


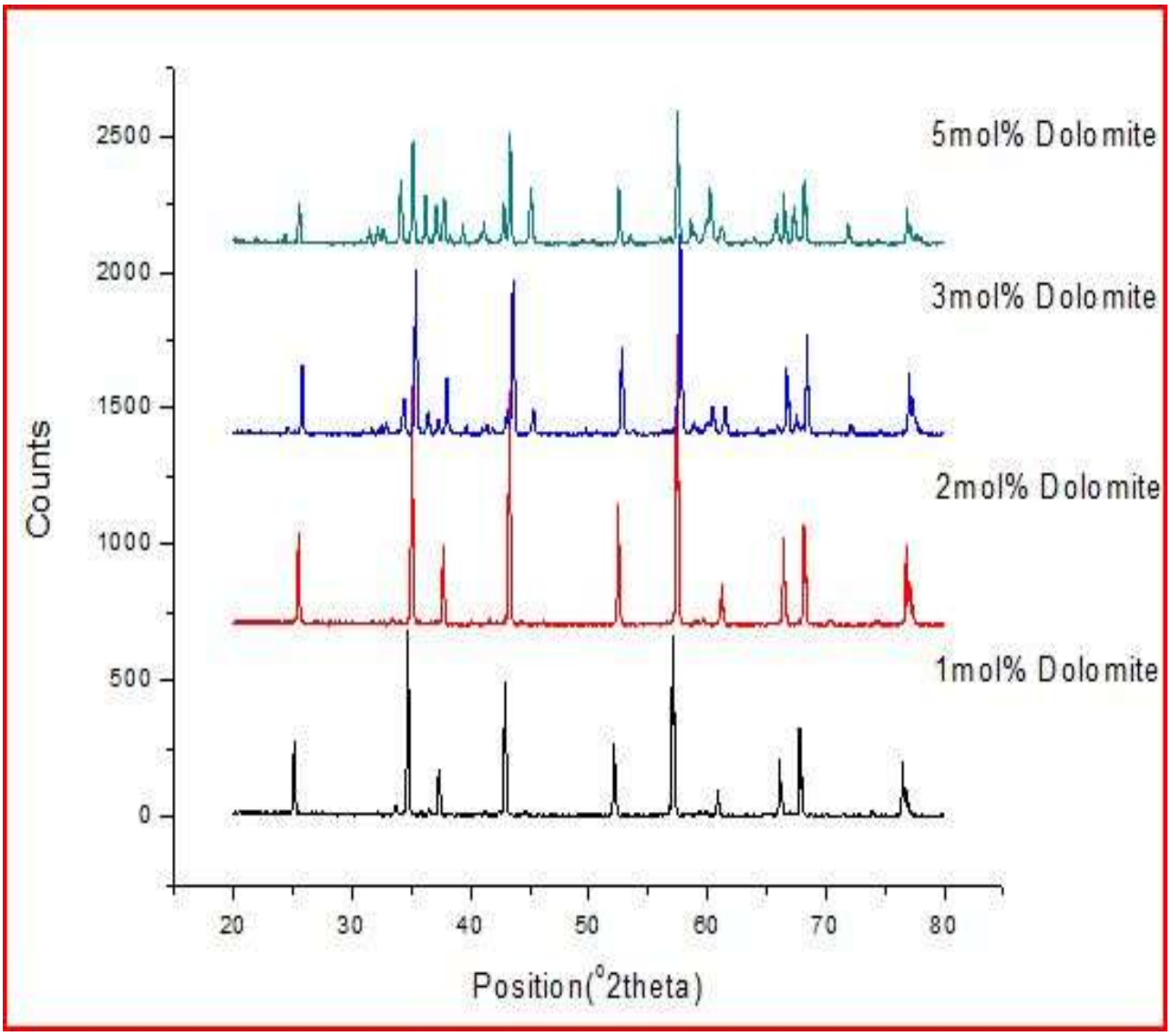
Fig 4.2.4:- XRD Diffraction Pattern of 5mol% of dolomite in Alumina

Fig 4.2.4 shows the peaks and which peak indicates which phase present in the pellet. The above figure and the below stated data indicate that alumina along with spinel and alumina rich Calcia phase ($CaAl_{12}O_{19}$) is present in the sample.

Table 4.2.4:- Pattern List of 5mol% of dolomite Doped Alumina

Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
84-1613	69	Calcium Aluminum Oxide	-0.040	0.386	$CaAl_{12}O_{19}$
82-1468	61	Aluminum Oxide	-0.048	0.718	Al_2O_3
84-0377	42	Magnesium Aluminum Oxide	0.122	0.147	$MgAl_2O_4$
73-1959	51	Magnesium Aluminum Oxide	0.090	0.284	$MgAl_2O_4$

4.2.5 XRD Peaks of 1, 2, 3 and 5mol% dolomitedoped In Alumina Combined



The rather very small peaks in the XRD pattern of 1mol% of dolomite grow into relatively big peaks as the concentration of dolomite increases. This indicates the formation of more amounts of spinel and Calcium Hexaluminate. As the concentration of dolomite increases the amount of Calcia and Magnesia increases which react with Alumina to give more amount of spinel and Calcium Hexaluminate. This is shown by the formation of prominent peaks.

4.3 Linear Shrinkage

The diameter of the green pellets was measured using vernier calipers and again after firing their diameters were measured. The difference was calculated to get the linear shrinkage.

Mol% of dolomite	Diameter of Green Pellet(cm)	Diameter of Fired Pellet(cm)	Linear Shrinkage (%)
1	12.18	9.56	21.51
2	12.15	9.81	19.25
3	12.25	10.12	17.38
5	12.21	10.58	13.35

The calculation of Linear Shrinkage suggests that more the concentration of dolomite in Alumina the less is the shrinkage in the pellets.

4.4 Dilatometry

Fig 4.4.1 and Fig 4.4.2 shows the dilatometric curve of 2mol% and 5mol% dolomite doped in alumina respectively. The first curve shows the shrinkage starts at 1100^{o}C whereas in the second curve the shrinkage starts at around 1000^{o}C. Fig 4.4.3 shows the combined dilatometric curves of 2mol% and 5mol% dolomite. The formation of spinel and Calcium Hexaluminate leads to a shrinkage at a lower temperature in case of 5mol% of dolomite. In 2mol% dolomite the amount of spinel and Calcium Hexaluminate formed is less hence the shrinkage occurs at a higher temperature.

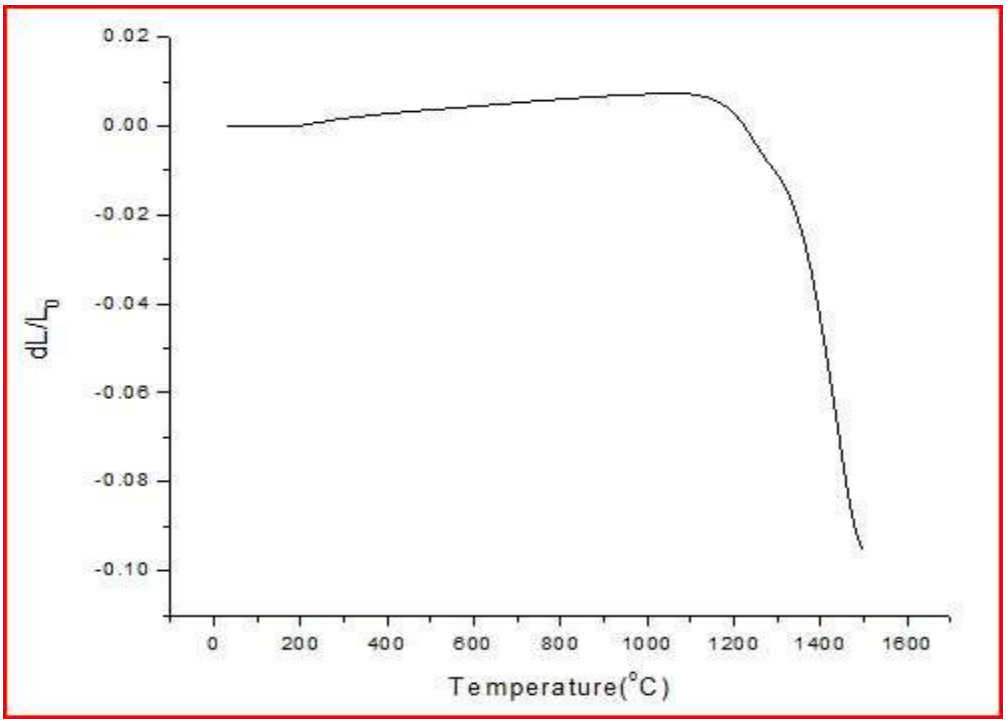


Fig 4.4.1:- Dilatometric Curve of 2mol% dolomite

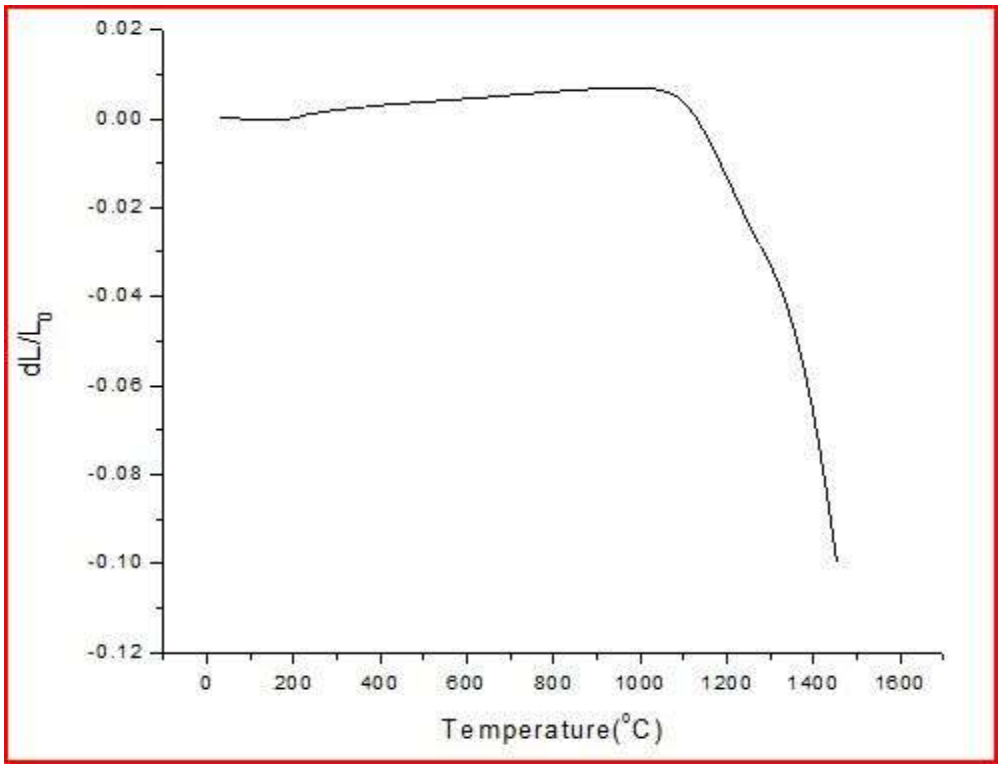


Fig 4.4.2:- Dilatometric Curve of 5mol% dolomite

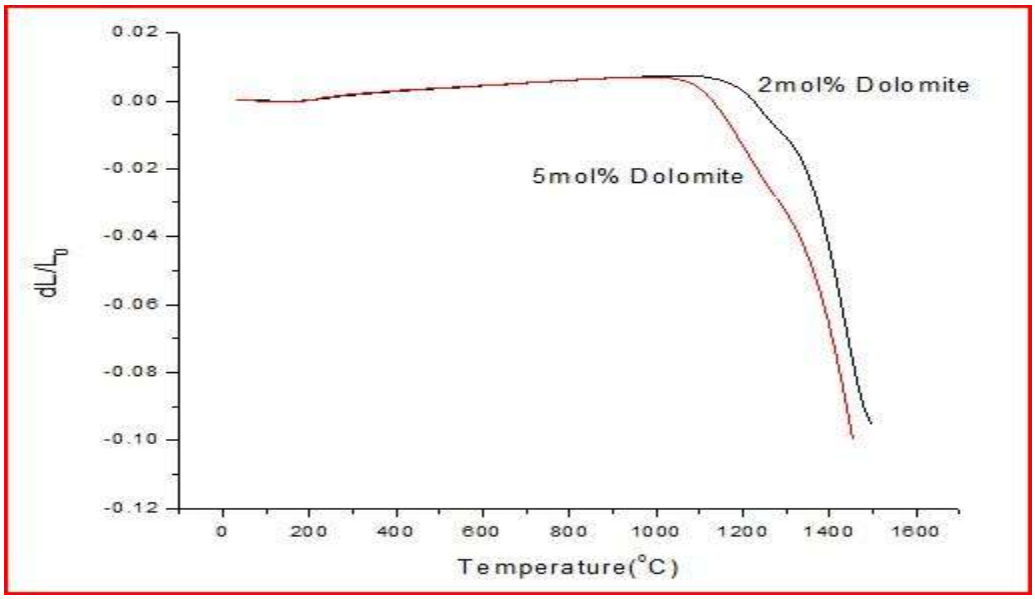


Fig 4.4.3:-Comparisonof 2mol% and 5mol% dolomite Dilatometric Curves

4.5 SEM Images and Their Analysis

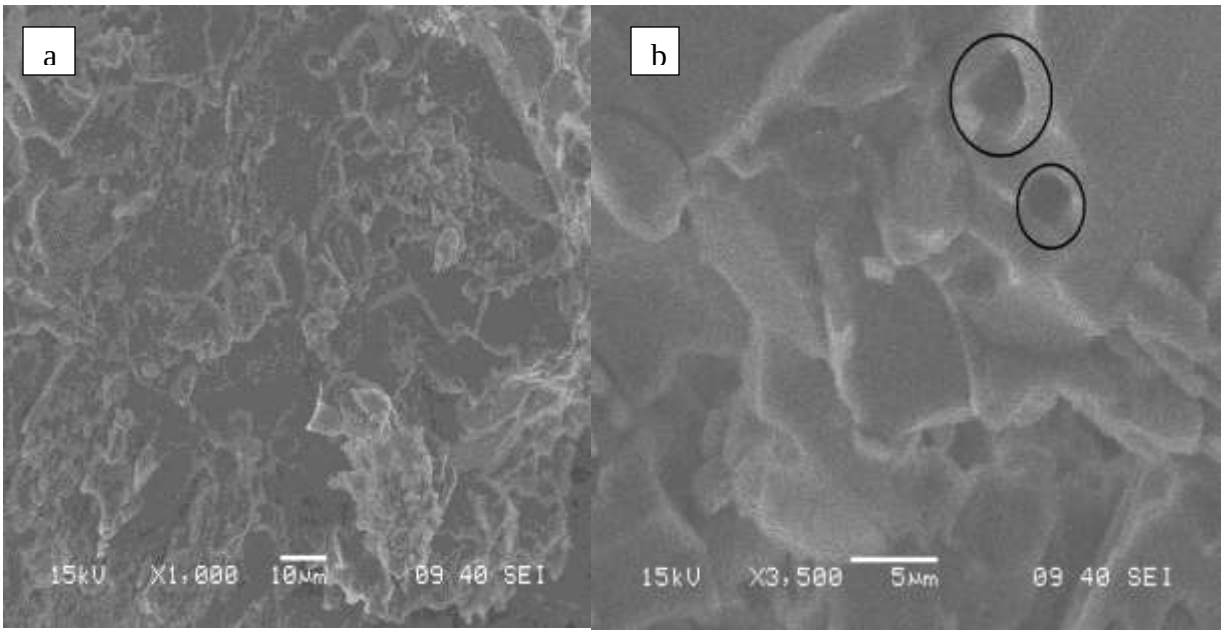


Fig 4.5.1 (a)& (b):- SEM Images of 2mol% dolomite Doped Alumina

The pores the fig 4.5.1 (b) are clearly seen to been formed at the grain boundaries rather than inside the grains. But the amount formed is very less.

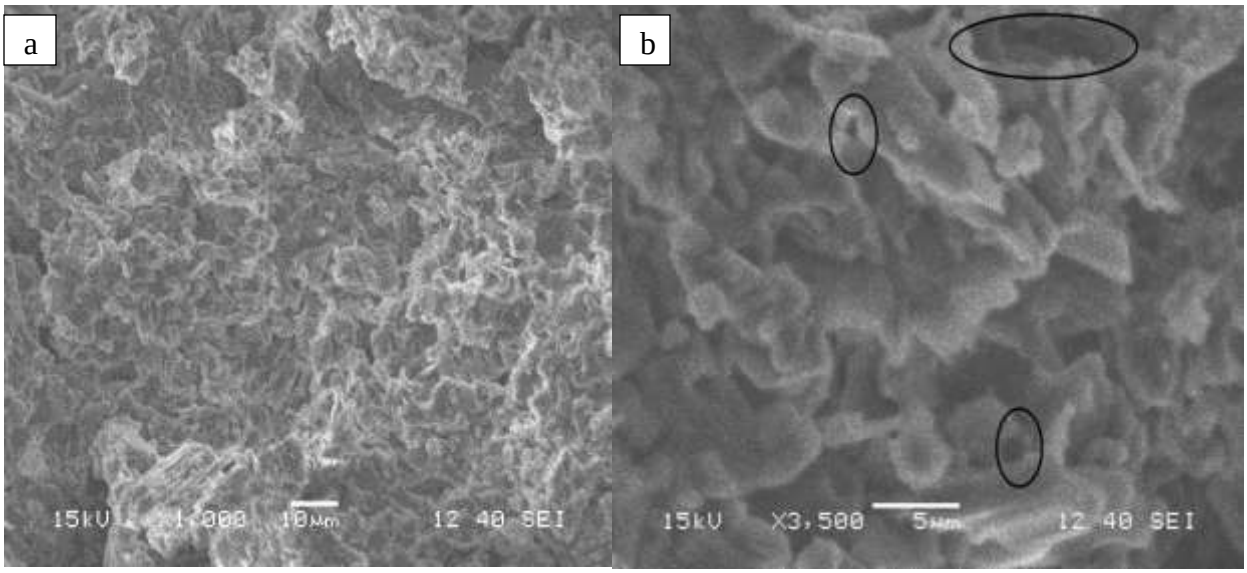


Fig 4.5.2 (a) & (b):- SEM Images Of 5mol% of dolomite Doped Alumina

As the dolomite concentration increases in the sample the pores start to form at the grain boundaries. This is shown in the figure 4.5.2 (b). The amount of spinel and Calcium Hexaluminate formed increases in this sample.

Chapter 5

Conclusion

5.1 Conclusion

From the above experiments and their results we obtain the following conclusions.

1. spinel and Calcium Hexaluminate phases were formed when dolomite was doped in Alumina. This was confirmed by the XRD Analysis. However the amount formed was not significant in case of 1mol% and 2mol% dolomite but it was significant in case of 3mol% and 5mol% dolomite.
2. The Bulk Density of the sample increases as the sintering temperature increases but decreases with the increase in the amount of dolomite. This due to evolution of large amount of Carbon Dioxide (CO_2). This large amount of evolution causes pore formation which decreases the Bulk Density.
3. The pores start to segregate at the grain boundaries when the concentration of dolomite is increased. This is shown by the SEM images.
4. From the Dilatometric curves it is seen that the onset of shrinkage occurs at a lower temperature as we go on increasing the amount of dolomite.

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