Sol-Gel Synthesis of $MgAl_2O_4$ Spinel And Optimization of Process Parameters by Taguchi Method

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Submitted by

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CERTIFICATE

This is to certify that the thesis entitled "Sol-gel technique for synthesis of $MgAl_2O_4$ spinel:application of Taguchi method for optimization of process parameters" has been carried out under the guidance of **Dr. Sathi Banerjee, Dept. of Metallurgical and Material Engineering, Jadavpur University Kolkata** by **Aishik Birbanshi** during the academic session 2017-2019 in partial fulfillment of the requirement for the award of the degree of **Master of Metallurgical Engineering in Industrial Metallurgy** in the **Department of Metallurgical and Material Engineering, Jadavpur University**, **Kolkata- 700032**. In our opinion the work fulfils the requirement for which it is submitted. It is further certified that materials obtained from other sources have been acknowledged in the thesis.

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CERTIFICATE OF EXAMINATION

The forgoing thesis is hereby approved as credible study of engineering subject carried out and represented in a manner of warrants its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by the approval of the undersigned does not necessarily endorse any statement made, opinion, opinion expressed or conclusion drawn therein but approved the thesis only for the purpose for which it has been submitted.

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1)

2)

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Date: **Signature ofExaminers**

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AISHIK BIRBANSHI

Abstract

Page No.

ABSTRACT

Refractories are very important in today's emerging science and technology field of high-temperature materials. These have a significant role in many technological advances in the modern world. The steel and iron sector has been benefitted a lot from these new age refractories. The consumption of good quality iron and steel is which depends on the quality and performance of refractories is also an index of growth of a country in the field of technology. This study concerned about the synthesis of $MgAl_2O_4$ spinel at low temperature and optimizing the process parameters to get the best result at a low cost. $MgAl_2O_4$ spinel has some limitations. To overcome the drawback researchers try to incorporate more amount of Mgo in the Alumina matrix. Aluminum nitrate, magnesium nitrate and citric-acid mixed with proper proportion. The mixture was then dried at 70-80^{0}C and then heat treated at different temperature. Synthesis temperature was 650ºC, 700ºC, 800ºC with different calcination time like 4,5&6 hours respectively in the tube furnace. The final synthesized materials were then sent to various testing such as XRD, FTIR, SEM, Microhardness test. From that results, we have come to a conclusion that even at low-temperature spinel can be formed and this material can be used as a refractory material which will be cost effective in the long run industrial production.

CHAPTER I

INTRODUCTION

1.Refractory materials

1.1.Basicconcepts

Refractory materials are good in various scientific and technological applications. Refractories are non metallic inorganic materials. Refractories are adept to withstand at elevated temperatures which requires for steel melting and other high temperature operations. Some important features are listed below.

- Melting temperature is very high.
- It can withstand high temperature heating to low temperature cooling operations.
- corrosion and erosion resistant due to molten metal, glass, slag, hot gases,etc
- Thermal stability is good
- Exquisite room temperature and high temperature and mechanical properties.

Major application areas of the refractories material

- Kilns
- Furnaces
- Boilers
- Incinerators

1.2 Definition of refractories

According to the ASTM C71 the definition of the refractories are that materials which is nonmetallic in nature having admirable physio-chemical properties for that it has a good engineering application for a structure or as a component of a systems which is exposed to environment above 5380^0C . Drastic technological advancement in the iron and steel making industries changes the operation practice. For this reason, the furnace capacity and operating temperature has been changed.

1.3 Classification of refractories:

Refractories can be classified as follows:

(a) Based on raw materials:

- Acidic refractories (e.g. zircon, fireclay and silica)
- Basic refractories(e.g.dolomite,Magnesite,magnesia-carbon,alumina-magnesia–carbon, chrome-Magnesite and Magnesite-chrome)
- Neutral refractories (e.g. alumina, chromites, Silicon carbide ,carbon)

(b) Based on manufacturing process:

- Shaped refractories (available in the form of different brick shapes ,and includes the oxide and non-oxide systems)
- Unshaped refractories (includes mortars, castables and other monolithics).

1.4 Required features

According to the application the refractories has been chosen in the steel industries. Some features are listed below.

- heavy load of molten metal
- very high temperature(>1600ºC)
- corrosive slag attack
- abrasion and thermal/mechanical spalling caused by molten metal and slag
- very high corrosion resistance
- good thermal spalling resistance
- excellent mechanical characteristics even at high temperature
- ease of application
- enhanced lining life
- less down time and environmental friendliness

2. Alumina(Corundum)

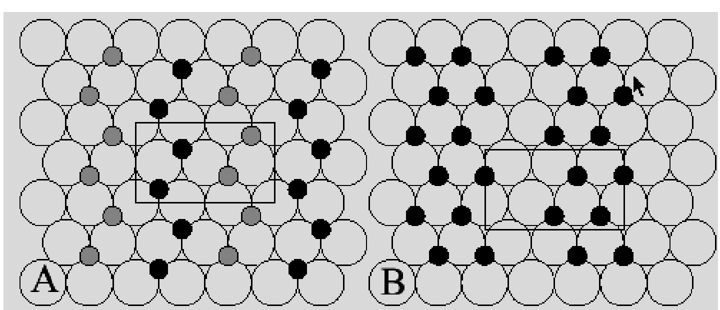
Corundum is a common natural crystal form of aluminum oxide(alumina). Rubies and sapphires are used for ornamentation having various colours for trace impurities in their corundum structure. Rubies are having red colour and having trace element chromium. Sapphire having different colours with different trace element likes iron and titanium.

2.1 CrystalStructure

α-alumina oxide is a common crystalline form of alumina known as corundum. It has a trigonal bravice lattice spacing group of R-3c. Primitive cell having two formula units of Aluminum oxide. The oxygen ion fill the hexagonal close-packed structure and Alumina ions filling the two third of octahedral sites. Alumina also having other phases like chi,gamma,delta and theta alumina. Alumina crystallizes in other forms also, most importants are alpha (stable), kappa (metastable) and gamma (metastable).

2.1.1 KappaAlumina

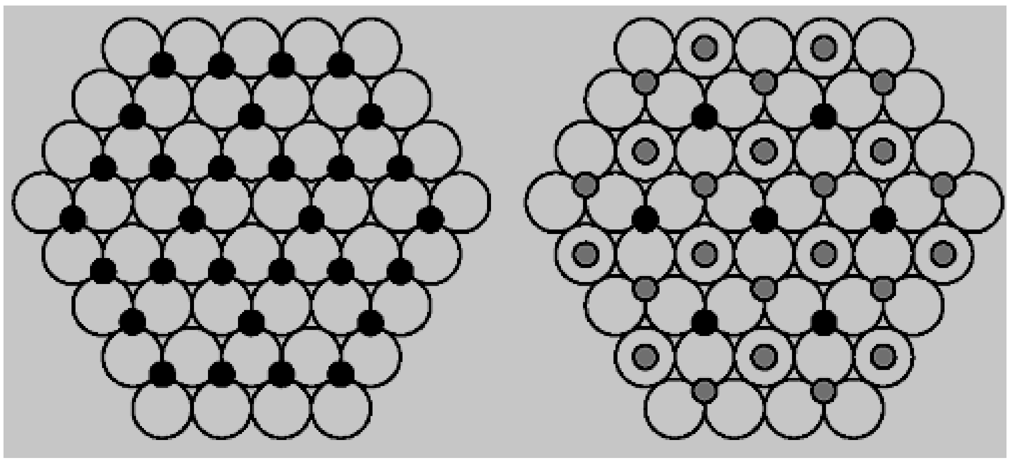
The crystal structure of Kappa aluminum is orthorhombic. Its close-packed planes of oxygen in an ABAC stacking sequence along the c-axis.1/4 of the Al ions share the tetrahedral interstitial positions and 3/4 occupy octahedral positions. The tetrahedrally coordinated Al ions make a zig zag lines along [100] in the structure is shown in the below figure (left). Other vacancy lines in the structure along [100] can be seen in figure(right).



Schematic drawing of the first two layers in the kappa alumina structure. Octahedral Al ions are black, tetrahedral are grey [1]

2.1.2 GammaAlumina

Gamma alumina having cubic structure with a space group of Fd-3m and it is based on the FCC . . . ABCABC stacking of oxygen.



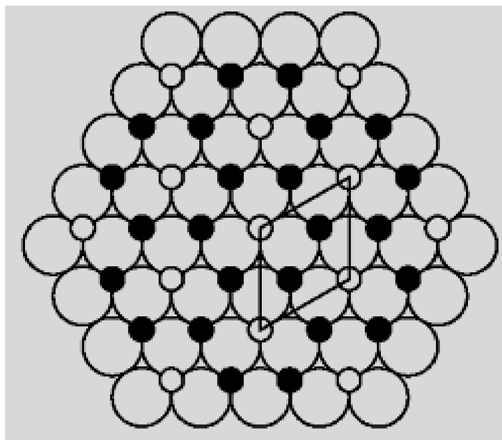
Schematic drawing of the first two layers in the gamma alumina structure [2]

The structure is called a defect cubic spinal structure. To full fill the stiochiometry unit cell

Contains 32 oxygen and 64/3 alumina ions.

2.1.3 AlphaAlumina

Alpha alumina is the only stable alumina phase at all temperatures. It has a trigonal structure (R-3c) and it has ABAB stacking of oxygen planes along the c-direction with Al ions in 2/3 of the octahedral interstitial positions.



Schematic drawing of the first layer in the alpha alumina structure [3]

3. Spinel

$MgAl_2O_4$(Magnesium Aluminate) spinel has a cubic crystal system and it is the member of the large spinel group . Spinel compounds are genearly the member of the group of minerals which are oxides of Magnesium, iron, Maganese or Aluminum. The term spinel was derived from a Latin word spina(Thorn) referring to its pointed octahedral crystal formation. The specialty of these spinel is very hard in nature, having various colour and transparent also. Spinels have a wide range of application in various engineering field, like as high temperature application due to high melting point, good refractories, mechanical strength, Corrosion resistance properties.

3.1 Structure, Property and Phase Diagram

3.1.1 Spinel Structure

- Formulae – $(A^{2+})(B^{3+})_2O_4$ or AB_2O_4 or $AO.B_2O_3$
- Type of packing of the anions is FCC
- The spinel unit-cell is made by eight FCC cells made by oxygen ions. The configuration is 2×2×2. The structure consists of 32 oxygen atoms, 8 A atoms and 16 B atoms.
- According to the cataonic position in interstitial position spinel structure is normal or inverse

3.1.2 Normal Spinel

- Chemical formula: $(A^{2+})(B^{3+})O_4$
- Examples are many aluminates such as $MgAl_2O_4$, $FeAl_2O_4$, $CoAl_2O_4$ and a few ferrites such as $ZnFe_2O_4$ and $CdFe_2O_4$.
- In this structure, all the A^{2+} ions occupy the tetrahedral sites and all the B^{3+} ions occupy the octahedral sites.

3.1.3 Inverse Spinel $B(AB)O_4$

- Chemicalformula: $(A^{2+})(B^{3+})_2O_4$ but for more convenience written as $B(AB)O_4$.
- Most of the ferrite has this structure such as Fe_3O_4(or $FeO.Fe_2O_3$), $NiFe_2O_4$, $CoFe_2O_4$ etc.

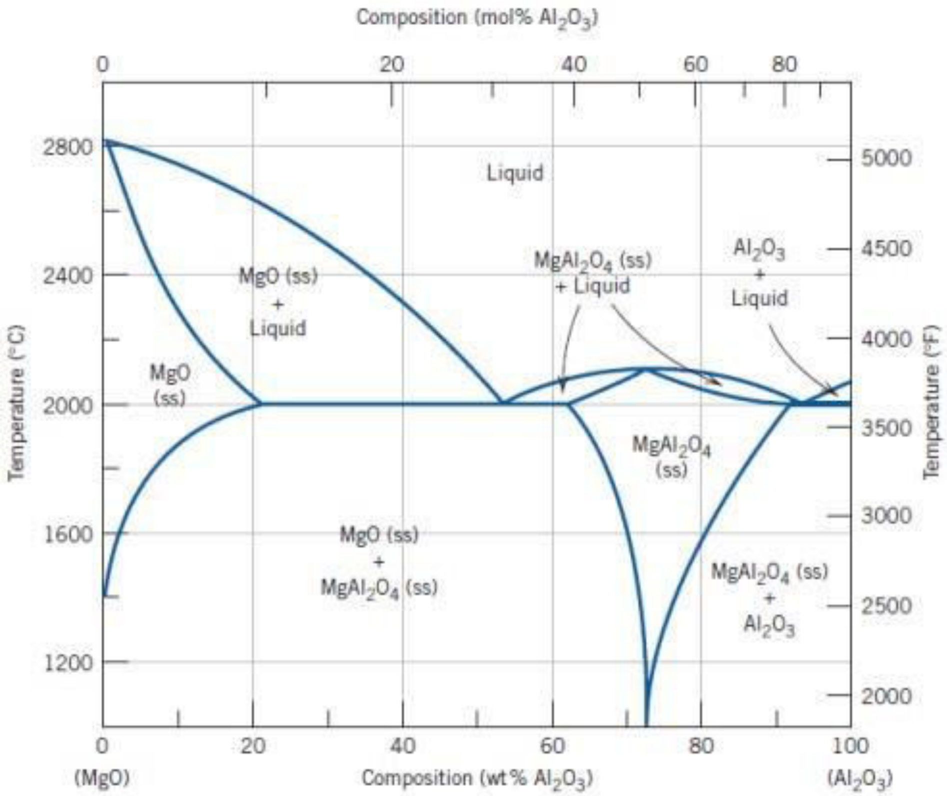
  - In this structure, ½ of the B^{3+} ions occupy the tetrahedral sites and remaining ½ B^{3+} and all A^{2+} ions occupy the octahedral sites.

3.1.4 Physical property

- Density(g/cm) 3.58
- Thermal conductivity(W/mK) 5.9
- Thermal expansion coefficient (dl/LK 10) 7.6

3.1.5 Spinel phase diagram

- Melting point of pure magnesia is 2800°C.
- Melting point of pur alumina 2054°C.
- Magnesia can dissolve up to 2% alumina, the maximum solubility happened at 2000°C. The name was given to this solid solution of alumina in magnesia is"periclase."
- Magnesia has no solubility in alumina.
- "Spinel" is the name which is associated with the compound $MgAl_2O_4$, but it is also the name of a phase in the magnesia-alumina binary system with solubility ranging from 40% alumina (at 2000°C) to 84% alumina (at 1800°C). The spinel phase with a composition of 50% alumina melts simultaneously at 2200°C.
- At 2200°C, an 82% magnesia alloy is partially solidified, having equal parts of periclase and liquid.
- At 2000°C, a 68% magnesia alloy transforms on cooling from a liquid phase to a two solid phases. One of the solid phases is periclase with 2% alumina content and the other spinel contains 40% alumina.
- At 2000°C, a 73% alumina alloy is half liquid and half spinel. • At 1800°C, a 95% alumina alloy solidifies on cooling into two solid phases, one is a spinel of 84% alumina, and the other is pure alumina.
- At 1000°C, 75% magnesia alloy has equal parts periclase, with a composition of 100% magnesia, and spinel with a composition 50% magnesia.



MgO–Al_2O_3 phase diagram Reference

4. Statement of Problem:

It is clear from the literature study that alumina can act as refractory material for iron & steel industry. In this studies we will try to find out the low temperature process treatment for spinelization followed by characterization of mixture of magnesium oxide-aluminium oxide ($MgAl_2O_4$) prepared through solution combustion method and the process parameters are optimized by Taguchi and ANNOVA to determine the best parametric condition to get the least grain size because smaller grain can make good refractory properties and proper agglomeration of the spinel. It has been seen from the literature survey that using proper process optimizing tools can reduce the production cost as well as it can identify the most effective parametric condition for the feasible low temperature synthesis. Intricate structural and morphological studies has been undertaken to check if it shows desired refractory properties for low temperature synthesis. This can reduce energy and process hazards during long run industrial manufacturing of the spinel.

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CHAPTER II

LITERATURE REVIEW

1. $MgAl_2O_3$ Spinel as a refractory material:

Refractories has a dominant role in metallurgical, glassmaking and ceramic industries[1,2]. Problem faced during the steel making process in steel ladel refractories is corrosion by steel slags(acidic/basic in nature),abration driven by liquid metal, generation of oxidized carbon layers which will cause of major detoriation of strength at high temperature and molten steel penetration[3-5].The performance depends on the selection of raw materials from which the spinel was formed. Now a day's magnesia-alumina spinel made from pure raw material shows great high temperature strength, high melting point(2135),high chemical inertness and good dimensional stability[6-8], it also shows great slag resisting strength due to Mgo-Mgo bond.For these properties, it is greatly used as a refractory material[9]. Humidity sensor[10]. Spinel has a wide range of applications in metallurgical, chemical, electro technical, catalysis, electronic and glass industries [11-12]. Over the last few decades various novel techniques have been applied for the synthesis of $MgAl_2O_4$ spinel including Sol- Gel[13], spray drying[14], freeze-drying[15], mechanical activation[16], organic gel- assisted citrate process[17]. Wet chemical process did not get much success due to the requirement of costly raw materials although it can be done at relatively low temperature[18-21]. The conventional method for preparation of $MgAl_2O_4$ spinel requires to calcine the mixture of metal oxides at elevated temperatures (1625ºC for 2hours), which causes a large no of aggregates and inhomogeneous compositions[22,23]. In spite of other methods the combustion synthesis for preparation of binary oxides got many advantages which includes homogeneity, high purity, formation of crystalline oxide powders in shorter time span and lower amount of external energy[24-27]. Magnesium aluminate spinel, which is the only stable compound in the $MgO\text{-}Al_2O_3$system, has long been considered an important ceramic material. Many studies have reported its properties, applications and different processing methods [28].

2. Different Types of Synthesis Method for spinel:

2.1. Organic precursors method :

Pacurariu et all used magnesium and aluminium glycolate prepared through 1,2-ethanediol oxidation with presence of aluminum and magnesium nitrates. The aqueous solution of aluminum and magnesium nitrates and the 1,2-ehhanediol has been taken in a stoichiometric proportion, had been heated in air upto 100 ^{0}C . After completion of the experiment a white colour powder obtained which had been washed out with aceton-water mixture and filter paper followed by full emission of nitrogen di-oxide [29-32].

2.2. Combustion method:

It is based on the redox reaction between aluminum and magnesium nitrate which used as a oxidizing agent and fuel which acts as reductive reactant. The fuels which were used urea, glycine and –alanine for the sake of study of the influence for their reducing characteristics and length of the chain which is the effect of temperature and crystalline size. Reducer and oxidizer ratio also plays a significant role in the combustion, it controls the temperature and time of the reaction. The redox reaction generates CO2, H2O and N2 gases. The mixed solution is heated upto 100^{o}C for the water evaporation. The dried mixture was heated in a open system at 300^{0}C, ignition takes place and produce a white fragile foam like substance which is very easy to convert in powder form [33] .

2.3. Sol-Gel method:

Aluminum and magnesium nitrate and citric acid has been taken in a stoichiometric ratio dissolve into a small amount of water after complete mixing a transparent homogeneous mixture obtained after that Ammonia solution added to it in the form of droplets to change the ph of the solution and make a homogeneous solution. To make a high viscous gel the solution has been evaporated slowly. After that that mixture heated in a range of temperature 120-140^{o}C for 24 hr to get a dried gel. And the final gel precursor were calcined at various different temperature [34] .

3. Concept involves behind optimization:

An optimization problem starts with a set of independent parameters and incorporates conditions and restrictions that may defines acceptable set of values of variables or parameters which has to be minimized or maximized according to the systems requirement. Basically optimization of process parametric design has been used where the process steps are unknown or it is very complex in nature, especially where the experiment no is in large scale. Full factorial design is one of an experimental design consists of two or more factors with discrete levels and during the experiment it will consider all possible factors. It helps to understand the contribution of each factor in the systems response variable. A common experimental design having 2 factor with levels each. So if there are k factors each at 2 level the design should have 2^k runs. Taguchi method is an another statistical method developed by Taguchi and Konishi[35]. Previously it was developed to enhance the quality life of goods manufactured, later this has been applied for many other engineering fields.

4. TAGUCHI METHOF DESIGN OF EXPERIMENT:

Taguchi method is a quality control tool to optimize process parameters of any system. It has some advantages over traditional quality improvement tool such as full factorial design. Best performance level of any product/process can be calculated by proper designing of the process parameter and from that optimal condition has been selected to find out the impact of uncontrollable factors(Noise factor). Signal to Noise ratio (S/N Ratio) has been used to measure the effect of the noise on the system. A robust system always has a high S/N ratio. This helps to identify the possible combination of factors and find out the best combination. But sometimes large no of experiment to test is costly and time consuming. The model developed by Taguchi simplified, standardized and minimize the no of factor of combination which would require checking of the factor effect [36]. In classical process parametric design, it is complex and not easy to use. The experiment volume will increase with the increase of process parameter. Taguchi method which uses special designed orthogonal array to understand the entire process parameter with less no of experiment.

5. No of steps involved in Taguchi method:

1) Finding out the main problem and its effects.

2) Finding out the noise factor, testing condition and quality characteristics.

3) Finding out the objective function which has to be optimized.

4) Selection of orthogonal Array and construct a Matrix

5) Run the Matrix operation.

6) Conduct and verify the experiment.

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CHAPTER III
EXPERIMENTAL WORK

3.1 PREAMBLE

In this section the details experimental procedure for the study of Al_2O_3 synthesis and alumina and magnesium spinel synthesis has been discussed by solution combustion method. The amounts and ratio of the Al_2O_3, MgO and citric acid has been used for preparing the different batches in certain ratio were selected through the literature survey. We will compare the characteristics of alumina and spinel in different treatment temperature. The raw material used in this work viz. aluminum nitrate, magnesium nitrate and citric acid were bought form the market of analytical grade.

3.2 MATERIAL PREPARATION

3.2.1 Preparation of spinel:

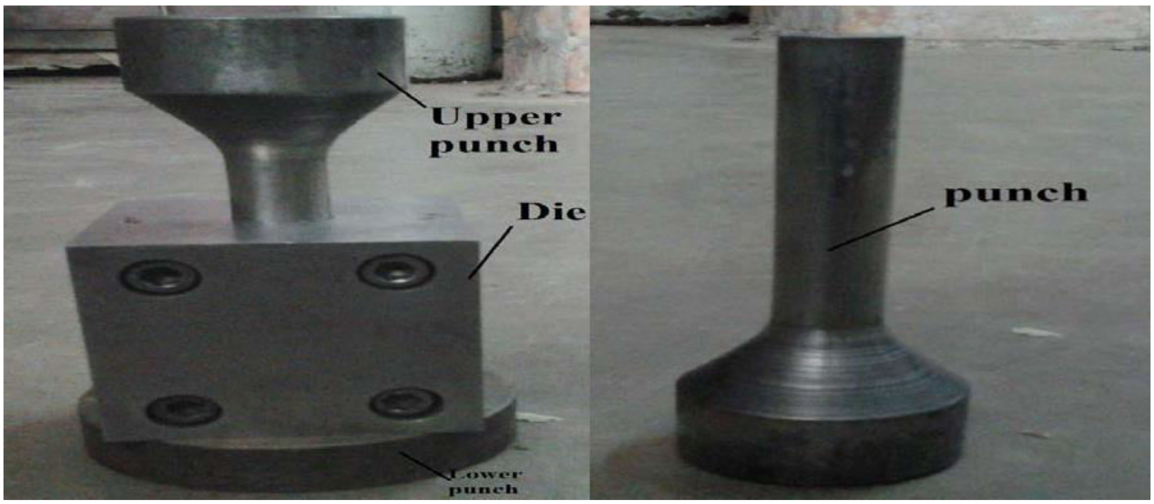
Magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$), Aluminum nitrate ($Al(NO_3)_3.9H_2O$) and Citric Acid as a fuel has been taken at the ratio of 1 :2: 1.25, 1:5 & 1:1.75. The mixture was then mixed with very small amount of de ionized water. De ionized Water was used to mix with the chemicals uniformly. Then the mixture was dried at 80ºC for 3-4 hours with the help of hot plate. After completing drying operation the mixture converted into fine powder. The powder was then divided into 3 equal parts. Each part was then passed through a heat treatment for specific temperature for 4, 5&6 hours respectively. The treatment temperatures chosen for processing were 650ºC, 700ºC, 800ºC.

Ceramic powder mixing bowl and mixing hamme r

Drying machine

3.3 PRESSING/COMPACTION FOR MICRO HARDNESSTEST

The powder mixtures were poured into a 12mm diameter mould cavity in a die system consisting of two punches (a stationary lower punch/ base and a moveable upper punch) and the central block consisting of the cylindrical mould cavity. The entire die system was placed in a manually operated hydraulic pressing machine. Pressing was performed by applying an uniaxial pressure of 1500kg/cm^2. Cylindrical pellets of alumina and spinel of different heat treated powders were thus obtained.



Die and Punch System

Hydraulically controlled high-pressure pressing machine

3.4 CURING

The compacted samples were cured at 1200^0C for about 1 hours. This was done in order to complete the followings:

- Eliminate the residual water, volatile matters and phenols if still present in sample.
- Develop sufficient strength and proper binding of the constituents so that the tablets could be gone through micro hardness test.

Pot furnace

3.5 CHARACTERISATIONS /TESTS:

3.5.1. Differential Thermal& Thermo gravimetric Analyzer:

Differential Thermal & Thermo gravimetric Analysis is a very important characterization method for characterization of material. In DTA/DSC-TGA we can find any phase change or any chemical/physical changes in the system where enthalpy change takes place which are measured by controlling temperature at a particular rate of heating or cooling. Diamond DT-TGA is used to analyze DSC by suitable software to measure heat flow Vs temperature plot. This system can measure both weight change and heat flow at the same time, any phase change can be identified precisely as most of the phase change occurs without change in weight.

DTA/DSC-TGA instrument

DTA/DSC-TGA analysis was carried out with:

MODEL NO. : Pyris Diamond TG/DTA

MAKE : PerkinElmer (SINGAPORE)

Nitrogen Atmosphere(150ml/min)

Platinum crucible used with alpha alumina powder as reference.

3.5.2 XRD analysis of different batches (identification of phases):

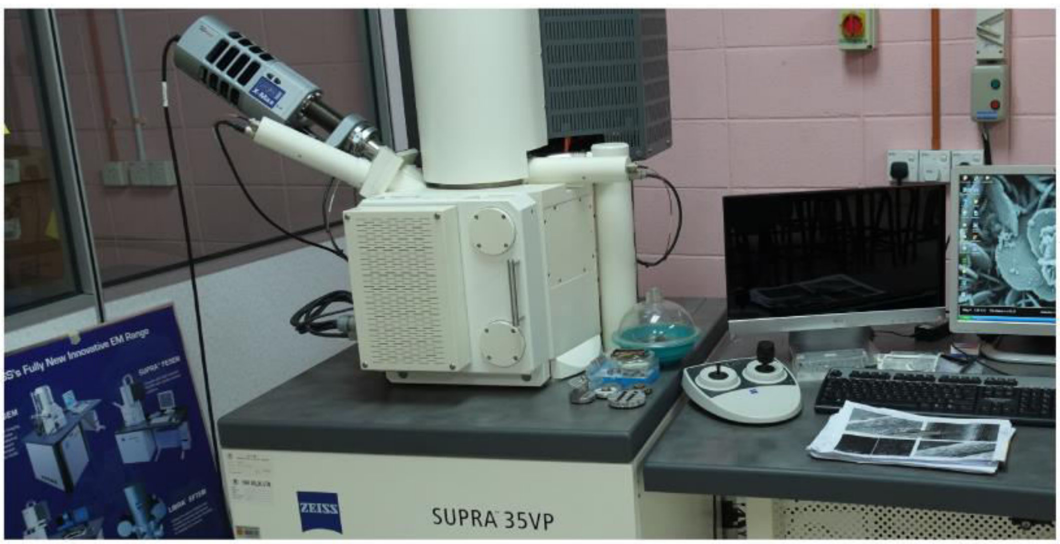
X-ray diffraction machine

X- Ray Diffraction analysis was done with BrukerD8 Advance of all the samples under identical conditions with CuKα radiation whose-

- Tube voltage is 40kV
- Tube current is 40mA.
- Scan Range:10º-90º
- Scan Mode:Continuous
- Speed:1º/min

These settings were used throughout the entire XRD analysis. We get from XRD spectrum the diffraction intensity Vs 2θ plot, where θ is the Bragg's angle in degrees. We get from XRD plot the d-values of the samples along with the values of flex width, 2θ and intensity of the consecutive peaks. The calculated d-values for the respective peaks in the XRD plot of $MgAl_2O_4$ (spinel), pure Al_2O_3, and were compared and matched with standard JCPDS data to identify the phases corresponding to each of the peaks.

3.5.2 FESEM analysis:



Field Emission Scanning Electron Microscopy (FESEM)

FESEM gives us topographical and elementary information at a magnification of 10X to 300000X, it has virtually unlimited depth of field, when it is compared with conventional scanning electron microscopy. FESEM produces clear less distorted electrostatically images with a spatial resolution down to 1-1/2 nanometer.

Some advantages of FESEM:

1. It has the ability to examine smaller-area contamination spots at electron accelerating voltages compatible with energy dispersive spectroscopy(EDS).

2. Reduce the penetration rate of low-kinetic-energy electrons to the probes near to the material surface.

3. Accelerating voltage range is 0.5 to 30kilovolts.

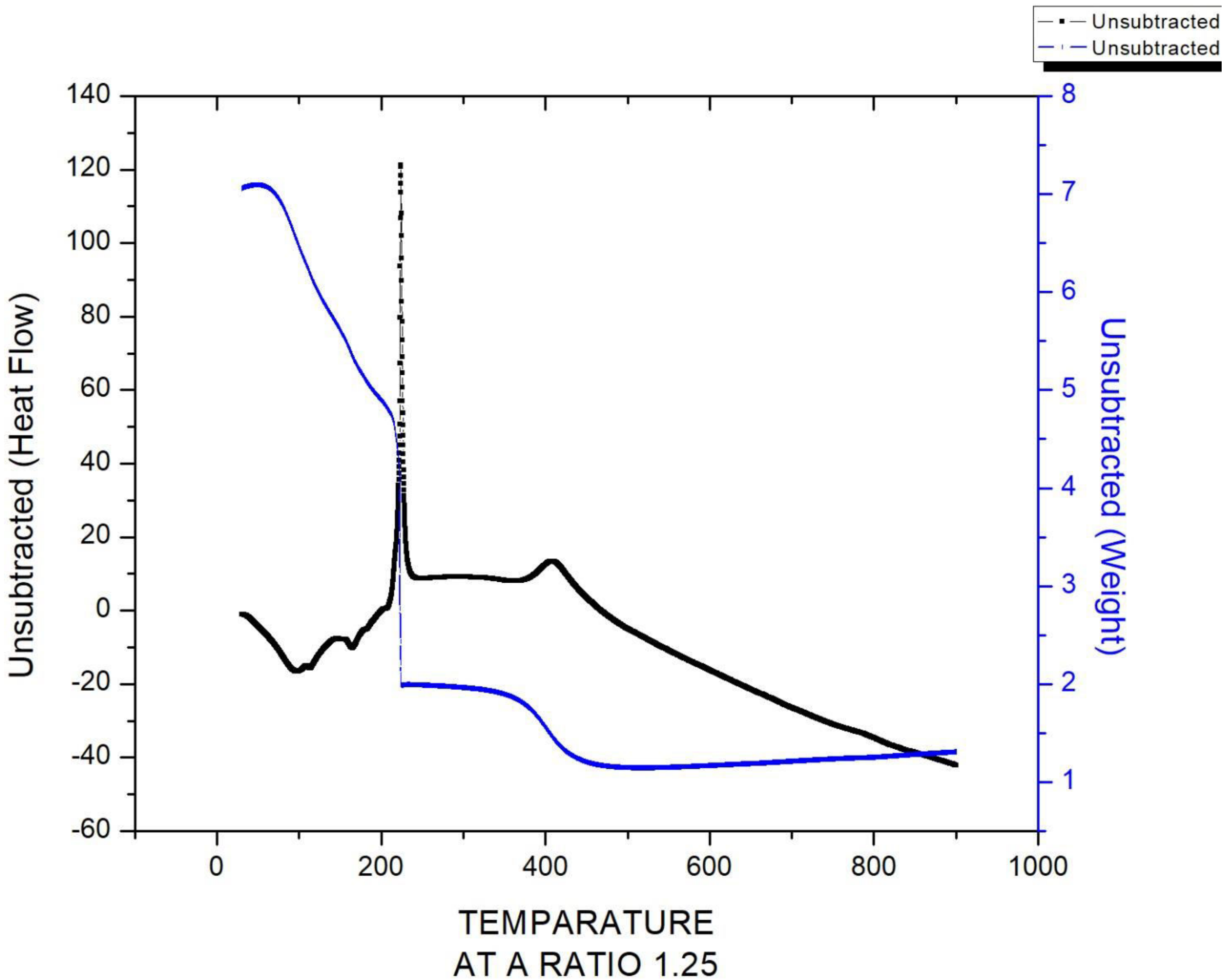
4. No need of conducting coating

5. Ultra high magnification is achievable.

CHAPTER-IV

RESULTS AND DISCUSSIONS

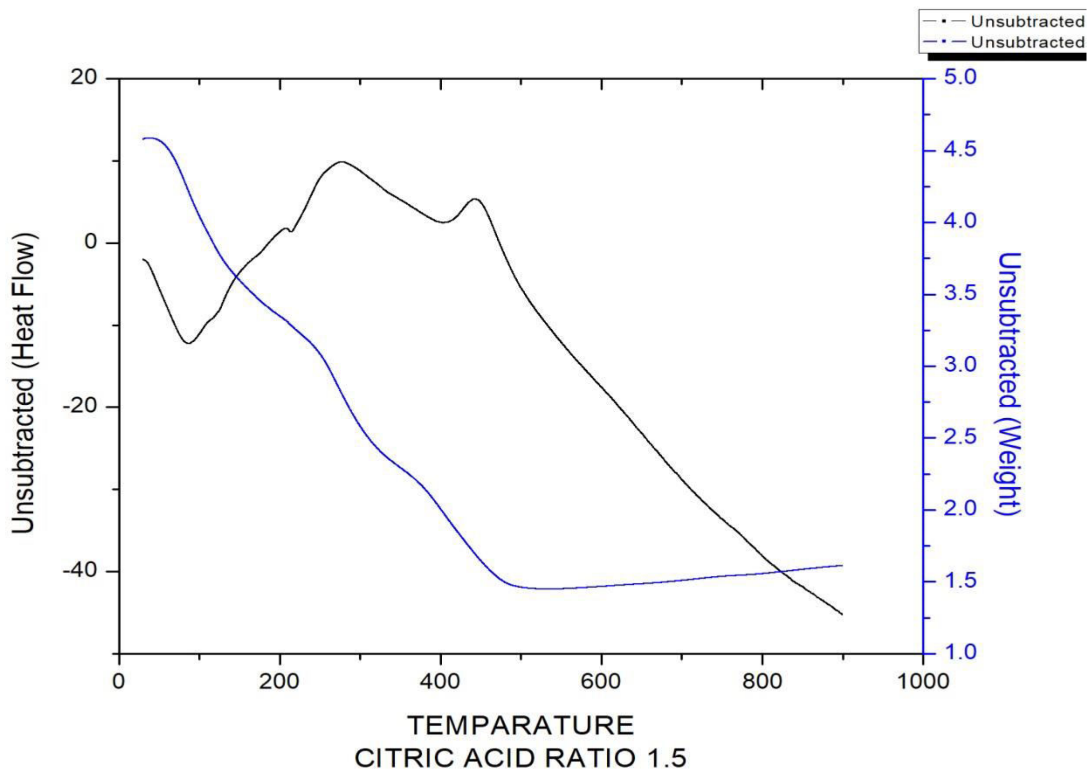
4.1 DTC/TGA Analysis of various compositions



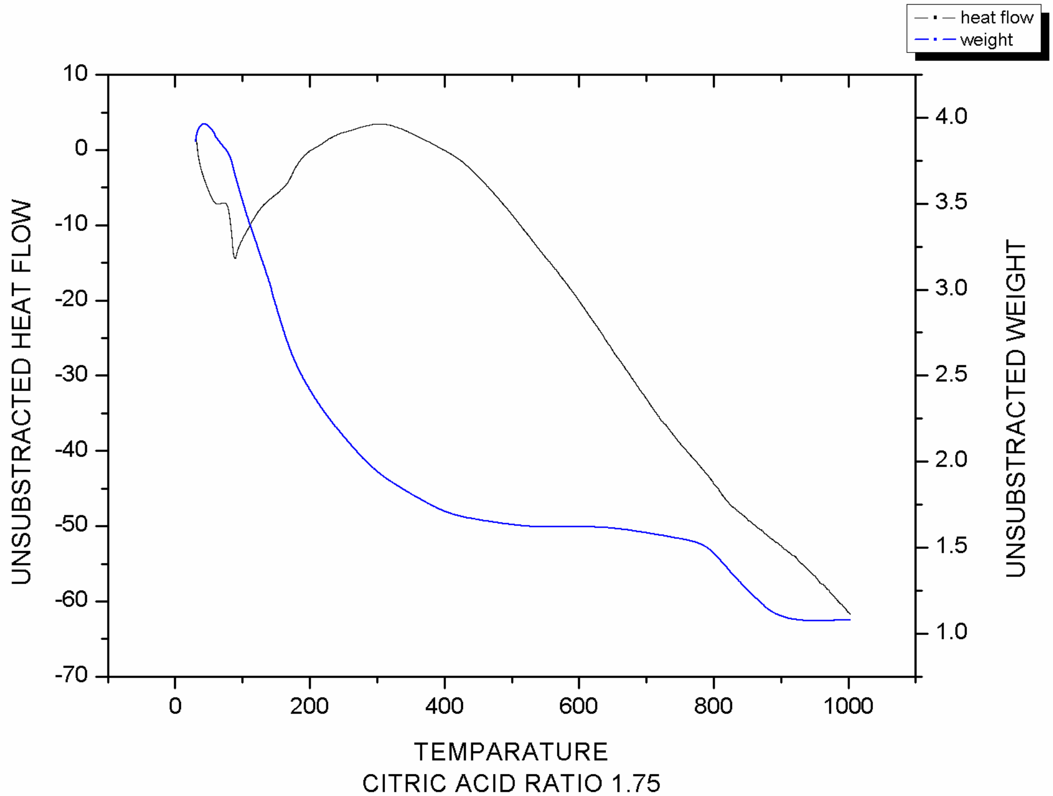
DTA/TGA of spinel with heating rate of 10ºC/min

Thermal analysis of precursors material of alumina and MgO has been observed at the heating rate of 10ºC/ min from room temperature to 900ºC (Fig 1). TG (BLUE colored) plot indicates a constant weight loss from room temperature to 900ºC with three steps. Initial drop of weight occurred due to evaporation of moisture and physically held volatile content up to the 90ºC.

100ºC onwards there is a drastic drop of weight due to dissociation of chemically held moisture content. Form 400ºC onwards the change in weight is observed almost at a constant rate nearly up to 900ºC. For DTA plot there are three drop of curve at 180ºC, 220ºC, 410ºC. All the drops are due to endothermic reaction. Release of chemically held moisture occurs in these regions. At 600ºC onwards crystallization of Al_2O_3 occurs which has been indicated by exothermic trends.



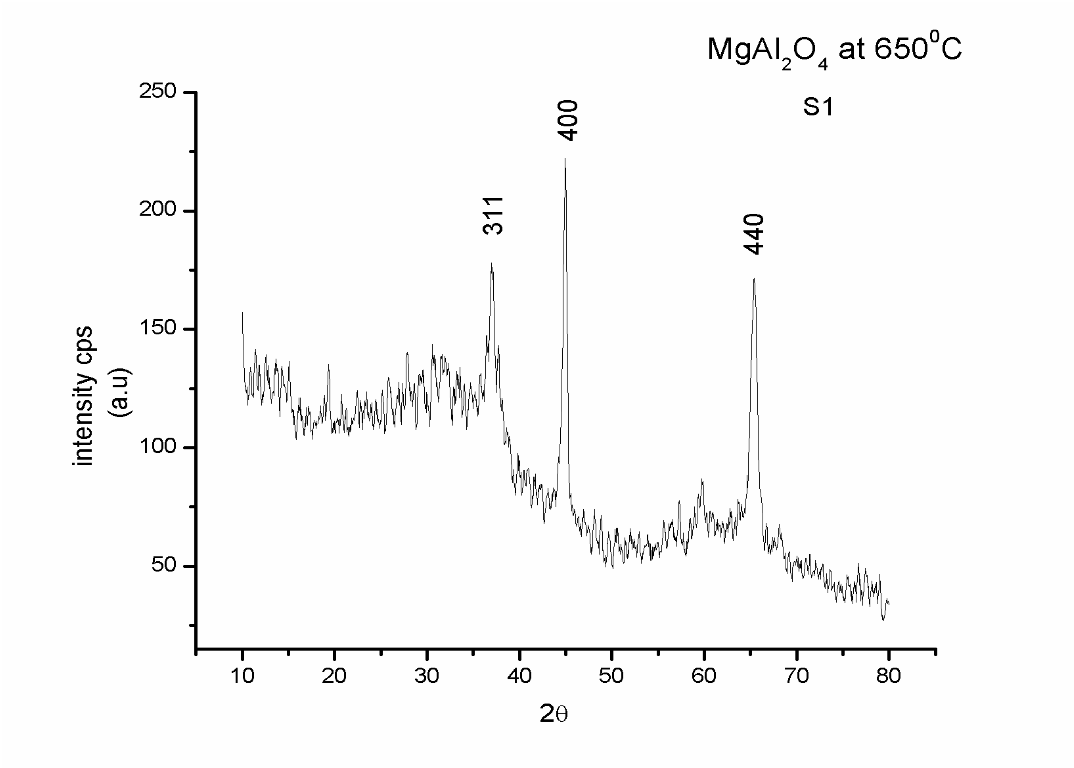
Thermal analysis of precursor's material of alumina and MgO has been observed at the heating rate of 10ºC/ min from room temperature to 900ºC (Fig 1). TG (BLUE colored) plot indicates a constant weight loss from room temperature to 900ºC with three steps. Drastic drop of weight occurred due to evaporation of moisture and physically held volatile content and dissociation of chemically held moisture content up to the 440ºC. Form 440ºC onwards the change in weight is observed almost at a constant rate nearly up to 900ºC. For DTA plot there are three drop of curve at 100ºC, 300ºC, 490ºC. All the drops are due to endothermic reaction. Release of chemically held moisture occurs in these regions. At 500ºC onwards crystallization of Al_2O_3 which has been indicated by exothermic trends.



DTC/TGA of spinel with heating rate of 10ºC/min

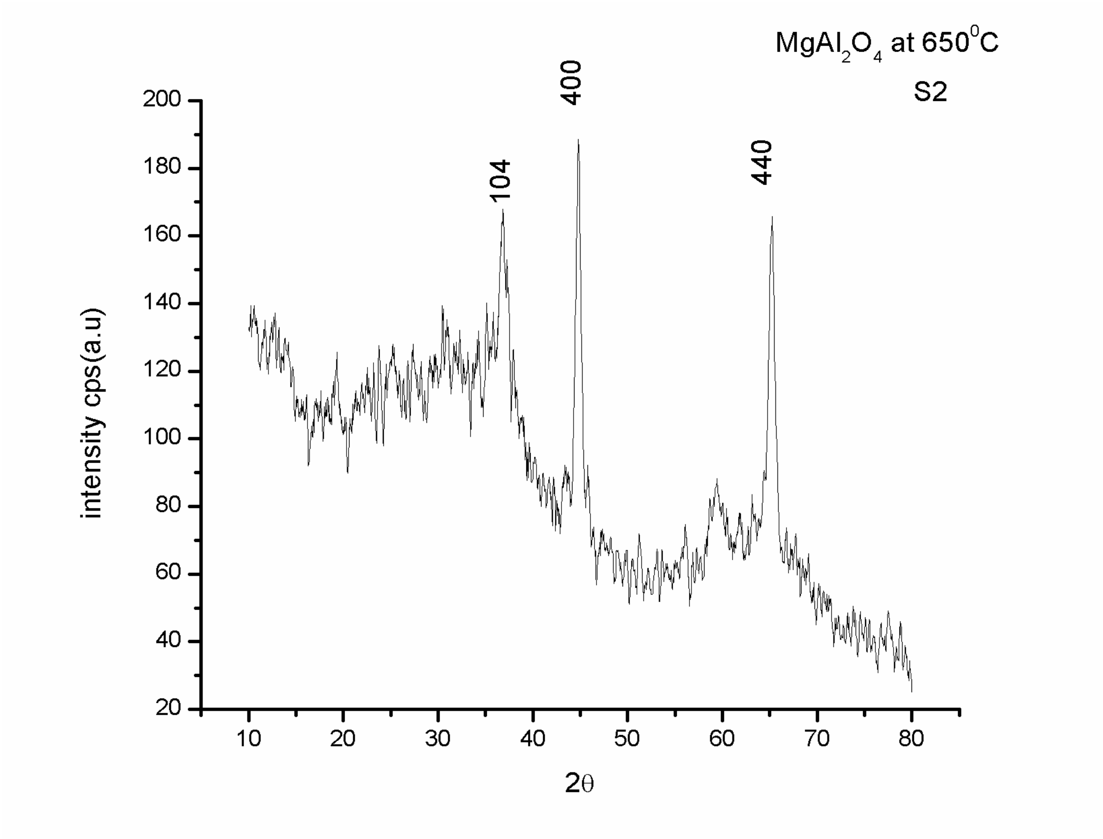
Thermal analysis of precursors material of alumina and MgO has been observed at the heating rate of 10ºC/min from room temperature to 900ºC (Fig 1). TG (BLUE colored) plot indicates a constant weight loss from room temperature to 900ºC with three steps. Drastic drop of weight occurred due to evaporation of moisture and physically held volatile content and dissociation of chemically held moisture content up to the 440ºC. Form 440ºC onwards the change in weight is observed almost at a constant rate nearly up to 800ºC. Again further weight loss up to 850^0C then a constant graph has been observed .For DTA plot there are three drop of curve at 150ºC, 340ºC and then a constant slope. All the drops are due to endothermic reaction. Release of chemically held moisture occurs in these regions. At 780ºC onwards crystallization of Al_2O_3 which has been indicated by exothermic trends.

4.2 XRD ANALYSIS OF SYNTHESIS OF MgAl2O4



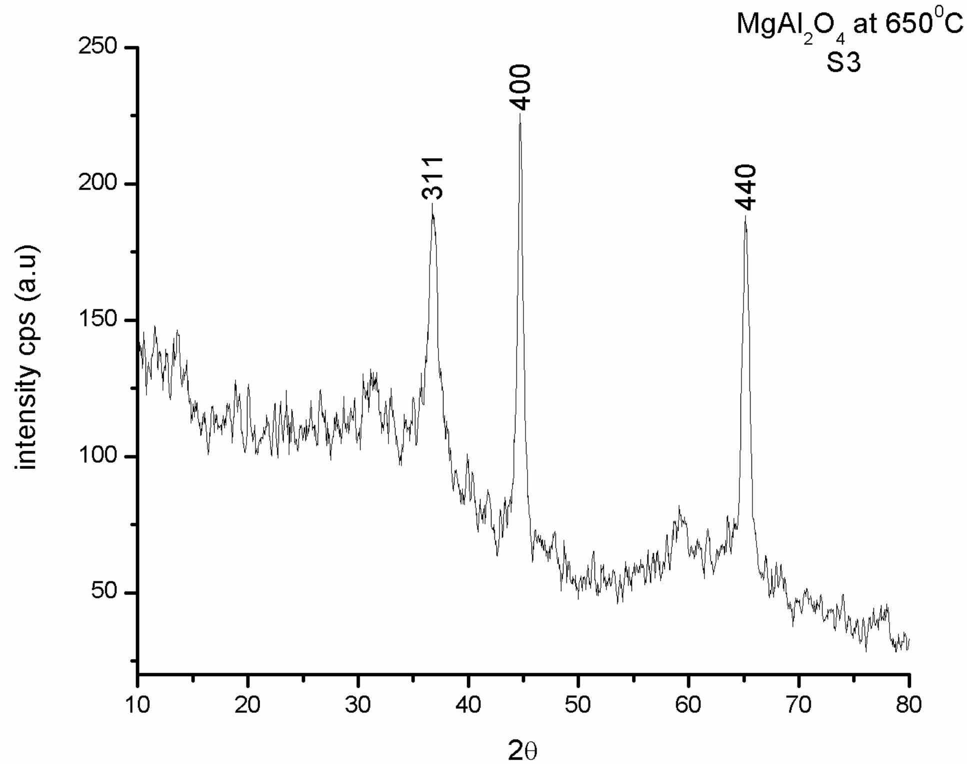
MG:AL:CITRIC ACID(1:2:1.25)

Standard d-value	Obtained d-value	Plane	Phase
2.4363	2.4276	311	$MgAl_2O_4$
2.0201	2.0150	400	$MgAl_2O_4$
1.4284	1.4258	440	$MgAl_2O_4$



MG:AL: CITRIC ACID (1:2:1.50)

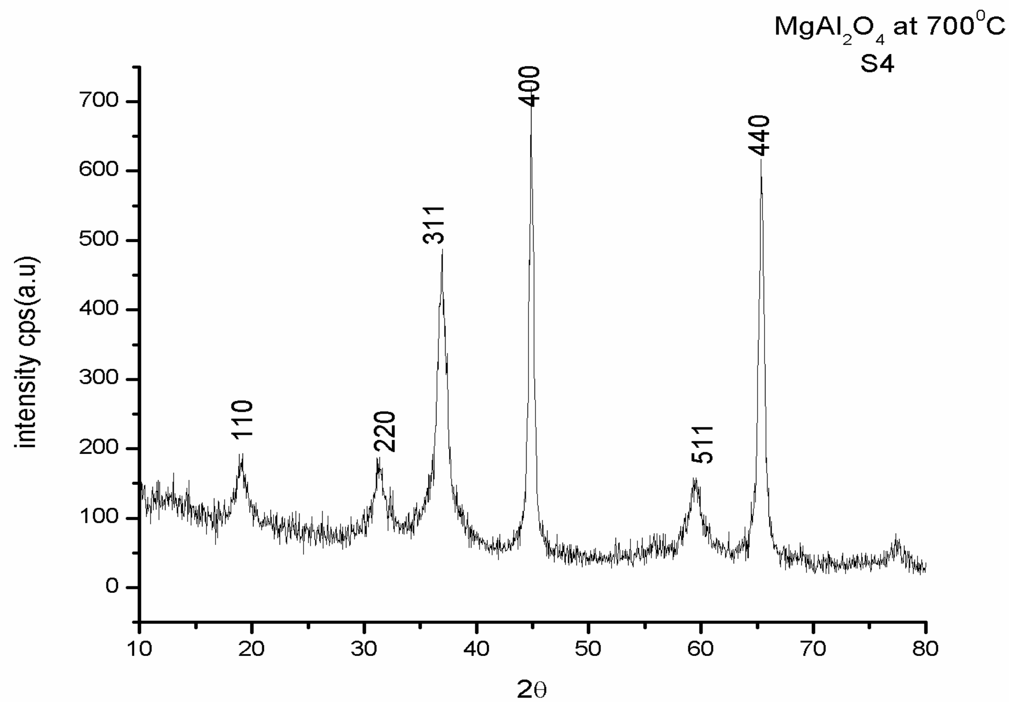
Standard d-value	Obtained d-value	Plane	Phase
2.0201	2.0214	400	$MgAl_2O_4$
1.4284	1.4307	440	$MgAl_2O_4$
2.5520	2.5472	104	Alpha&Gama Al_2O_3



MG:AL: CITRIC ACID (1:2:1.75)

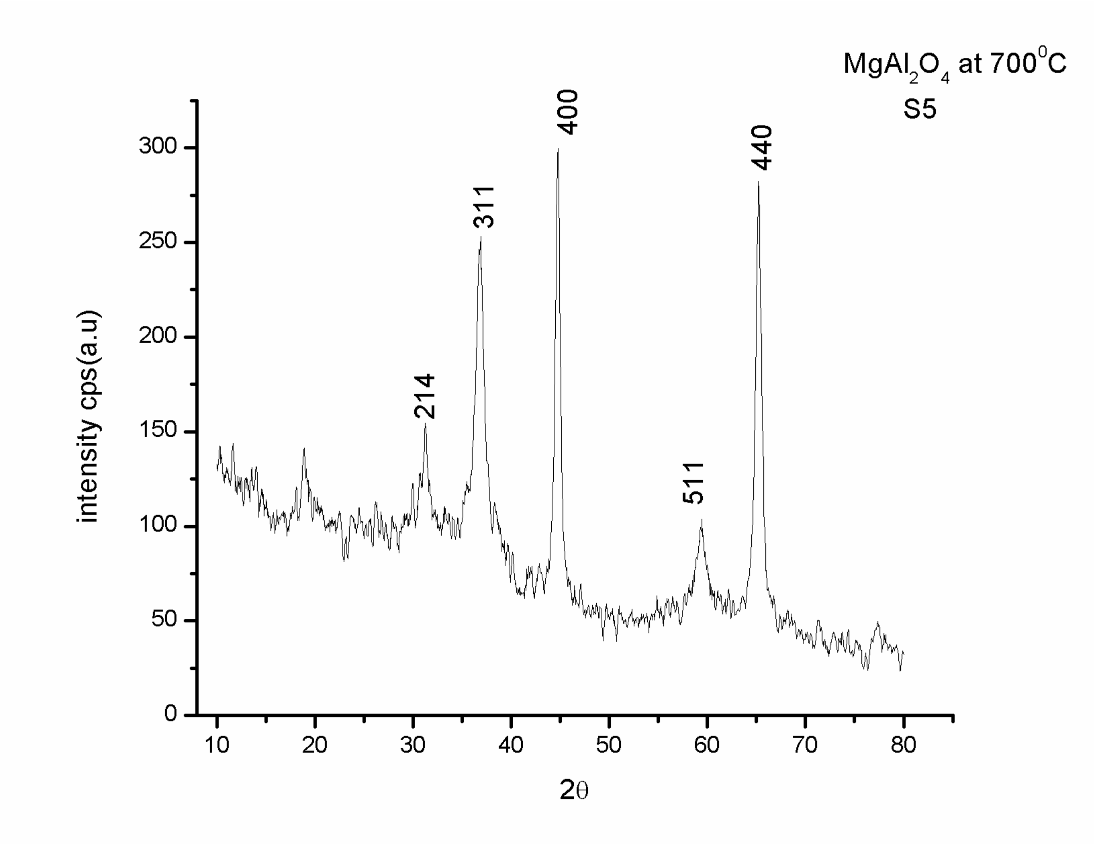
Standard d-value	Obtained d- value	Plane	Phase
2.4363	2.4276	311	$MgAl_2O_4$
2.0201	2.0257	400	$MgAl_2O_4$
1.4284	1.4317	440	$MgAl_2O_4$

.



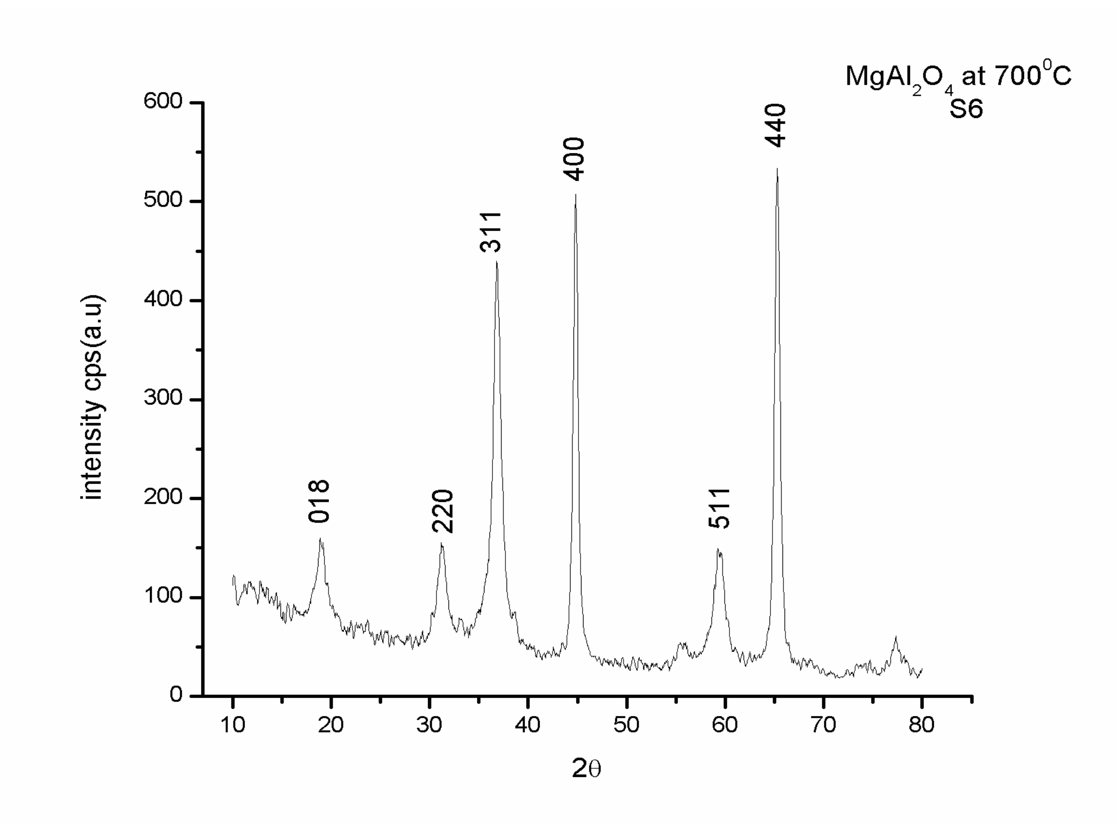
MG: AL: CITRI ACID(1:2:1.25)

Standard d-value	Obtained d-value	Plane	Phase
2.8569	2.8554	220	$MgAl_2O_4$
2.4363	2.4271	311	$MgAl_2O_4$
2.0201	2.0192	400	$MgAl_2O_4$
1.5561	1.5488	511	$MgAl_2O_4$
1.4284	1.4268	440	$MgAl_2O_4$
2.3804	2.3790	110	Alpha&Gama Al_2O_3



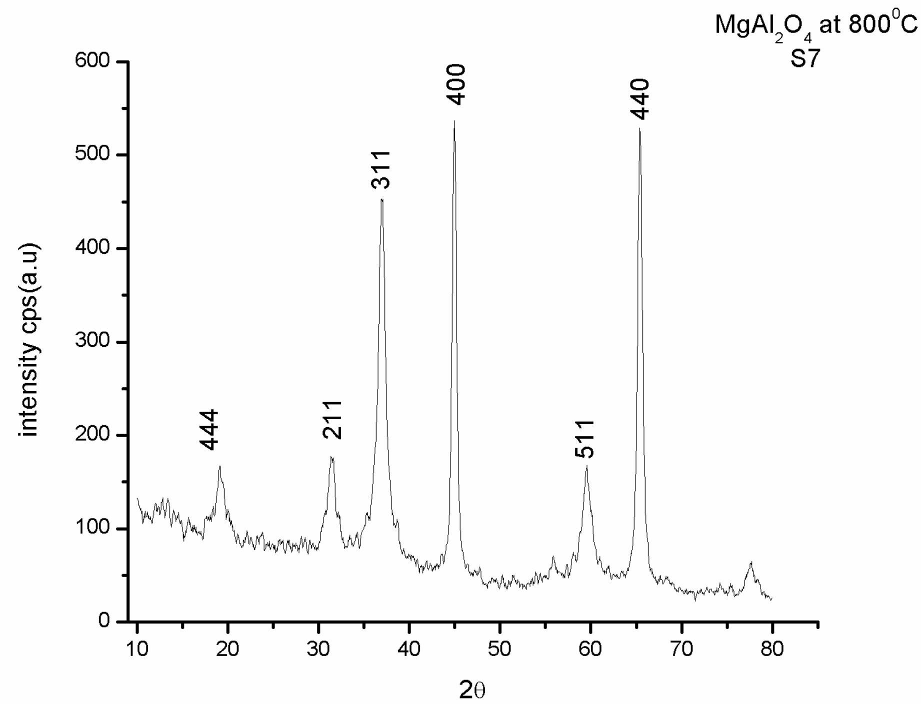
MG: AL: CITRI ACID (1:2:1.50)

Standard d-value	Obtained d-value	Plane	Phase
2.4363	2.4276	311	$MgAl_2O_4$
2.0201	2.0257	400	$MgAl_2O_4$
1.5561	1.5571	511	$MgAl_2O_4$
1.4284	1.4317	440	$MgAl_2O_4$
1.4045	1.4032	214	Alpha&Gama Al_2O_3



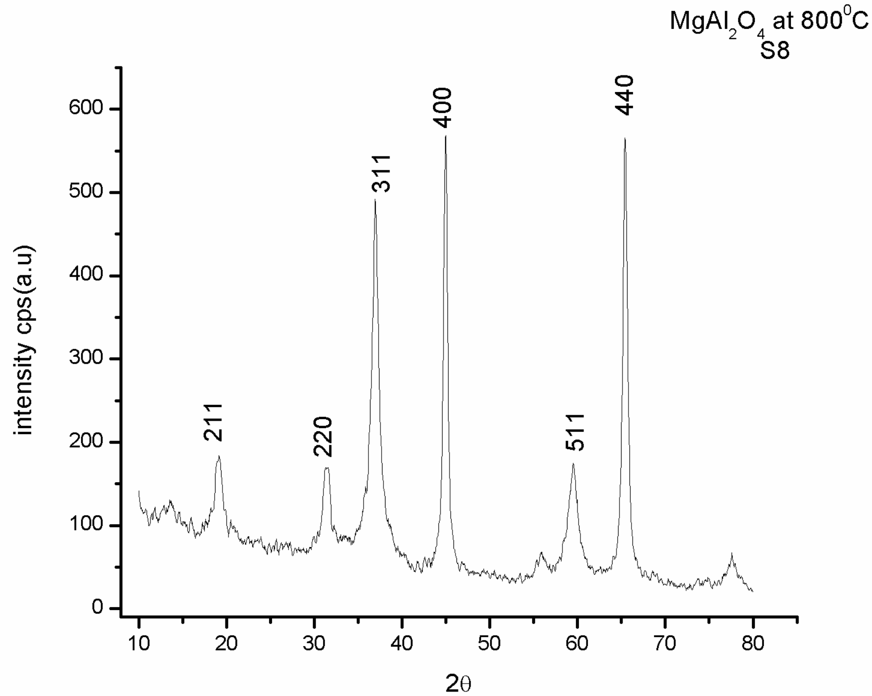
MG: AL: CITRI ACID (1:2:1.75)

Standard d-value	Obtained d-value	Plane	Phase
2.8569	2.8510	220	$MgAl_2O_4$
2.4363	2.4435	311	$MgAl_2O_4$
2.0201	2.0214	400	$MgAl_2O_4$
1.5561	1.5499	511	$MgAl_2O_4$
1.4284	1.4297	440	$MgAl_2O_4$
1.5115	1.5098	018	Alpha&Gama Al_2O_3



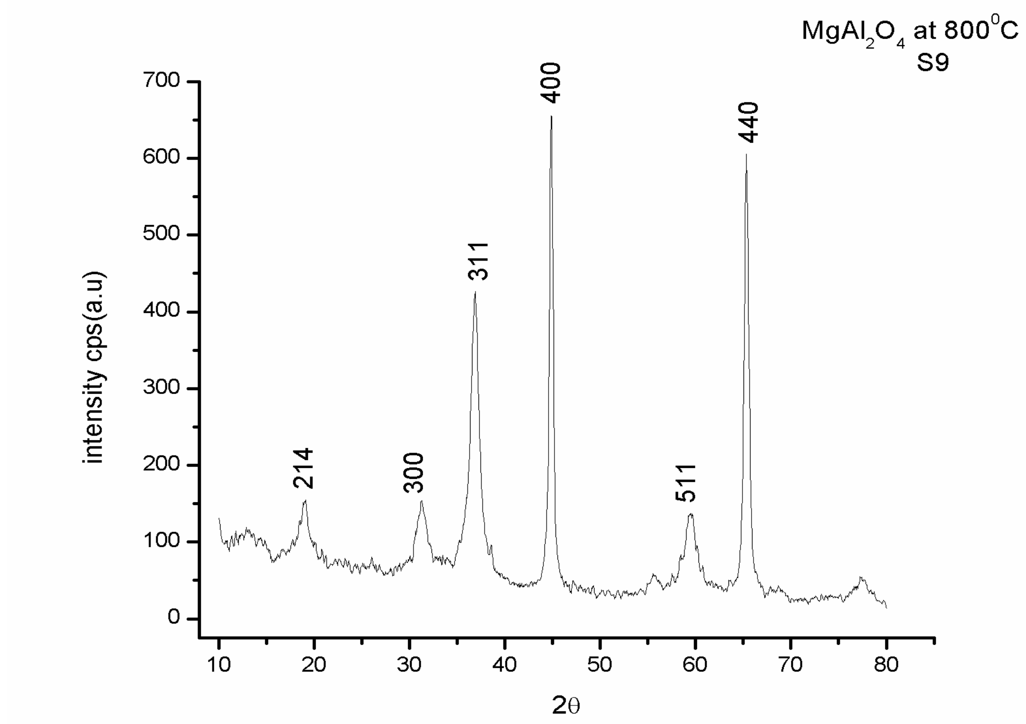
MG: AL: CITRI ACID (1:2:1.25)

Standard d-value	Obtained d-value	Plane	Phase
2.4363	2.4276	311	$MgAl_2O_4$
2.0201	2.0150	400	$MgAl_2O_4$
1.5561	1.5523	511	$MgAl_2O_4$
1.4284	1.4268	440	$MgAl_2O_4$
1.5472	1.5396	211	Alpha&Gama Al_2O_3
1.1663	1.1659	444	$MgAl_2O_4$



MG: AL: CITRI ACID (1:2:1.50)

Standard d-value	Obtained d-value	Plane	Phase
2.8569	2.8644	220	$MgAl_2O_4$
2.4363	2.4307	311	$MgAl_2O_4$
2.0201	2.0171	400	$MgAl_2O_4$
1.5561	1.5523	511	$MgAl_2O_4$
1.4284	1.4258	440	$MgAl_2O_4$
1.5472	1.5398	211	Alpha&Gama Al_2O_3



MG: AL: CITRI ACID (1:2:1.75)

Standard d-value	Obtained d-value	Plane	Phase
2.4363	2.4371	311	$MgAl_2O_4$
2.0201	2.0192	400	$MgAl_2O_4$
1.5561	1.5595	511	$MgAl_2O_4$
1.4284	1.4287	440	$MgAl_2O_4$
1.4051	1.3998	214	Alpha&Gama Al_2O_3
1.3743	1.3723	300	Alpha&Gama Al_2O_3

Key note: All the above data of XRD analysis is compared with standard JCPDS library Serial no- (77-0435) for $MgAl_2O_4$

Result analysis by Taguchi optimization method and ANNOVA analysis:

TEMAPARATURE	TIME	RATIO OF CITRIC ACID	GRAIN SIZE
650	4	1.25	114.960
650	5	1.50	131.500
650	6	1.75	130.456
700	4	1.25	115.069
700	5	1.50	131.477
700	6	1.75	102.450
800	4	1.25	104.814
800	5	1.50	104.726
800	6	1.75	131.453

The above data from the table used Analysis of variance (ANOVA) is used to evaluate the response magnitude in % of each parameter in the orthogonal experiment. It is used to identify and quantify the sources of different trial results and Tukey method also used to identify the confidence level and a comparison between the parameters to understand their effect in the chemical reaction.

Calculation of ANNOVA:

One-way ANOVA: TEMP, TIME, RATIO

Method:

Null hypothesis = All means are equal

Alternative hypothesis At least one mean is different

Significance level $\alpha = 0.05$

Equal variances were assumed for the analysis.

Factor Information

FACTOR	LEVELS	VALUES		
FACTOR	**3**	TEMPRATURE	TIME	RATIO

Analysis of Variance:

Source	DF	Adj SS	Adj MS	F-Value	P-value
Factor	2	3053835	1526918	1046.84	0.00
Error	24	35006	1459		
total	26	3088842			

Factor	**N**	**Mean**	**StDev**	**95% CI**
TEMP	9	716.7	66.1	(690.4, 810.0)
TIME	9	5	0.866	(-21.275, 31.275)
RATIO	9	1.5	0.2165	(-24.7745, 27.7745)

Tukey Pair wise Comparisons:

Grouping Information Using the Tukey Method and 95% Confidence

FACTOR	**N**	**MEAN**	**GROUPING**	
TEMP	9	716.70	A	
TIME	9	5.00		B
RATIO	9	1.500		B

From the above Tukey data table it has been seen that the effect of time and ratio same or in other terms they are not significantly different.

Difference of levels	Difference of means	SE of difference	95% CI	T-value	Adjusted P-value
TEMP-TIME	-711.7	18.0	(-756.6, -666.7)	-39.53	0.000
RATIO-TEMP	-715.2	18.0	(-760.1, -670.2)	-39.72	0.000
RATIO-TIME	-3.5	18.0	(-48.4, 41.4)	-0.19	0.979

Individual confidence level = 98.02%

From the above table it is clear that the P-value of the interaction between TEMP-TIME, RATIO-TEMP is less than .05 so they have a significant interaction during the reaction.

Using Taguchi method to get the optimum result from the system:

We have used here L-9 orthogonal array for the requirement of the system optimization

TEMP	TIME	RATIO
1	1	1
1	2	2
1	3	3
2	1	2
2	2	3
2	3	1
3	1	3
3	2	1
3	3	2

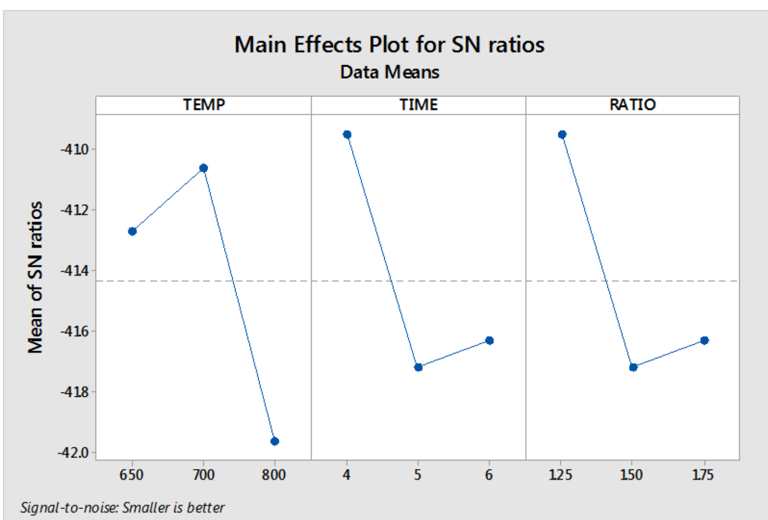
FACTOR=3(TEMP, TIME, RATIO OF CITRIC ACID)

LEVEL=3

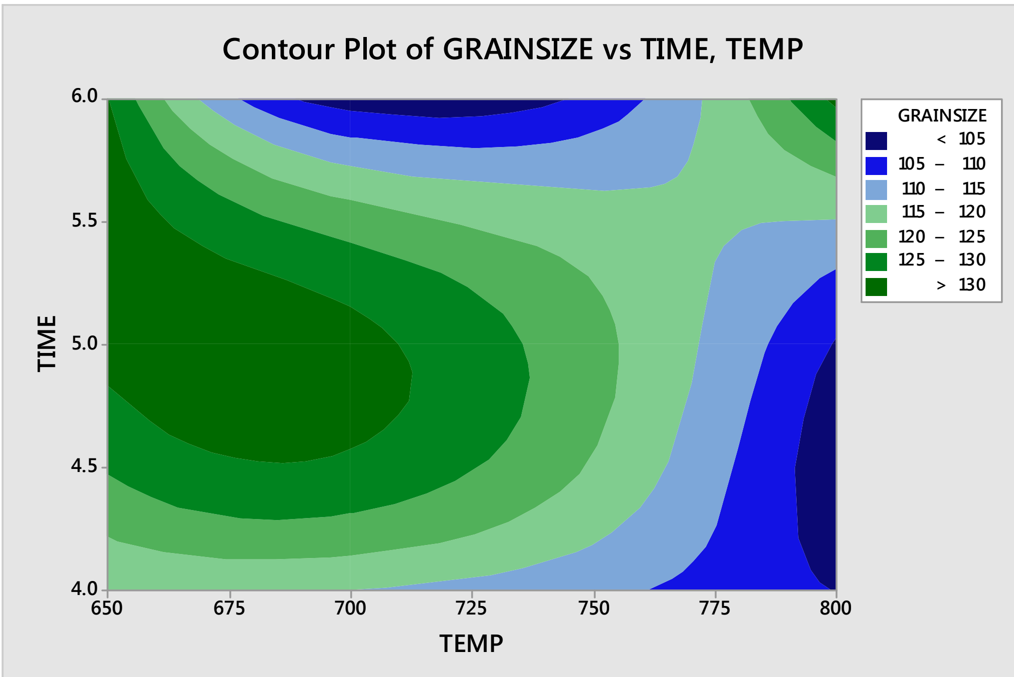
	TEMP	TIME	RATIO
LEVEL1	650	4	1.25
LEVEL2	700	5	1.5
LEVEL3	800	6	1.75

Purpose of the Taguchi method to get the optimum result and least grain size as small grain size gives better sintering property, low porosity, less prone to corrosive attacks. For the fulfillment of the experiment we we choose "Smaller is better" as a target to minimize the response.

The formula is $S/N = -10 * \log(\Sigma(Y^2)/n)$). where Y = responses for the given factor level combination and n = number of responses in the factor level combination.



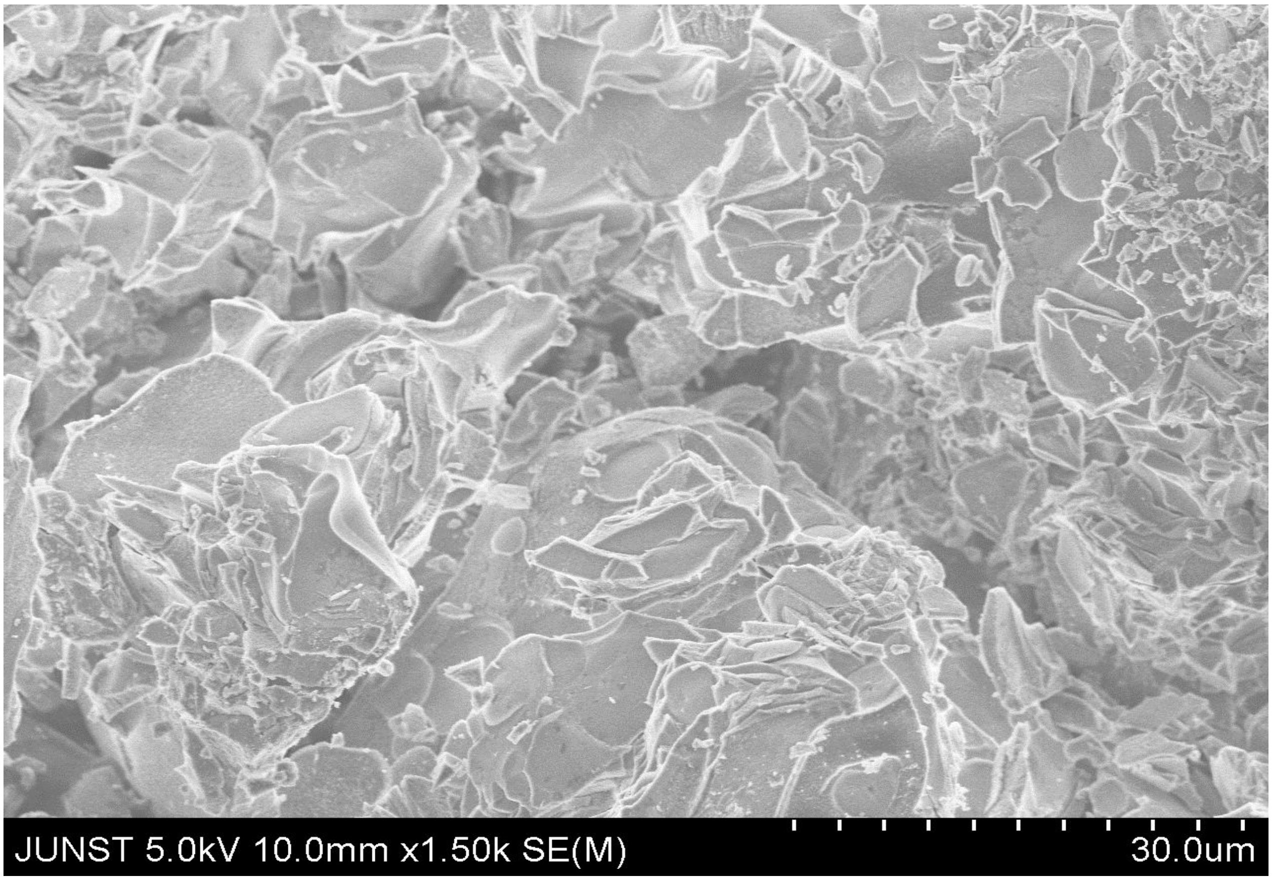
From the SN graph it has been seen that output result will be minimum at operating condition at 800^0C, 5hr with a ratio of 1.5. For the above set of data obtained output/grain size is 104.726nm.



Z-axis –Grain size, X-axis- Temp, Y-axis-time

The contour plot shows how the grain size changes with the change of time and temperature variables. From the graph we can have a quick interpretation about the system variables.

The above result which is obtained from Taguchi method (800^{0}C,5hr,1.5), this sample has been sent for FESEM analysis to justify the result. The FESEM image is given below:



The micrograph revealed granulated agglomerated mass dispersed in various zone. The spinel formation shows layered overlapping structure due solid state bonding of alumina and magnesia quite distinct in figure. The particle seems to be micron meter level on spinelization.

REFERENCES

1. Preparation And Characterization Of Mgo Nanoflakes By Wet Precipitation Method Mageshwari K., And Sathyamoorthy R. * Pg & Research Department Of Physics, Kongunadu Arts And Science College, Coimbatore, Confluence 2012 Conference proceedings.

2. Ft-Ir/Pas And SemEdx Studies On Aluminosilicates Modified ByCs(I), Th(Iv) And U(Vi)Z. Hubickia, E. Ziebac;¤, G. Wojcika And J. RyczkowskibAdepartmentOf Inorganic Chemistry, BdepartmentOf Chemical Technology University Of Maria Curie-Skłodowska,Pl. M. Curie-Skłodowskiej 3, 20-031 Lublin, Poland Cscanning Electron Microscopy Laboratory, John Paul Ii Catholic University Of Lublin Faculty Of Mathematical And Natural Sciences, Al. Racławickie 14, 20-950 Lublin, Poland Vol. 116 (2009).

CHAPTER - V

CONCLUSION

Studies have been conducted on the synthesis of the Magnesia-Alumina spinel formation at different heating temperature. The homogeneous Magnesia-Alumina dispersion for solid-solution conversion is fabricated by solution combustion route prior to heat treatment. Also the homogeneous Magnesia-Alumina spinel with enhanced structural change is successfully synthesized by Molecular level mixing process. Various conclusions that can be drawn from these investigations are–

- From DTA/TGA data clear crystallization of alumina and spinel formation has been clearly identified and it will starts from 550^0C and stable spinel has been observed above 700^0C.

- From Taguchi optimization it has been seen the role of temperature-ratio(fuel as citric acid) plays an important factor for the experiment.

- The variation of heating temperature in the alumina matrix plays an important role in the change of the characteristics, crystallization and morphology of the particle.

- From the FESEM, we observed the granular agglomerated formation of alumina.

- From the experiment we can say that low temperature synthesis can be done with proper selection of temperature with fuel ratio.

CONFERENCE

&

PUBLICATION

1.Conference attended:

Oral presentation on Synthesis and characterization of spinel using Thiourea as a fuel at NML,Jamshedpur.

32nd National Convention of Metallurgical & Materials Engineers & National Seminar on Advances in Engineering Materials for Sustainable Development on January 18-19, 2019 organized by The Institute of Engineers(India) in association with TATA STEEL and CSIR-National Metallurgical Laboratory, Jamshedpur.

2. Sol-gel technique for synthesis of $MgAl_2O_4$ spinel:application of Taguchi method for optimization of process parameters, Manuscript is under process.