Synthesis of Nano Magnesium aluminate by Solution Combustion Process Using Mixed Fuel Approach (Urea + Sucrose)

Chanveer Gogi, Parag Shah, Venkatesh D, Sangamesh P.K, Baburao N. Sherikar

Abstract— **In this work nano $MgAl_2O_4$ powders were prepared by solution combustion process by mixed fuel approach using magnesium nitrate hexahydrate $Mg(NO_3)_2.6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$) as oxidizers with mixtures of urea (NH_2CONH_2), sucrose ($C_{12}H_{22}O_{11}$). Fuel urea is taken as stoichiometric fuel and sucrose as excess nonstoichiomertic fuel. The effect of sucrose fuel addition as excess on phase, structure and characteristics (e.g. crystallite size morphology,) of the as-resulted powders were investigated. The crystallite sizes were determined by using Scherer formula and Williamson -Hall equation. The experimental results revealed that the formation of pure crystalline phase of magnesium aluminate was confirmed for two bacthes of mixteres cases by comparing the obtained peaks of XRD pattern with the peaks of standard XRD pattern of JCPDS card number 21-1152. The crystallite size of the powders was significantly decreased from 80 nm to 30 nm as the sucrose content rose from 0.00, 0.50, (0, 3.5 wt%), excess with 4 grams of urea, 2.56 grams of magnesium nitrate and 7.5 grams of aluminum nitrate.**

Index Terms—**Combustion, Sucrose, $MgAl_2O_4$, Urea.**

I. INTRODUCTION

Magnesium aluminate spinel ($MgAl_2O_4$) a class of double oxide material is of great importance from the industrial point of view due to their important properties. Because of its high refractoriness, low thermal expansion coefficient, high thermal shock resistance and high chemical stability $MgAl_2O_4$ is an important refractory material used in steel (steel ladles) and cement industries (burning and transition zones) and also in the checker bricks of glass furnace regenerators [1]. l and in the biological applications. Magnesia alumina Spinel can also be used in advanced application like high-temperature arc-enclosing envelops, humidity and infrared sensors, transparent windows, domes and armour material [2].

The physical properties, mechanical and thermal properties depend on the crystallite size, shape size, orientation of the powder. Synthesis of magnesium aluminate in nano powder form further increase the performance properties [2,3].

Nano-powders are attracting the scientists, researchers, industrial people due to their unique properties compared with their bulk counterpart due to high surface area [5-6]. Magnesium aluminate nano powders were prepared by solid state method [7], sol gel [8], co-precipitation[9-11],reverse micro emulsion method [12], polymerized complex method [13],gel-combustion method [14], self propagating high temperature synthesis (SHS) technique[15], SPS Processing[16] hydrothermal, microwave assisted combustion and other methods [17] , by several groups with using different chemical precursor and varying the process parameters like temperature, concentration etc.

The preparation techniques mentioned above are slow, non homogeneous, require costliest precursors, energy and time consuming but Prof K.C Patil of Indian Institute of Science Bangalore introduced a novel synthesis method called Solution Combustion Synthesis which is discovered two decade ago is simple easy, fast homogeneous no energy and time consuming process to prepare nanopowders of oxide materials. Many ceramic oxide nanopowders were prepared by SCS method using single fuel [18,19] and mixed fuel [20,21]. Magnesium aluminate nano powders were also prepared by SCS with single[18] and mixed fuels[22] in literature. Till now no reports have been made on the synthesis of nano magnesium aluminate by solution combustion process using urea and sucrose mixed fuel with calculation of enthalpy and adiabatic flame temperature and correlating them with experimental results.

In this work nano $MgAl_2O_4$ powders were prepared by solution combustion process by mixed fuel approach using magnesium nitrate hexahydrate $Mg(NO_3)_2.6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$) as oxidizers with various mixtures of urea (NH_2CONH_2) sucrose ($C_{12}H_{22}O_{11}$). Fuel urea is taken as stoichiometric fuel and sucrose as excess nonstoichiomertic fuel. The effect of sucrose fuel addition as excess on phase, structure and crystallite size of the as-resulted powders were investigated.

II. EXPERIMENTAL DETAILS

A. *Raw materials used.*

Magnesium nitrate hexa-hydrate (Mg (NO3)2.6H2O).(Universal laboratories), Aluminium nitrate Nona-hydrate

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(Al (NO3)3.9H2O),(Universal laboratories), Urea (NH_2CONH_2), Sucrose ($C_{12}H_{22}O_{11}$).(Alchem).

B. Solution Combustion Synthesis of $MgAl_2O_4$

The $MgAl_2O_4$ was prepared by using Magnesium nitrate, ($Mg(NO_3)_2.6H_2O$), Aluminium nitrate nonahydrate ($Al(NO_3)_3.9H_2O$), as oxidizers and urea as stoichiometric fuel and ,sucrose as exothermicity reducing fuel. Variation of sucrose fuel has been made and coded as in Table I. The reactants were mixed in deionized water in molar ratio and mass as shown in Table I. Deionized water was used for homogeneous mixing of reactants at atomic level. These solutions were then kept in a furnace pre heated to 500°C. First on heating to 200°C the water was evaporated making frothing of solution then suddenly evolution of gases occurred with huge amount of flame due to combustion reaction occurring due to redox reaction between fuel and oxidizer. The combustion reaction characteristics and the combustion details like expected product, yield obtained , amount of chemicals taken and moles of chemical precursor and number of moles of sucrose fuel taken are shown in Table I. The combustion details like nature of combustion ,combustion time, combustion sound ,color of the flame, flame type, are shown in Table II. The real images of combustion reactions taking place for all compositions of sucrose are shown in Fig 1 . Combustion calculations were done according to paper [23]. Combustion reactions with compositions of codes MASU00(urea+0.0sucrose) & MASU50 (urea+0.5g sucrose) show volume type combustion with white colored flame. All obtained powders characterized by XRD SEM. Under the equilibrium conditions the reaction equations in these fuels-nitrate systems for preparation of $MgAl_2O_4$ by mixed fuels for sucrose can be represented as below.

$Mg(NO_3)_2.6H_2O+2Al(NO_3)_3.9H_2O+6.66CH_4N_2O+$

$0C_{12}H_{22}O_{13} \longrightarrow MgAl_2O_4+10.6N_2+6.6CO_2+$

$37.2H_2O$.....(1)

$Mg(NO_3)_2.6H_2O+2Al(NO_3)_3.9H_2O+6.66CH_4N_2O+$

$0.203C_{12}H_{22}O_{11} \longrightarrow MgAl_2O_4+10.6N_2+9.038CO_2+$

$9.43H_2O$.....(2)

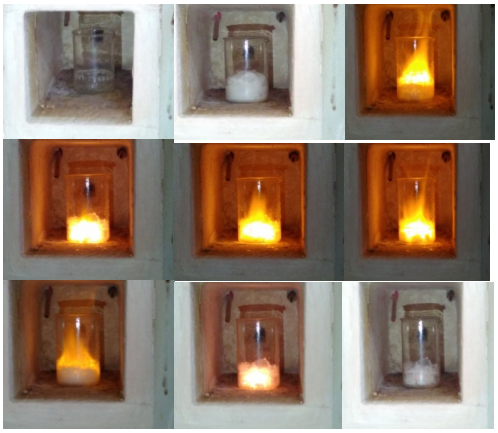

Fig. 1. Images of solution combustion of U+ 0.50 (g) of Sucrose.

C . Phase Analysis by X-ray diffraction (XRD)

X-ray diffraction studies were carried out for phase confirmation and calculating crystallite size of the milled samples, using D8-Advance-Bruker machine with Cu-K_α (wavelength of Cu-K_α (λ) ~1.5406 Å) radiations for all the measurements. Ni filter was used to attenuate K_β lines. The crystallite size of powders was calculated using Scherer's formula where an assumption was made that the particle is spherical in shape [24]. The Scherer's formula gives [25]

$$\beta_\theta = \frac{K'.\lambda}{L.Cos\theta} \quad \text{.....3}$$

where, β_θ is the full width at half maximum (FWHM) of diffracted peaks in degrees, L stands for the liner dimension of particles in meters, θ refers to Bragg's angle in degrees and K' is the shape factor, generally known as a numerical constant and evaluated [26] as 0.93 and depends on shape of crystallites. From this expression, it is clearly seen that diffracted beam gets broadened as the size of crystallite reduces..

The crystallite size of powders was also calculated by Williamson and Hall (W-H) equation which recommends combining the domain size and lattice micro strain effects on line broadening. The method refers to the cases when lattice deformation and the domain effect are simultaneously operative and their collective effects yield the final line

Table I Amount of fuel and oxidizer, used for the combustion reaction to produce $MgAl_2O_4$ by mixed fuel approach maintaining stoichiometric urea fuel and Sucrose as excess fuel condition.

Sl.no	Sample codes	$Mg(NO_3)_2$.$6H_20$ (g)	$Al(NO_3)_3.6H_2O$ (g)	Fuel Urea (g)	Fuel sucrose(g)	Expected powder (g)	Obtained Powder (g)	No. of moles
1	**MASU00**	2.56	7.5	4	0	1.42	1.36	0.00
2	**MASU50**	2.56	7.5	4	0.50	1.42	1.416	0.20

Table II: Characteristics of the combustion reaction for varying excess fuel sucrose –nitrate system at stoichiometric urea fuel condition to prepare the $MgAl_2O_4$

Excess of sucrose(g)	Sample	Combustion type	Spark/sound	Gases	Color	Reaction	Combustion time
0.0	$MgAl_2O_4$ by Urea+sucrose	Flame	No Sparking/cracking sound	Gases with fine powder	White	Foam formation	6min 21sec
0.50	$MgAl_2O_4$ by urea+sucrose	Flame	Sparking , loss of solution and cracking sound	Huge Gases with fine powder	grey	No Froth formation	5min 56 sec

broadening FWHM (β), - the total of grain size (β) and lattice distortion (ε).When compared with the sample-dependent broadening, this relation assumes infinitesimal instrumental contribution. The W-H equation is represented as

$$\beta cos\theta = \frac{k\lambda}{D} + 4\varepsilon sin\theta \quad \text{.....4}$$

Where ε is the strain associated with the nanoparticles. Eq.8 represents a straight line between 4 sinθ (X-axis) and βcosθ (Y-axis). The slope of the line gives the strain (ε) and intercept (kλ/D) of this line on Y-axis gives crystallite size D).

C. Phase analysis of $MgAl_2O_4$ powders prepared by urea fuel with excess additions of sucrose fuel

Fig. 2 and 3 show XRD patterns of the as synthesized powder for MASU00 (0.00g) and MASU050(0.5g of sucrose with different amount of excess fuel respectively. The formation of phase pure crystalline $MgAl_2O_4$ is confirmed by comparing the peaks with standard peaks of JCPDS card no 21-1152 for both the cases. The intensity of the peak varies with change in excess amount of fuel used. On comparison of the above phases, it is clear that peak intensity has gradually decreased along with increase in broadening of the peaks from MASU00 to MASU50. The decrease in crystallite size and increase in broadening is very high for MASU50 sample which can be clearly seen from Fig. 3. While synthesizing $MgAl_2O_4$from using U+0.0sucrose to U+0.5 sucrose ,during combustion exothermicity gradually decreases due to unavailability of oxygen molecules for complete combustion thus adiabatic flame temperature decreases and this leads to formation of nano powders of crystallite size ranging from 61nm to 30nm due to arresting of sintering by low temperature and increased moles of gases evolved burst the foam to nanopowders..

The decrease of crystallite size of $MgAl_2O_4$ powder with increasing amount of sucrose Fuel combustion system can be seen from Figure 2 and 3 . The crystallite size is inversely proportional to the excess addition of sucrose amount. The crystallite size decreases from 42 nm to 11 nm with increase in fuel addition by Scherer's formula. The crystallite size decreases from 62 nm to 14.5 nm by Williamsons Hall plot.

Decrease in crystallite size may be due to the low temperature generated due to decrease in exothermic temperature. William Hall plot shows the values higher than Scherer's formula this is due to exclusion of broadening formed by strain of sample. There is huge difference in crystallite size of the powders without sucrose fuel with sucrose fuel.

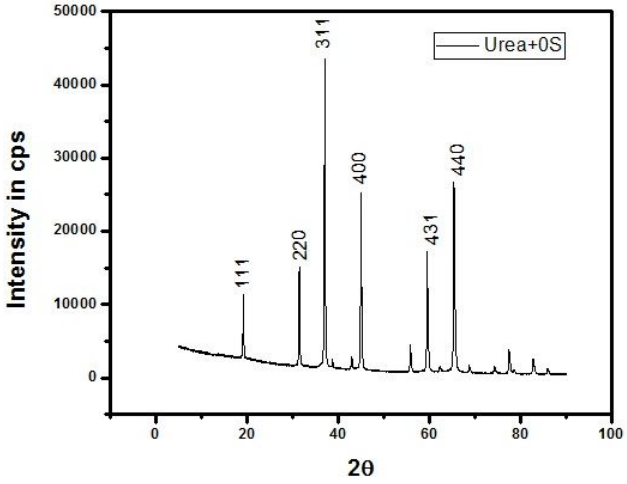

Fig. 2. XRD pattern of $MgAl_2O_4$ using fuel mixture (urea+0.0Sucrose)

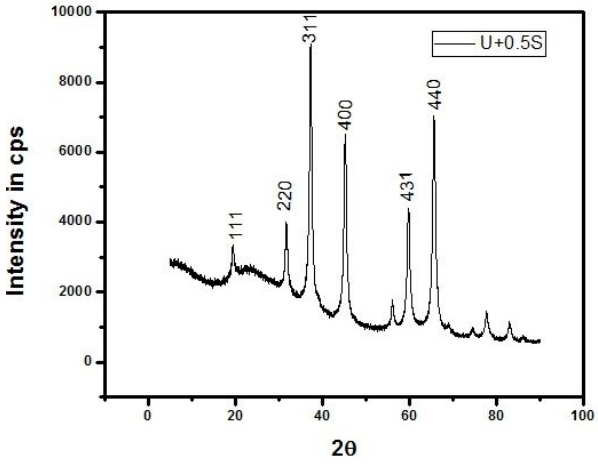

Fig. 3. XRD pattern of $MgAl_2O_4$ using fuel mixture (urea+0.5g Sucrose)

CONCLUSION

The phase pure nano Magnesium-Aluminate spinel is successfully synthesized for the first time at low temperature by solution combustion process using mixture of urea and

sucrose fuels. Addition of 0.5g (0.20mole) Sucrose fuel reduces the exothermicity of combustion reaction there by creates formation of nano particles reducing the crystallite size from 42 nm to 11 nm. The effect of mixture of fuel is studied using urea+sucrose keeping urea constant and varying the amount of sucrose on powder properties like crystallite size is studied.

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