

Synthesis And Characterization of Spinel (MgAl₂O₄) Using Sol- Gel Technique

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Abstract--Spinel(MgAl₂O₄) is synthesized by citrate sol-gel process. This paper presents a study concerning the effects of amount of magnesium nitrate and aluminium sulphate in spinel. In order to quantify the effect of magnesium nitrate and aluminium sulphate comparative study between different compositions produced by sol-gel process is done. To study the effect of comparison of two different compositions of magnesium nitrate and aluminium sulphate, Green pellets formed at a pressure of 10tons and sintered at 1350°C for 3 hours. Mechanical properties were measured for all compositions.

Keywords:- spinel, magnesium nitrate, aluminium sulphate, citric acid, sol-gel process.

I. INTRODUCTION

Spinel (MgAl₂O₄) is known since long for its excellent refractoriness, a good thermal shock resistance, high mechanical strength at elevated temperatures and a chemical inertness. Spinel is widely used in metallurgical, electrochemical and chemical industrial fields. The production of high purity and reactivity of spinel is influenced by synthesis technique. In addition to the solid state synthesis which suffers from the inhomogeneity and high synthesis temperatures, many unconventional techniques have been used for the synthesis of spinel.

Alumina and magnesia react together to produce spinel. Alumina magnesia spinel with varying amount of alumina and magnesia (either alumina-rich or magnesia-rich side) is a very important material in various applications in various industries. Magnesia aluminate spinel (MgAl₂O₄) is an excellent refractory oxide of immense technological importance as a structural ceramic. It possesses useful physical, chemical and thermal properties, both at normal and elevated temperatures. It melts congruently at 2135°C, shows high resistance to attack by most of the acids and alkalis and has low electrical losses. Due to these desirable properties, it has a wide range of application in structural, chemical, optical and electrical industry. It is used as a refractory in lining of steel making furnaces, transition and burning zones of cement rotary kilns, checker work of the glass furnace regenerators sidewalls and bottom of the steel ladles, glass furnaces and melting tanks.

Nanocrystalline spinel is synthesized by citrate sol-gel process. The precursor gel yields an amorphous oxide phase at 550°C and begins to crystallize to the spinel at 600°C. the initial crystallization temperature of the spinel powder is 600°C. The formation process of spinel may contain two stages. First, the decomposition of the compound of nitric and citric to γ -Al₂O₃ and MgO. Second, the solid state reaction between γ -Al₂O₃ and MgO to spinel [1]. Magnesium aluminate spinels have been developed by reaction sintering of calcined alumina and calcined

magnesia and its densification behavior was studied in presence of Dy₂O₃. It was found that Dy₂O₃ additive does not have significant effect on the spinelisation but favors the densification of the spinel. Microstructure of sintered spinel without any additive is non-uniform with some exaggerated grain growth and thereby helps in the densification process [2]. Magnesia and alumina powders along with tetravalent oxide additives were analyzed for their role in reactive densification spinel in a single stage firing process in order to achieve a better binding system for magnesia based refractories. These tetravalent oxides on reaction with magnesia form spinel solution with spinel as they have similar crystal structure [3]. Ali Saberi et al. have studied the influence of heat treatment atmosphere in synthesis of nanosize spinel powder employing sol-gel citrate route. It shows that the argon treatment confronts the problem of sudden heat generation in sol-gel citrate method to synthesize nanosize spinel particles in the range of 20-100nm [4]. It was found that the spinel is formed at several hundred degrees lower than the temperatures reported for the conventional powder preparation methods [5]. Spinel nanoparticles of MgAl₂O₄(white), CoAl₂O₄(blue), were synthesized by a sol-gel route with propylene oxide as a gelation agent. This method has proven to be an effective route to synthesize mixed oxide nanoparticles [6]. Powder samples of spinel (Co₂SnO₄) were successfully synthesized by a sol gel technique at three different temperatures: 900, 1300 and 1400°C for 1, 5 and 8 hours [7]. Spinel nanoparticles can be prepared by boehmite so as the chief precursor, with magnesium salt intimately mixed to it and heat treated.

The γ -Al₂O₃ with incipient spinel character, is an important intermediate in this preparation [8]. The polymorph of Al₂O₃ influences the synthesis and sintering of MA [9]. Polycrystalline magnesium aluminate spinel has advantage that it consist optically isotropic cubic structure, so that light scattering at grain boundaries is less critical than with optically anisotropic systems [10]. To improve the strength of polycrystalline ceramics the grain refinement should be increased to the nano range [11]. Polycrystalline nanosized zinc aluminate has been synthesized by sol-gel technique using oxalic acid as a chelating agent. Mixing at the molecular level between the precursor materials seems to be the key factor reducing the sintering temperature and sintering time, thus avoiding severe sintering with concomitant loss of surface area [12].

An attempt has been made to synthesize spinel by using an unconventional technique, sol-gel process.

II. MATERIALS AND METHODS

A. Materials: Magnesium nitrate (Mg(NO₃)₂·2H₂O), aluminium sulphate, citric acid and polyvinyl alcohol as a binder is used.

B. Experimental Procedure: Figure 1 shows typical sol-gel process for preparation of spinel. A stoichiometric

amount of magnesium nitrate, aluminium sulphate was dissolved in distilled water, after that stoichiometric amount of citric acid was added, and after complete mixing, a homogenous solution was obtained. This solution was slowly evaporated until a highly viscous colloid was formed.

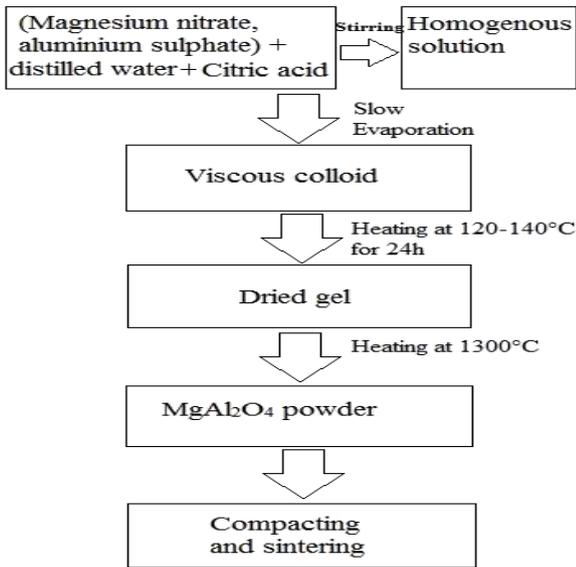


Fig. 1: Typical sol-gel process (flow chart)

The viscous colloid was then heated in 120-140°C for 24 hours to get a dried gel. Finally, the dried gel precursor was calcined at different temperatures to obtain spinel powder. Spinel powder was compacted in power press under suitable pressure. The sintering was done after compacting.

1) *Sample Preparation:* Powders of magnesium nitrate (Mg(NO₃)₂·2H₂O), aluminium sulphate and citric acid were used for this study. Appropriate amount of Magnesium nitrate, aluminium sulphate and citric acid were accurately weighted for five different samples and homogenous solution was made.

Table. 1: Sample compositions

Sample	Magnesium Nitrate Wt %	Aluminium Sulphate Wt %	Magnesium Nitrate Gms	Aluminium Sulphate Gms
M25Al75	25	75	56.25	168.75
M30Al70	30	70	67.5	157.5
M50Al50	50	50	112.5	112.5
M70Al30	70	30	157.5	67.5
M75Al25	75	25	168.75	56.25

2) *Spinel Powder Preparation:* Homogenous solution was allowed to evaporate slowly to form a viscous colloid, which was heated at 120-140°C for 24 hours to get a dried gel. Spinel powder was obtained by heating dried gel at 1300°C for 3 hours.

3) *Compacting:* The powder was again mixed using mortar to get fine powder. A binder i.e. polyvinyl alcohol was mixed with the powder and was poured into cylindrical die (110 mm high, 20 mm inner diameter and 80 mm outer diameter) for making green pellets at a forming pressure of

10tons. For each batch composition pellets were prepared, and then pellets were dried for drying binder at 200°C for 1 hour.



Fig. 2: Compacting press

4) *Sintering:* The solid compacted pellets were baked in furnace at temperature 1350°C for 3 hours and then allowed for atmospheric cooling. In sintering the samples were heated slowly from room temperature and maintained at 400°C for 3 hours. Preheating is essential to burnout the binder. The temperature is then increased gradually to 1350°C and maintained for 3 hours. During processing, the spinel powder has exposed to atmosphere, which contains oxygen and moisture also and it would oxidize at high temperature. Moreover, the moisture would react chemically with the oxide and such reaction would reduce the bonding force of spinel and further deteriorate the mechanical properties of composites. To avoid the oxidation of aluminium powder at high temperature and to abbreviate the preparation procedure, the degassing and sintering procedures of the compacts have been incorporated together. The stepped heating procedures of the degassing and sintering has introduced into the experiment.

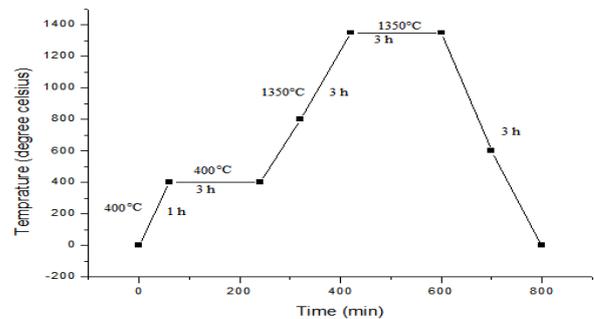


Fig. 3: Sintering scheme

III. EXPERIMENTS

The density and microhardness of pellets sintered was measured. Microhardness was determined using electronic microhardness testing machine. The density of bodies after sintering was measured by Archimedes method.

IV. RESULTS AND DISCUSSIONS

A. *Density:* The density values for all compositions of spinel samples are shown in table 2.

Table. 2: Density values of samples

Sample	Density(g/cm ³)
M25Al75	3.72
M30Al70	3.64
M50Al50	3.56
M70Al30	3.45
M75Al25	3.42

From results tabulated it is observed that the density of spinel decreases with increase in wt% of magnesium nitrate. For the sample M50Al50, which contains same wt% of magnesium nitrate and aluminium sulphate, density value is average. Further with samples exceeding with wt % of magnesium nitrate in comparison with aluminium sulphate, the density decreases by large value for sample M70Al30. The exsolution of alumina is observed as wt % of magnesium nitrate increases in spinel samples.

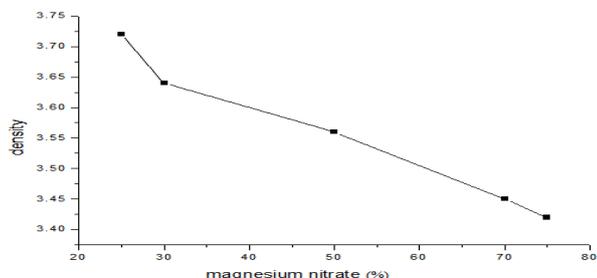


Fig. 4: Magnesium nitrate (wt %) Vs density

B. Microhardness: The micro hardness is checked by using electronic micro hardness testing machine. Table 3 shows hardness values for all the compositions of spinel.

Table. 3: Microhardness values of samples

Sample	Microhardness (Gpa)
M25Al75	15.44
M30Al70	15.29
M50Al50	14.32
M70Al30	13.93
M75Al25	13.83

The hardness value for sample M50Al50 is 14.32 Gpa, as compared to sample M30Al70 it is decreased by large value. By referring table 3, it is observed that value of microhardness for spinel decreased as exsolution of alumina is observed in samples M50Al50, M70Al30 and M75Al25 with increase in wt% of magnesium nitrate in spinel. The decreasing trend of microhardness value is shown in the figure 5.

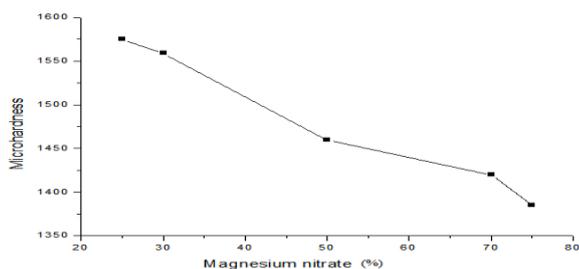


Fig. 5: Magnesium nitrate (wt %) Vs microhardness

From the figure 5 it is observed that the sample M75Al25 shows a lower value of microhardness. The microhardness decreases with increase in wt % of magnesium nitrate.

C. Microstructures: The surface for microstructural analysis was prepared by grinding, polishing and etching. The scanning electron photomicrographs of magnesium aluminate spinel. The average grain size is 15µm, the spinel grain shape is angular and pores are present in the intergranular spaces

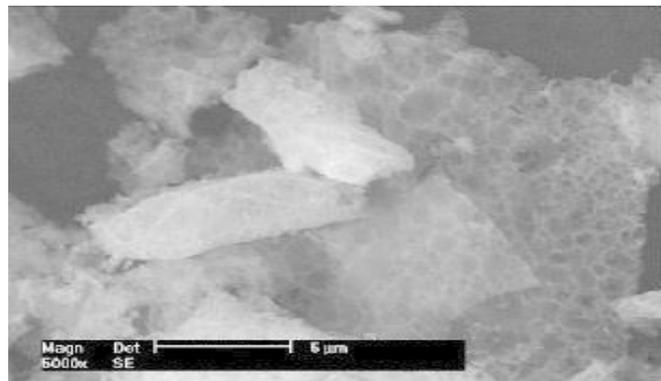


Fig. 6: SEM photograph of M25Al75

Figure 6 shows microstructure of M25Al75. The microstructure is more uniform and with very few intergranular pores. The structure is dense for lower amount of magnesium nitrate in spinel.

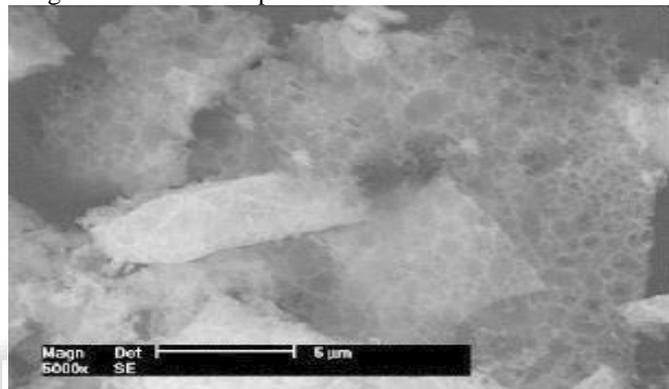


Fig. 7: SEM photograph of M30Al70

The microstructure of sample M30Al70 is less dense as compared to sample M25Al75. It consists of few intergranular pores. It has been seen that as wt% of magnesium nitrate in spinel increases, microstructure becomes less dense.

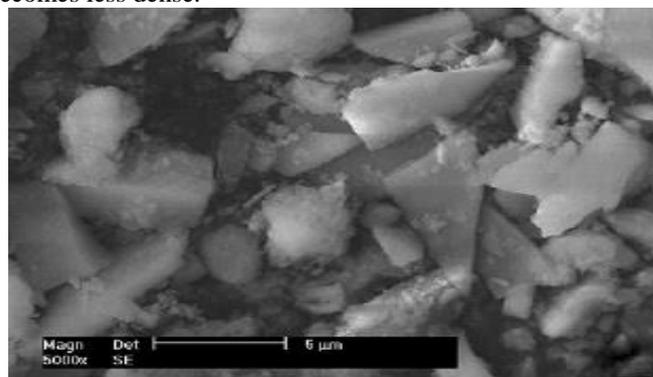


Figure 8: SEM photograph of M50Al50

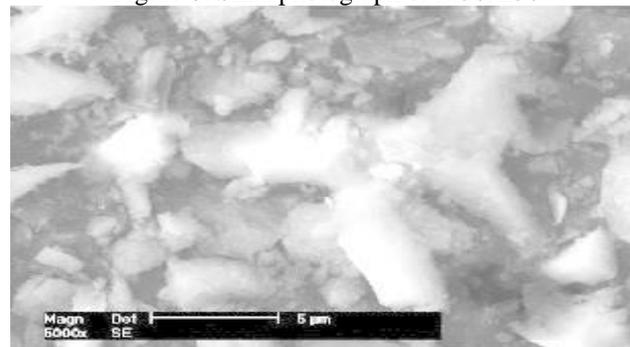


Fig. 9: SEM photograph of M70Al30

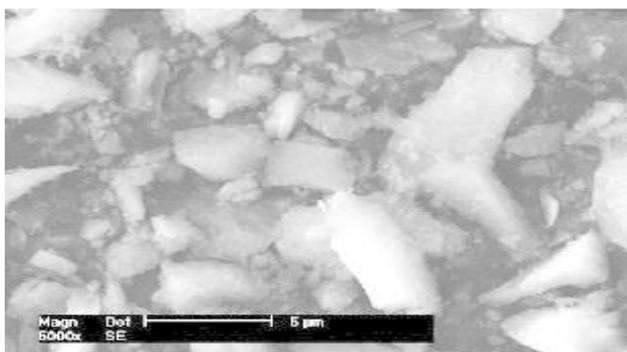


Fig. 10: SEM photograph of M75Al25

Microstructure of M50Al50, M70Al30 and M75Al25 shows the exsolution alumina in spinel sintered at 1350°C. The microstructure is not uniform in case of sample M70Al30 and sample M75Al25. Increase in wt% of magnesium nitrate affect the densification of spinel.

V. CONCLUSION

The results of spinel synthesized by sol-gel technique are as follows

- Results of sample M30Al70 show the formation of spinel takes place at 1350°C.
- The density was greatly affected with increase in wt % of magnesium nitrate.
- The microhardness decreases with increase in wt% of magnesium nitrate.
- Uniformness and dense structure of grains of spinel decreases with the increase in wt% of magnesium nitrate.

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REFERENCES

- [1] Haijun Zhang et al. "The low temperature preparation of nanocrystalline MgAl₂O₄ spinel by citrate sol-gel process." Material letters, (2003), Elsevier.
- [2] H S Tripathi and S Singla, "Synthesis and densification behaviour of magnesium aluminate spinel:effect of Dy₂O₃." Ceramics international, (2009), Elsevier.
- [3] R Lodha, G Oprea and T Troczynski, "Role of Ti⁴⁺ and Si⁴⁺ ions in spinel formation and reactive sintering of magnesia-rich ceramics.", Ceramics international, (2010), Elsevier.
- [4] Ali Saberi et al. "The novel approach to synthesis of nanosize MgAl₂O₄ spinel powder through sol-gel citrate technique and subsequent heat treatment.", Ceramics international, (2008), Elsevier.
- [5] H Reveron et al. "chemical synthesis and thermal evaluation of MgAl₂O₄ spinel precursor prepared for industrial gibbsite and magnesia powder.", Material letters, (2001), Elsevier.
- [6] Hongtao Cui and Marcos Zayat, "Sol-gel synthesis of nanoscaled spinels using propylene oxide as a gelation agent.", Journal of sol-gel science and technology, (2005), Springer.
- [7] J A Aguilar et al, "Optimal parameters for synthesizing single phase spinel type Co₂SnO₄ by sol-gel technique:

Structure determination and microstructure evaluation.", Journal of alloys and compounds, (2013), Elsevier.

- [8] A Banergee, S Das and S Misra, "Structural analysis on spinel (MgAl₂O₄) for application in spinel bonded castables.", Ceramics international, (2007), Elsevier.
- [9] Zhihui Zhang and Nan Li, "Effect of polymorphism of Al₂O₃ on the synthesis of magnesium aluminate spinel., Ceramics international, (2004), Elsevier.
- [10] Karel Maca and Martin Trunec, "Processing and properties of fine grained transparent MgAl₂O₄ ceramics.", (2007), Ceramics Silikaty.
- [11] Homas mroz and Lee M, "Nanostructured infrared transparent magnesium aluminate spinel with superior mechanical properties.", Goldman surmate corporation, (2012), Int. J. Appl. Tech.
- [12] Xiuhua Wei and Donghua Chen, "Synthesis and characterization of nanosized zinc aluminate spinel by sol-gel technique.", Material letters,(2005), Elsevier.