Available online at www.sciencedirect.com

SCIENCE DIRECT

ELSEVIER

Materials Letters 58 (2004) 2283–2289

materials letters

www.elsevier.com/locate/matlet

Sintering behaviour of $MgAl_2O_4$—a prospective anode material

S. Angappan, L. John Berchmans, C.O. Augustin*

Central Electrochemical Research Institute, Karaikudi-630 006, India

Received 30 June 2003; accepted 9 January 2004

Available online 13 March 2004

Abstract

Awareness in environmental hygiene and escalation in the energy cost in electrometallurgical industries have necessitated a reauditing of the production technologies, more so in the case of aluminium as it is a highly energy intensive process. Metal aluminates are of interest due to their technological applications in aggressive environments. The preparation of the metal aluminates usually involves the solid state reaction (SSR) of the corresponding metal oxides or sulphates at high temperatures. The present investigation is the preparation of $MgAl_2O_4$ using the metal oxides by solid state synthesis. The compacts were sintered at high temperatures and their properties such as particle size, density, porosity, hardness, ac electrical conductivity and dielectric behaviour were evaluated. The phase formation and structural properties have been ascertained by XRD, FTIR, TG/differential thermal analysis (DTA) and scanning electron micrograph (SEM) studies. The sinterability characteristics of the materials strongly dependent on the temperature of the processing. The XRD patterns confirm the phase formation of $MgAl_2O_4$. The FTIR spectra show the structural details of the synthesized compound. From the SEM micrographs, it is revealed that the agglomeration process progresses with the increasing temperature. The ac electrical conductivity and dielectric behaviour of aluminates strongly depend upon sintering time, temperature and spinel formation.

Keywords: Non-consumable anode; Aluminium; $MgAl_2O_4$ synthesis; Sintering; Characterisation

1. Introduction

Mixed metallic oxides having the general formula AB_2O_4 (A and B are transition metal ions) and crystallizing with spinel structure ($Fd3m-O_h^7$) are gaining attention in recent years [1]. The structure consists of a cubic close-packed array of oxide ions in which the magnesium ions occupy 1/8 of the tetrahedral (A) sites and the aluminium ions occupy half of the octahedral (B) sites [2]. Magnesium aluminate ($MgAl_2O_4$) is an excellent material of immense technological importance as a structural ceramic. It possesses useful physical, chemical, and thermal properties, both at normal and at 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 applications in structural, chemical, optical and electrical fields. It is used as a refractory 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 [3]. Many refractory oxide materials have been tried to replace conventional carbon anode in aluminium electrolytic cells [4]. Since metal aluminates have excellent high temperature and electrochemical properties in aggressive media, an attempt has been made to fabricate a suitable electrode material based on $MgAl_2O_4$ to serve as anode in cryolite-alumina bath.

A number of techniques such as conventional solid state reaction (SSR), sol–gel method, wet chemical method, self-heat-sustained (SHS) technique and spray drying (Atomisation) have been employed for the preparation of spinel $MgAl_2O_4$ [5–9]. The conventional SSR method is one of the methods for preparation of spinel oxides. The preparation of transition metal–alumina spinel is limited to fusion of the two component oxides at high temperatures (1000–1600 °C) [10]. The present work has been carried out to elucidate the sintering behaviour and their physical, electrical and morphological

* Corresponding author. Fax: +91-4565-227779, 227713.
E-mail address: caugustin@rediffmail.com (C.O. Augustin).

0167-577X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2004.01.033

properties of $MgAl_2O_4$ as an anode material in metallurgical applications.

2. Experimental

$MgAl_2O_4$ spinel was prepared by solid state reaction method. Stoichiometric quantities of oxides of MgO and Al_2O_3 powders were thoroughly mixed and compacted at a pressure of 4.0 tonnes/cm^2. Pellets of sizes 1- and 2. 5-cm diameter have been made using a hydraulic press. The compacts were placed in an electrically heated resistance furnace and heated continuously from ambient temperature to 1550 °C for about 50 h in air. During sintering process, the compacts have undergone phase transition forming $MgAl_2O_4$ spinel. The density of the green and sintered pellets was calculated by measuring weight and volume of the pellets. The porosity of the samples was calculated by liquid absorption technique. DC electrical conductivity has been carried out using a modified 4 probe method from room temperature to 1000 °C. The X-ray diffraction studies were carried out by the JOEL 8030 X-ray diffractometer (CuKα irradiation). FTIR analysis was performed using FTIR—Perkin Elmer, UK Paragon—500 between the range 400–1000 cm^{-1} with KBr medium. Differential thermal analysis and thermogravimetry (DTA/TG, Rigaku Thermalplus, TG 8120) were used to study the phase transition of green and sintered powders. A heating rate of 10 °C/min was used for the measurements from room temperature to 900 °C in air. Ac electrical conductivity measurement was carried out from 50 Hz to 10 KHz with the help of a computerised LCRTZ test system (CLCRTZIP-Model). The dielectric constant and dielectric loss tangent of the samples were calculated. The morphological studies were carried out using a scanning electron microscopy JEOL (JSM-35 CF) Japan make model.

3. Results and discussion

Density, porosity, hardness, electrical conductivity and crystalline size of the compounds are presented in Table 1. From the values, it is observed that the density of the sample was found to increase with increasing sintering temperature. The observed density is lower than that of the theoretical density (3.55 g/cm^3) because of the incomplete reaction of the starting materials during sintering process. Sintering is an agglomeration process where the individual molecules coalescence form a bulk mass by the expense of thermal energy. During the process of agglomeration, the pores are eliminated and the densification of the particles taking place which results in increase in density. The porosity decreases with increasing sintering temperature. The values of hardness for different samples show that the densification process progresses with increase in sintering temperature as observed in many materials [11–13].

Table 1
Density, porosity, hardness, electrical conductivity, crystalline size of $MgAl_2O_4$

Sintering temperature (°C)	Density (g/cm^3)	Porosity (%)	Vickers hardness (VHN)	Electrical conductivity (S cm^{-1})	Crystallite size (nm)
Green	2.41	32.1	180	1×10^{-7}	38.2
1000	2.8	21.0	260	0.6	42.1
1550	2.98	16.0	340	1.2	43.6

The crystal sizes of the samples were determined with the Debye-Scherrer equation. It is found that the average crystal size of the spinel increases from 38.2 to 43.6 nm as the sintering temperature increases. Preliminary results have shown that the annealing temperatures as high as 1000 °C is required to induce significant crystallization in the structure of the material [14]. The high temperature structural refinements for stoichiometric $MgAl_2O_4$ is due to the exchange of metal cations between the tetrahedral and octahedral sites as reported by Suzuki and Kumazawa [15] and Yamanaka and Takeuchi [16].

3.1. DC electrical conductivity

The values of electrical conductivity are presented in Table 1. It has been observed that the electrical conductivity increases with increasing temperature. The relationship between the DC conductivity with temperature is shown in Fig. 1. The plot is linear where the conductivity of the material is increased with increasing temperature. The increase of conductivity may be due to the presence of Al^{3+} ions at octahedral sites, which increase the hopping rate of electrons in the structure of the compound. Considering the Arrhenius plot, the activation energy increases with increasing temperature while it decreases with increase in sintering temperature of the material. The carrier concentration remains constant throughout the temperature range measured and the Arrhenius plot ($\log\sigma T$ vs. $1000/T$) for small polaron conduction should be linear following the relation [17]

$$\sigma = \frac{C}{T}\exp\left(\frac{-E_{\sigma T}}{kT}\right)$$

where E is the activation energy of the conduction process, k is the Boltzmann constant and T is the absolute temperature. The pre-exponential constant C includes the carrier concentration.

3.2. Dielectric properties

The dielectric properties of spinels depend upon several factors, including the method of preparation, chemical composition, and grain size. The results are presented in Fig. 2(a, b). Fig. 2(a) indicates that the dispersion is sharp at lower frequencies and almost levels off at higher frequencies. This behaviour may be due to the existence of

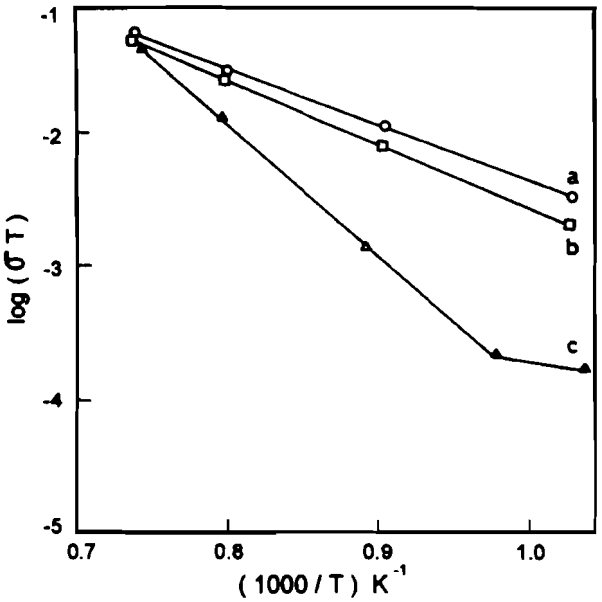

Fig. 1. Plot of $\log(\sigma T)$ vs. $10^3/T\,K^{-1}$ for $MgAl_2O_4$ sintered at (a) 973 K, (b) 1273 K, and (c) 1823 K.

interfacial polarization [18]. The normal dielectric behaviour of spinel was explained by Maxwell-Wagner interfacial type polarization, which is in agreement with Koops theory [19]. According to Maxwell-Wagner model, the dielectric structure of a spinel material is assumed to made up of two layers. First being a conducting layer consisting of large aluminate grains the other being a grain boundaries which are of poor conducting. This bi-layer formation is effected by the high temperature sintering. The variation of loss tangent, $\tan\delta$, with frequency of magnesium aluminate is shown in Fig. 2(b) . It shows a sharp increase at lower frequencies which declines for certain point and further increases with increase in frequency. There is a strong correlation between conduction mechanism and dielectric behaviour in the spinel, where the frequency of the hopping of electrons may be matching with the applied external field giving a loss maximum. The linear increase in $\tan\delta$ with frequency was attributed due to the presence of a large number of Al^{3+} ions on the octahedral sites whose frequency may match at higher range. The ac electrical conductivity, σ_{ac}, measured against frequency, shows good agreement with theoretical values obtained from the equation

$$\varepsilon' = \frac{4\pi\sigma_{ac}}{\omega\tan\delta}$$

The relationship between σ_{ac} against frequency is shown in Fig. 2(c). From the graph, it is found that the σ_{ac} increases with frequency but the dielectric constant ε' shows a

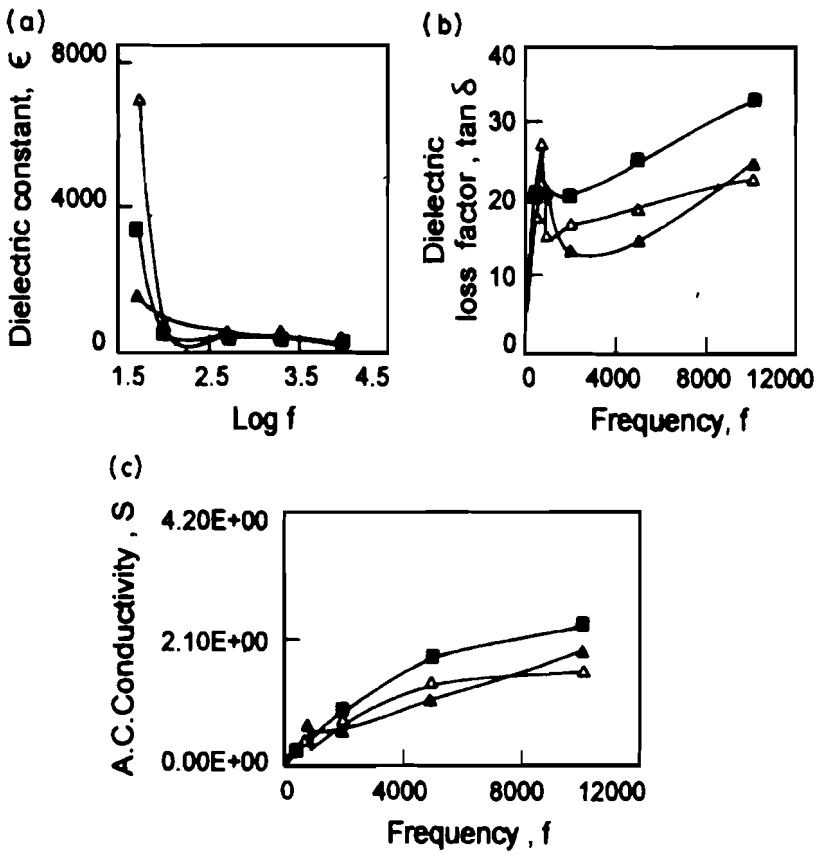

Fig. 2. Plot for (a) dielectric constant, (b) dielectric loss tangent and (c) AC conductivity of $MgAl_2O_4$ sintered at -△- 30, -■- 700 and -▲- 1000 °C.

decreasing trend, at lower frequencies, whereas at higher frequencies, the dielectric constant ε' found to increase. These results can be explained with the help of conduction mechanism. The Mg^{2+} ion shows strong preference for tetrahedral A site, whereas Al^{3+} ion shows its partial occupancy among A and B sites. The lesser occupancy of Al^{3+} ions in B sites, which is responsible for the hopping of electrons, which determines the polarization phenomena.

3.3. XRD

X-ray diffractograms of $MgAl_2O_4$ (Fig. 3(a–c)) reveal the formation of a single phase cubic spinel with fcc structure showing well-defined reflections of allowed planes, without any ambiguity [20] . The X-ray pattern confirms the existence of spinel structure with the reflection planes at 220, 311, 400, 511, 440, 533, 444, 711 and 642. At 1000 °C, the spinel formation increased and shown in the (531) plane with lattice constant 8.081 A°. Few high-temperature structural studies on spinel suggest that it undergoes a discrete con-

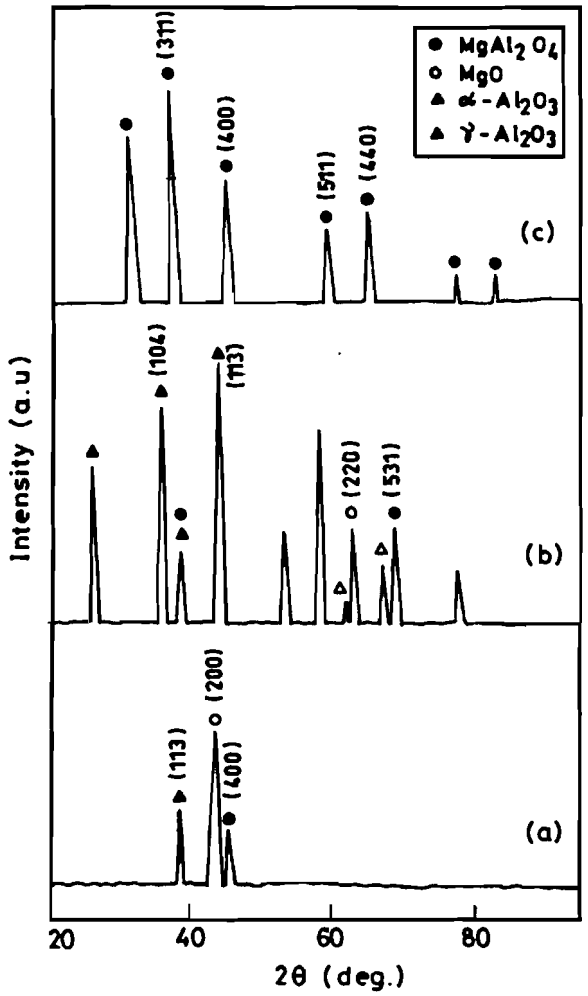

Fig. 3. XRD for $MgAl_2O_4$ sintered at (a) green, (b) 1000 °C (c) 1550 °C.

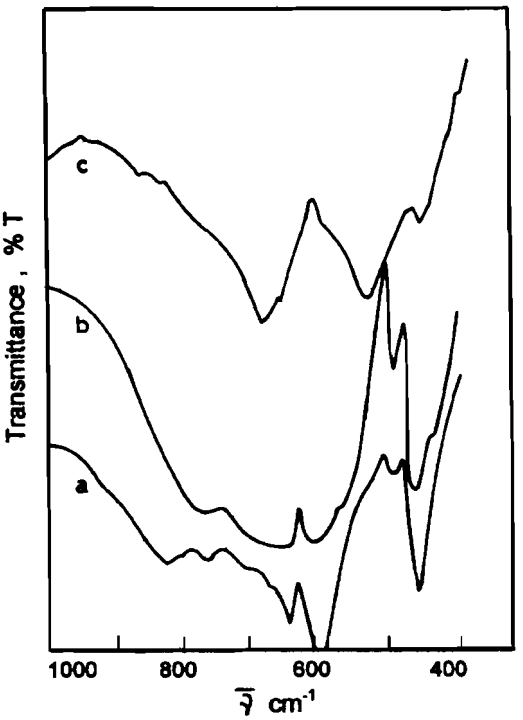

Fig. 4. FTIR for $MgAl_2O_4$ sintered at (a) green, (b) 1000 °C (c) 1550 °C.

vergent structural phase transition at temperatures between 600 and 700 °C. This anomalous changes in the structure at these temperatures have been reported by many authors [9,21,22]. The sample sintered at 1550 °C has shown a single phase spinel structure in the (311) plane, with lattice constant 8.101 A°. The samples sintered at 1000 °C have shown the presence of some unreacted α-Al_2O_3, γ-Al_2O_3 and MgO in the product, indicating incomplete formation of the aluminate. Quantitative analysis has done from the XRD patterns which revealed that the amount of $MgAl_2O_4$ formed was about 0%, 38% and 100 % for green, 1000 and 1550 °C, respectively. It has been reported that >90% spinel can be produced by solid state reaction by a precalcination process at 1100 to 1300 °C to convert more than 50% into reactive powders, by intermediate crushing, reforming and sintering up to 1700 °C [23,24].

3.4. FTIR

The FTIR spectra for the materials sintered at room temperature, 1000, and 1550 °C, are shown in Fig. 4(a–c). The position of ν_1 varied from 592.70 to 604.64 and that of ν_2 from 637.95 to 643.06 for MgO and Al_2O_3, respectively. The sample sintered at 1550 °C shows ν_1 at 694 cm^{-1}, ν_2 at 541.59 cm^{-1} and a shoulder appears at 465.72 cm^{-1} for $MgAl_2O_4$. The samples sintered at 1000 °C and room temperature show small bands at ν_3 and ν_4. The bands appeared from 449.58 to 456.19 and 492.11 to 495.70 are assigned to the spinel formation of $MgAl_2O_4$. It also reflected in the band at 465.72 in Fig. 4(c), it may be

explained that the metal–oxygen stretching frequencies in the range 400–1000 cm^{-1} are associated with the vibrations of MO–Al–O and M–O–Al bonds [25]. The high frequency band v_1 and low frequency band v_2 dependent on the preparation conditions [26] can be attributed to the tetrahedral and octahedral metal complexes [27], respectively. In $MgAl_2O_4$, the larger Mg^{2+} ion (1.6 Å) has the tetrahedral (v_1) coordination whereas the smaller Al^{3+} ion (1.4 Å) has octahedral (v_2) coordination [28]. The changes in v_1 and v_2 with increasing Mg^{2+} ion may be due to the changes in the Al^{3+}–O^2 complexes. The divalent Mg^{2+} ion in tetrahedral (A) site and trivalent Al^{3+} ion in octahedral (B) site gives a normal spinel at room temperature, whereas part of Al^{3+} ions occupied tetrahedral (A) site at 1000 °C, hence, under these conditions, $MgAl_2O_4$ behaves as a normal spinel.

3.5. TG/DTA measurements

TG and DTA curves of the magnesium aluminate spinel at room temperature and sample sintered at 1550 °C are shown in Fig. 5(a,b). The total weight gain amounts to 98% to 104% in green sample and 101% to 104% for the sample sintered at 1550 °C. The DTA curve obtained between 100 and 350 °C is mainly associated with the dehydration of water molecules which is represented in Fig. 5(a). The small two spikes appeared at 591 and 825 °C for green sample are responsible for the phase formation. The other two spikes at 342 and 374 °C for the sample sintered at 1550 °C indicating the early formation of $MgAl_2O_4$ phase. The appearance of these two spikes is indicating the compound formation. TG curves for the above samples reveal three different regions at 180 °C, 312 and 469 °C for green sample and 105, 325 and 411 °C for the sample sintered at 1550 °C. These three regions exhibit significant weight losses in the compounds. Above 500 °C, there is a gradual shift in the base line indicates that there is no significant weight loss was observed [21]. The DTA curve also indicates an exothermic peak which may be attributed to the formation of the single phase $MgAl_2O_4$.

3.6. SEM

Scanning electron micrographs (SEM) for green, and sintered samples at 700, 1000 and 1550 °C are shown in Fig. 6(a–d). From the figures, it is revealed that the sample sintered at 1550 °C has shown less porosity (16%) and has a

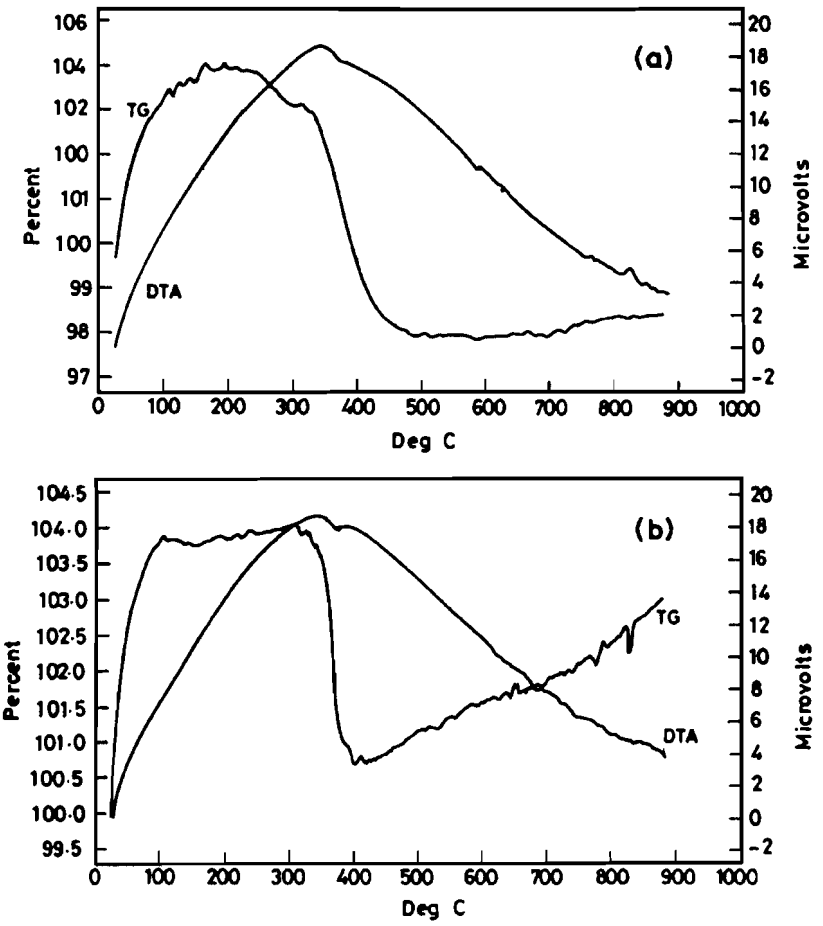

Fig. 5. TG/DTA curves for $MgAl_2O_4$ sintered at (a) room temperature, (b) 1550 °C.

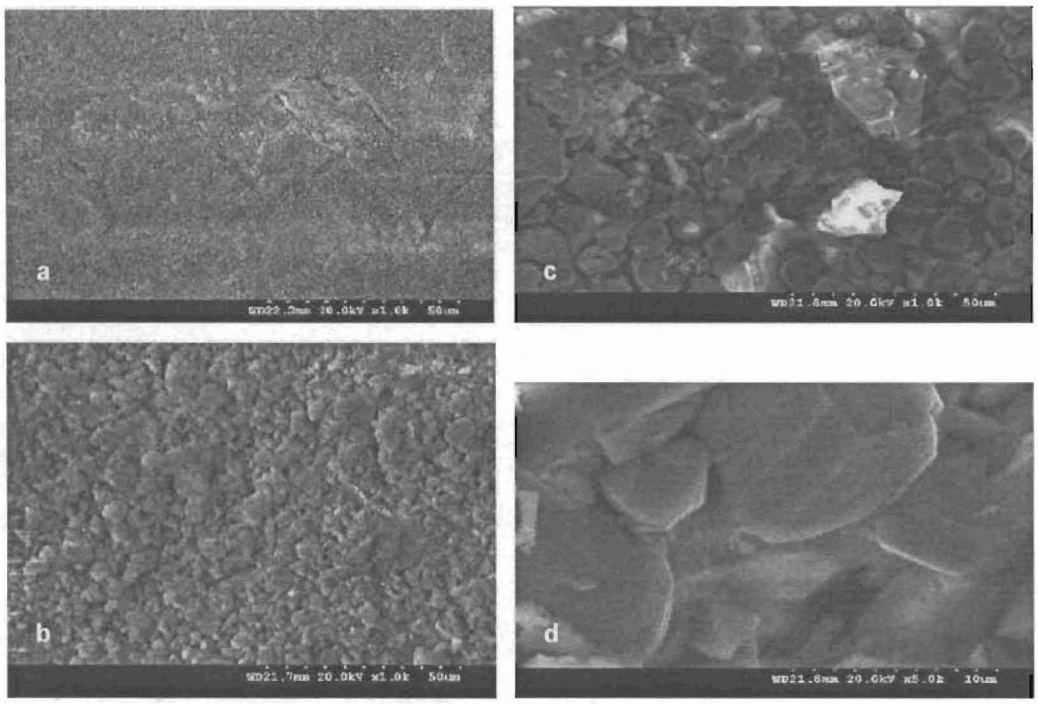

Fig. 6. SEM photograph for $MgAl_2O_4$ at (a) green, (b) 700 °C, (c) 1000 °C, (d) 1550 °C.

larger grain size. The morphological features revealed that the high temperature sintering allows uniform grain growth, whereas low temperature sintering favours uneven grain growth. High temperature sintering yields homogeneous, spherical-shaped particles of larger size, whereas low temperature sintering the particles show an irregular shape with a scattered morphology.

4. Conclusions

SSR method is found to be a suitable route for the synthesis of $MgAl_2O_4$ spinel. The synthesized $MgAl_2O_4$ shows an increase of crystallite size, density, hardness, electrical conductivity, and a decrease in porosity with sintering temperature. The results of XRD and SEM show that at 1550 °C, single phase the crystal structure of the spinel formed with distribution of the particles of uniform grain size with homogeneous in nature. The FTIR studies reveal that the formation of $MgAl_2O_4$ spinel with proper coordination of Mg^{2+} and Al^{3+} ions. From the above studies, it has been concluded that the synthesized $MgAl_2O_4$ is found to be a suitable anode for metallurgical industries to replace the conventional carbon anodes.

Acknowledgements

The authors express their sincere thanks to the Director, CECRI, and staff of EPM division for their support.

References

[1] A.R. Shitre, U.N. Devatwal, D.S. Birajdev, K.M. Jadhav, Indian J. Eng. Mater. Sci. 7 (2000) 464.
[2] C.N.R. Rao, J. Gopalakrishnan, New Directions in Solid State Chemistry, II edition, Cambridge Univ. Press, United Kingdom, 1997, p. 30.
[3] L.P. Ping, A.M. Azad, T.W. Dung, Mater. Res. Bull. 36 (2001) 1417.
[4] D.R. Sadoway, JOM 53 (2001) 34.
[5] L. Schreyeck, A. Wlosik, H. Fuzellier, J. Mater. Chem. 11 (2001) 483.
[6] A.D. Mazzoni, M.A. Sainz, A. Caballero, E.F. Aglietti, Mater. Chem. Phys. 78 (2002) 30.
[7] F. Meyer, R. Hempelmann, S. Mathur, M. Veith, J. Mater. Chem. 9 (1999) 1755.
[8] C.S. Narasimhan, C.S. Swamy, Phys. Status Solidi, A Appl. Res. 59 (1980) 817.
[9] L. Shuzhi, Z. Bangwei, S. Xiaolin, O. Yifang, X. Haowen, X. Zhongyu, J. Mater. Process. Technol. 89–90 (1999) 405.
[10] J.W. Mellor, Trans. Ceram. Soc. 36 (1937) 1.
[11] R. Sarkar, S.K. Das, G. Banerjee, Ceram. Int. 29 (2003) 55.
[12] C.H. Lu, Y.H. Huang, Mater. Sci. Eng. B 98 (2003) 33.
[13] N. Rezlescu, L. Sachelarie, E. Rezlescu, C.L. Sava, P.D. Popa, Ceram. Int. 29 (2003) 107.
[14] N. Yu, K.E. Sickafus, M. Nastasi, Mater. Chem. Phys. 46 (1996) 161.
[15] I. Suzuki, M. Kumazawa, Phys. Chem. Miner. 5 (1980) 279.
[16] T. Yamanaka, Y. Takeuchi, Z. Kristallogr. 165 (1983) 65.
[17] D.P. Karim, A.T. Aldred, Phys. Rev., B 20 (1979) 2255.
[18] B.P. Ladganonkar, C.B. Kolekar, P.N. Vasambekar, A.S. Vaingankar, Indian J. Eng. Mater. Sci. 7 (2000) 419.
[19] R. Sarkar, S.K. Das, G. Banerjee, Ceram. Int. 25 (1999) 485.
[20] B.P. Ladgaonkar, P.N. Vasambekar, A.S. Vaingankar, Bull. Mater. Sci. 23 (2000) 87.
[21] R.N. Panda, J.C. Shih, T.S. Chin, J. Magn. Magn. Mater. 257 (2003) 79.
[22] J. Wang, C. Li, Appl. Surf. Sci. 161 (2000) 406.
[23] G.A. Sigel, R.A. Bartlet, D. Decker, M.M. Olmstead, P.P. Power, Inorg. Chem. 26 (1987) 1773.