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Microwave assisted solid state reaction synthesis of $MgAl_2O_4$ spinel powders

Ibram Ganesh, Bakki Srinivas, Roy Johnson, Bhaskar P. Saha, Yashwant R. Mahajan*

Ceramic Materials Division, International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI),
Opposite to Balapur Village, Hyderabad, 500 005, India

Abstract

Stoichiometric $MgAl_2O_4$ spinel powders were synthesized by microwave assisted solid-state reaction (MWSSR powders) in a domestic microwave (MW) oven (2.45 GHz frequency, 700 W power) from aluminum tri-hydroxide and caustic MgO in the presence of carbon black (10–50 wt.% with respect to total raw mix). 20% C was found to be sufficient to produce spinel powder with 82% spinel content within 100 min while 50% C was able to produce 93% spinel containing powder within the same time. In conventional solid-state reaction (CSSR), in order to obtain the powder with the same amount of spinel phase (i.e., ~93%), the above raw mix was calcined at 1350 °C for 1 h and the total heating and cooling cycle time was more than 24 h. For the purpose of better comparison, three other stoichiometric $MgAl_2O_4$ powders were also prepared following conventional combustion synthesis using urea (CUCS powder) or sucrose (CSCS powder) as a fuel, and microwave assisted combustion synthesis using urea as a fuel (MWUCS powder), respectively. Effects of synthesis route on the powder properties were assessed by means of XRD, SEM, BET surface area, and particle size analysis. Among the various powders studied, the MWSSR powder was found to be superior as far as saving in processing time and power is concerned in addition to good sintering characteristics in terms of bulk density (B.D), apparent porosity (A.P) and water absorption (W.A).

Keywords: Combustion synthesis; $MgAl_2O_4$; Microwave synthesis; Solid-state reaction; Spinel

1. Introduction

$MgAl_2O_4$ spinel has been recognized as an important refractory material in the steel ladles and cement rotary kilns on account of its high melting point, high strength at elevated temperature, superior chemical resistance, and low coefficient of thermal expansion.[1,2] Generally, dense spinels are produced for the above applications by the double stage firing process as the single stage firing process results into low density product because of the volume expansion associated with the spinel formation from its constituents alumina and magnesia.[3,4] The double stage firing process consists of calcining of the raw mix at temperatures >1350 °C followed by grinding, compaction and sintering at >1600 °C.[1–4] Because of the use of double stage firing process, the production cost of spinels is very high. In order to reduce the production cost, several methods have been attempted in the past. One such method involves the use of certain mineralizers to reduce the calcination/sintering temperatures.[5,6] Recently, methods such as combustion synthesis, sol-gel, co-precipitation, etc., have been successfully used to produce powders, where spinel formation occurs at significantly lower temperatures.[7–11] Since, these techniques involve expensive raw materials and controlled processing steps, powders obtained by these methods can be used only for specialty products and are not commercially viable for refractory applications. The current annual worldwide spinel consumption is >2,05,000 tons.[12] This large requirement, calls for the development of simpler methods where spinel powder can be produced with desired spinel content in shorter time periods using basic ingredients such as Al_2O_3 and MgO by the solid–state reaction route at far lower temperatures.

Recently, various ceramic materials such as oxides, chalcogenides, carbides, nitrides, silicides, borides, glasses, etc., have been produced at an appreciably lower temperatures by the solid-state reaction of ceramic

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* Corresponding author. Fax: +91-40-24442699.
E-mail address: arcint@hd1.vsnl.net.in (Y.R. Mahajan).

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powders with the help of microwave energy as a heat source in a very short time periods as compared with conventional methods.[13–15] In the present, stoichiometric $MgAl_2O_4$ spinel powders were produced from aluminum tri-hydoxide and caustic MgO using carbon (10–50 wt.%) as a microwave susceptor in a domestic microwave oven (2.45 GHz frequency and 700 W power) within about 100 min duration. The powders were characterized and the properties of MWSSR powders have been compared with CSSR, CUCS, CSCS and MWUCS powders and the findings have been rationalized in terms of processing techniques.

Table 1
Physical properties and chemical composition of raw materials

Oxides present	$Al(OH)_3$	Caustic MgO
Al_2O_3 (wt.%)	64.5	–
MgO (wt.%)	–	82.86
Na_2O (wt.%)	0.3	0.093
CaO (wt.%)	0.03	0.908
SiO_2 (wt.%)	0.009	0.97
Fe_2O_3 (wt.%)	0.007	0.106
LOI (RT-1000 °C)	34.5	15.0
Specific gravity (g/cc)	2.42	3.58
Average particle size (μm)	85	5.22
BET surface area (m^2/g)	11.33	8.63

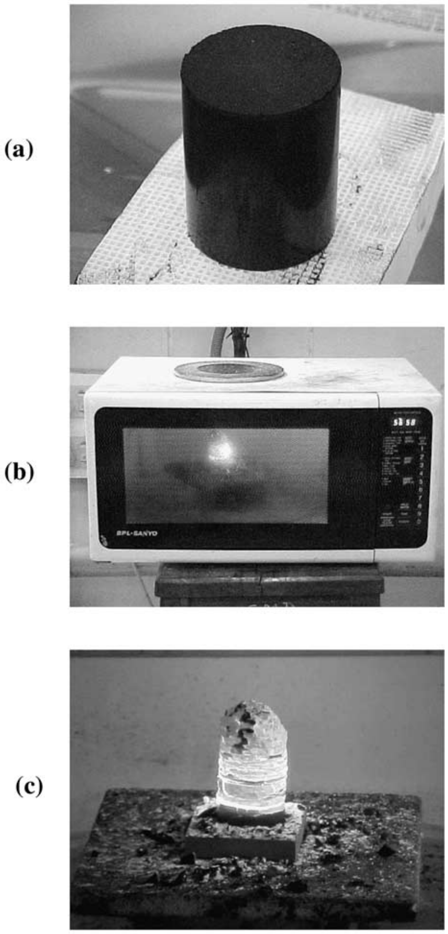

Fig. 1. Various stages of microwave assisted solid state reaction occurred in a microwave oven: (a) reaction mixture in the form of pressed pellet, (b) Microwave oven used, (c) pellet during the reaction.

2. Experimental

2.1. Powder synthesis

Specifications of raw materials used for the synthesis of CSSR and MWSSR powders are given in Table 1. In order to use microwave energy, it is required that at least one of the reactants should be a microwave susceptor. In the present study, carbon black was added to the reaction mixture to serve this purpose. In a typical experiment, the stoichiometric mixture of aluminum tri-hydroxide and caustic MgO was ground and mixed with 10–50 wt.% carbon black having residual mass of 0.5% after treating at 550 °C for 6 h in an air (Light grade, Industrial Graphites, Hyderabad, India). Carbon containing raw mix was compacted into cylindrical rods (25 mm diameter and 80–90 mm height) under the compaction pressure of 7.1 MPa. These compacted pellets were

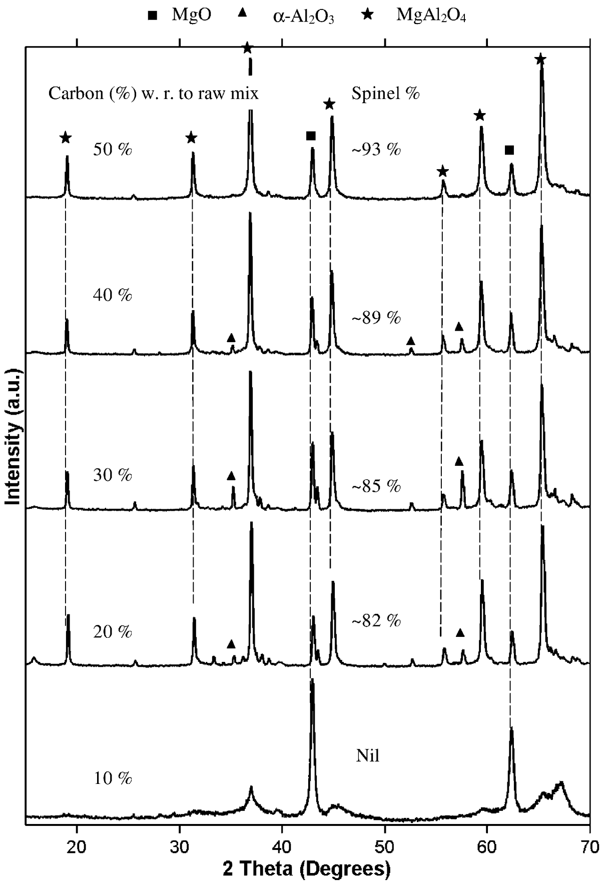

Fig. 2. X-ray diffraction patterns of microwave treated stoichiometric mixture of aluminum tri-hydroxide and caustic MgO in the presence of different amounts of carbon.

Table 2
Physical properties of $MgAl_2O_4$ powders produced by the various methods

S. No	Method	Code	Average particle size (μm)	BET surface area (m^2/g)	Crystallite size (nm)[a]
1.	Conventional solid-state reaction	CSSR	7.99	8.14	44.73
2.	Microwave assisted solid-state reaction	MWSSR[b]	5.43	36.03	66.03
3.	Conventional combustion synthesis using urea as a fuel	CUCS	14.24	8.06	43.51
4.	Conventional combustion synthesis using sucrose as a fuel	CSCS	3.17	65.8	22.21
5.	Microwave assisted combustion synthesis using urea as a fuel	MWUCS	4.58	0.1	55.47

[a] $MgAl_2O_4$ crystallite size, 311 plane was considered for crystallite size calculation using Debyez–Scherrer formula.[20]

[b] Powder obtained in the presence of 50 wt.% C

then exposed to microwaves in a modified domestic microwave oven (BPL India Limited, 700 W, input range 210–230 V-AC 50 Hz, MW frequency 2.45 GHz) operated at the highest power level for various time intervals till the black colour of the pellet disappears. Different stages of reaction occurred in a MW oven are shown in Fig. 1(a)–(c), respectively. Fig. 1(a) shows the pressed pellet of reaction mixture. The pellet was placed on a sintered SiC plate (45×45-mm size) on the top of an alumina plate inside the MW oven [Fig. 1(b)]. SiC plate enhances the reaction rate. Initially, experiments were conducted without using SiC as a bottom plate, however, the reaction could not be initiated when the C content was <30%, even at 30% or more, the reaction appeared to be sluggish. When SiC was used as a bottom plate, reaction was instantaneous and after about 30–40 min of MW irradiation, the entire pellet became red hot as can be seen from Fig. 1(c). After about 60 min of irradiation, the reaction was found to be completed and the pellet became fully white in colour. The resultant pellet was ground and made into a powder (MWSSR powder).

For the sake of better comparison, CSSR, CUCS, CSCS and MWUCS powders were synthesized as reported earlier.[2,6–8,16] The raw materials used in combustion reaction were analytical grade (Loba-Chemie, India).

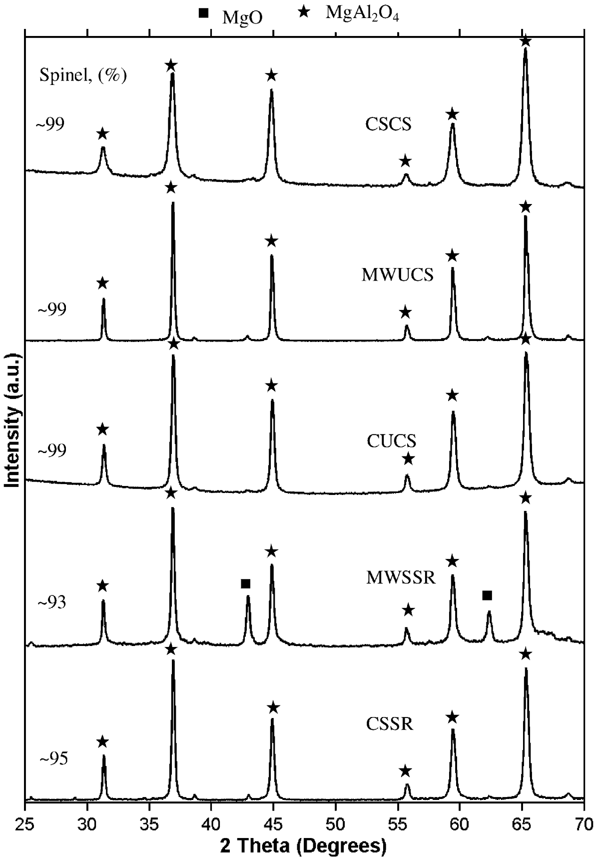

Fig. 3. X-ray diffraction patterns of CSSR, MWSSR, CUCS, CSCS and MWUCS powders.

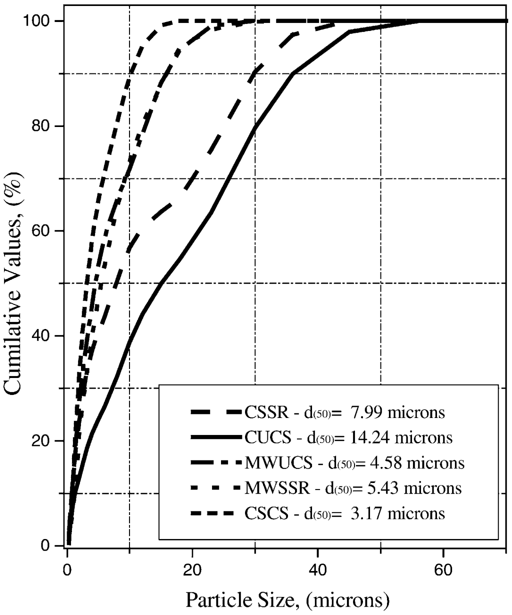

Fig. 4. Particle size distributions of 1 h ball milled CSSR, MWSSR, CUCS, CSCS and MWUCS powders.

2.2. Powder processing and characterization

All the synthesized powders were milled separately in a planetary ball mill (Fritsch, Pulverisette-5, containing alumina vessel and balls (12 mm dia.) for about 1 h under identical conditions (1:1 charge to balls ratio) and the resultant powders were granulated using PVA solution (5 wt.%) and dried overnight at room temperature. Thus obtained granules were then dry-pressed at 196 MPa in the form of pellets (30 mm dia. × 10 mm height) and sintered at 1625 °C for 2 h.[2,6–8,16] B.D, A.P, and W.A of sintered spinel materials were measured

Table 3
Properties of $MgAl_2O_4$ samples sintered at 1625 °C for 2h

S. No	Powder and its code	GD (g/cc)	BD (g/cc)	AP (%)	WA (%)	TD (%)	Crystallite size (μm)[a]	Lattice Parameter (a_o)[b]
1.	CSSR	2.10	3.36	1.76	0.51	94	84.59	8.068
2.	MWSSR	1.92	3.24	3.05	0.94	90.58	81.47	8.096
3.	CUCS	2.11	2.40	17.94	13.84	67.15	90.0	8.081
4.	CSCS	1.89	3.44	0.59	0.17	96	96	8.081
5.	MWUCS	1.91	2.63	14.05	9.13	73.57	94.92	8.081

[a] $MgAl_2O_4$ crystallite size, 311 plane was considered for crystallite size calculation.[20]

[b] The standard stoichiometric $MgAl_2O_4$ (i.e., 71.83 wt.% Al_2O_3 and 28.16 wt.% MgO, Fd3m structure, ICDD File No 211152) material shows the lattice parameter value of (a_o) 8.083 Å.[2,7,19]

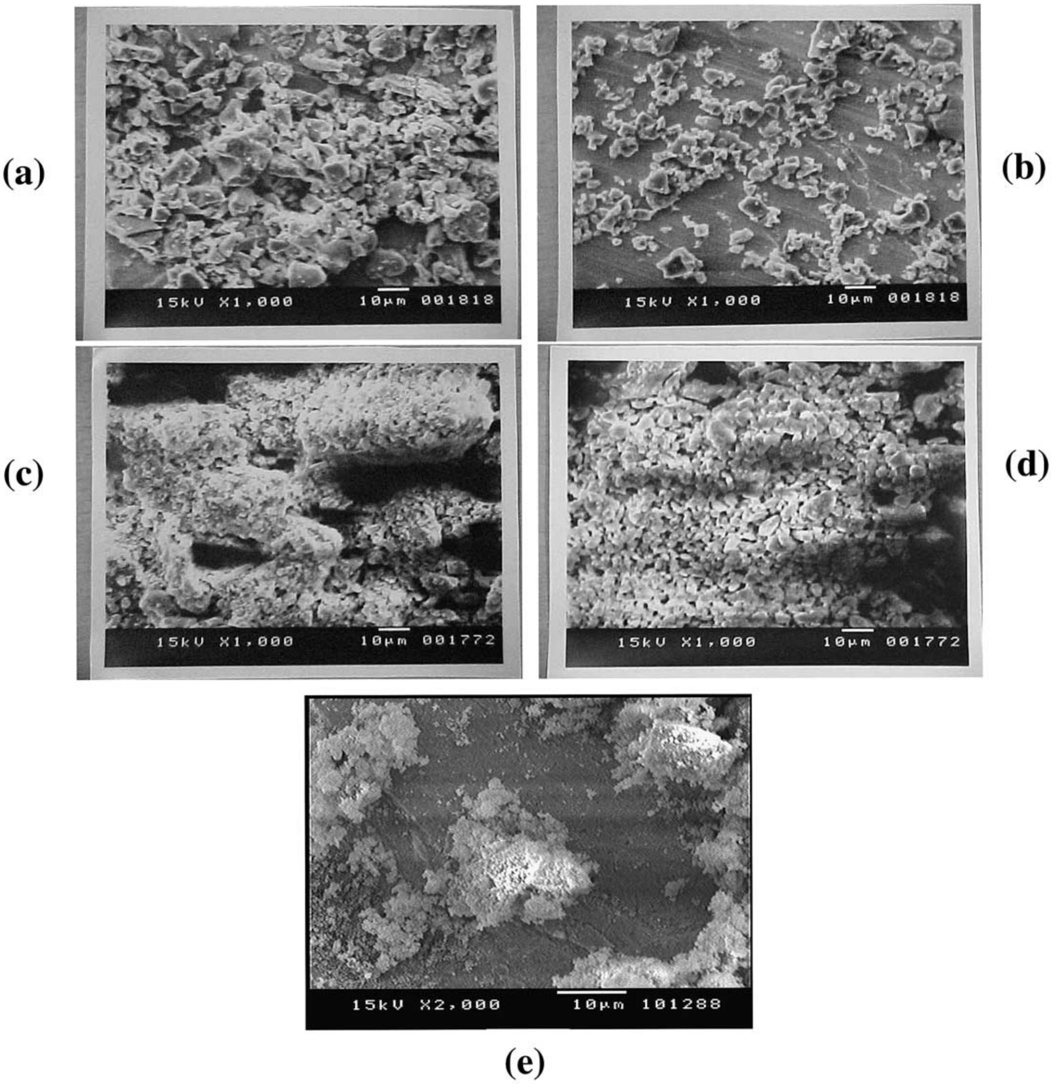

Fig. 5. SEM micrographs of 1 h ball milled (a)CUCS, (b)MWUCS, (c)CSSR, (d)CSCS and (e)MWSSR powders.

according to Archimedes principle. Phase analysis of the samples was carried out by X-ray diffraction (Brüker's D8 advanced system) using Cu-K_α radiation. Particle sizes of all the powders used were measured according to the Laser diffraction technique using particle size analyzer (Granulometer G 920, Cilas, France). The BET surface areas were measured according to a standard procedure mentioned elsewhere.[7]

3. Results and discussions

3.1. Powder characteristics

XRD patterns of various MWSSR powders are given in Fig. 2. As can be seen from Fig. 2, the powder corresponding to 10% C shows no effect on spinel formation whereas 20% C has resulted in the spinel content of up to 82%. As C content increased to 30, 40 and 50%, the spinel formation has further increased to 85, 89 and $>93\%$, respectively. This study clearly shows that even 20% C is sufficient to produce powder with 82% spinel formation from aluminum trihydroxide and caustic MgO in a domestic microwave oven. XRD patterns of CSSR, MWSSR (powder obtained with 50% C), CUCS, CSCS and MWUCS powders obtained by the different techniques are shown in Fig. 3. Among these powders CSSR and MWSSR powders show lower percentage of spinel phase, i.e., 95 and 93%, respectively, whereas, others show more than 99%.

The basic principle, chemical reactions and energy calculations involved in the combustion synthesis of $MgAl_2O_4$ powders from aluminum nitrate, magnesium nitrate and urea or sucrose were reported previously.[7,8] $MgAl_2O_4$ spinel powders synthesized by the different techniques are listed in Table 2 along with their particle sizes, BET surface areas, crystallite size values and codes given. Among the various powders synthesized, CSCS shows the highest surface area. The reason for this high surface area may be due to the greater amount of gas that evolved during sucrose combustion.[7] Thus

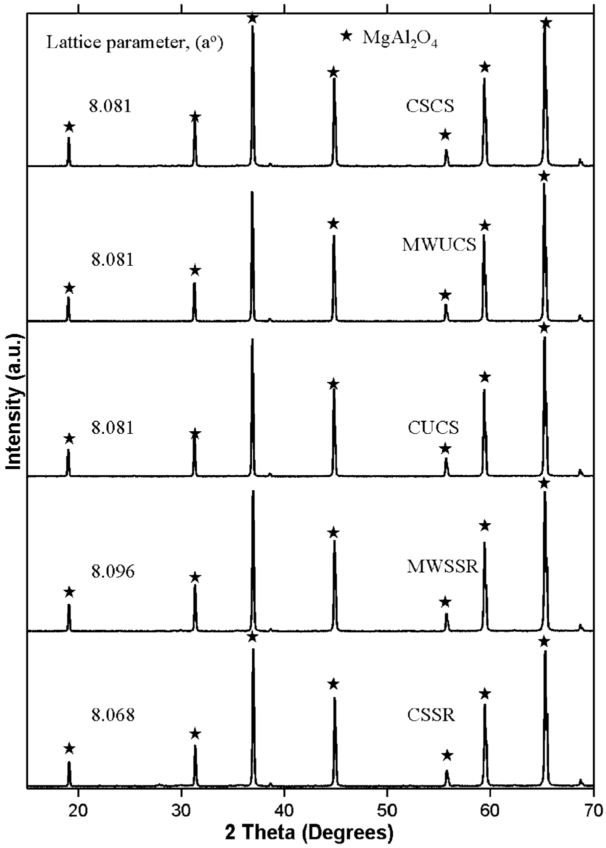

Fig. 6. XRD patterns of CSSR, MWSSR, CSCS, CUCS and MWUCS $MgAl_2O_4$ spinels sintered at 1625 °C for 2 h.

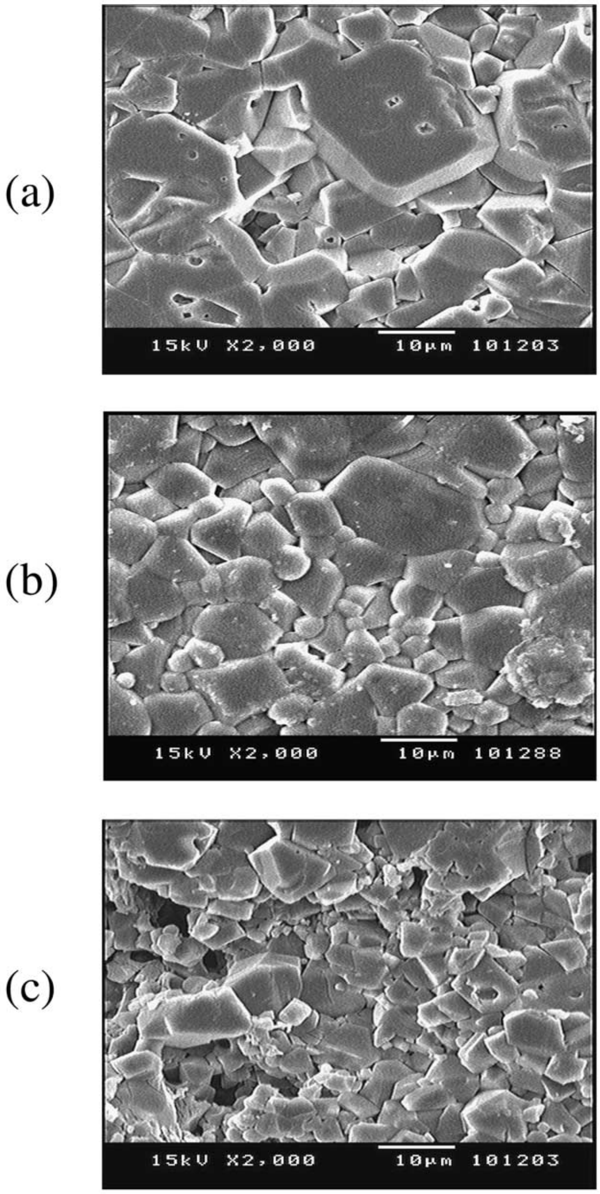

Fig. 7. SEM micrographs of etched surfaces of $MgAl_2O_4$ samples sintered at 1625 °C for 2 h; (a)CSCS, (b)CSSR and (c)MWSSR.

evolved gases generally helps in preventing the agglomeration of powder formed during the reaction, and deagglomeration is a strong function of surface area.[17] As can be seen from Table 2, MWSSR powder (hereafter MWSSR means powder obtained with the help of 50% C) show higher surface area than the CSSR powder. The reasons for this larger surface area may presumably due to the finer particle size of MWSSR powder. Among the various powders synthesized, CUCS and MWUCS show lower surface areas,[7,16] among which MWUCS has lower surface area. Two different adiabatic temperatures generated in the reactions in two different environments (i.e., in microwave oven and electric furnace) may be responsible for the difference in surface areas observed.[16,18]

The particle size distributions of powders milled for 1 h (in a planetary ball mill) are shown in Fig. 4. As can be seen from Fig. 4, CSCS, MWUCS and MWSSR powders show narrow particle size distribution compared with CSSR and CUCS powders. In general, microwave synthesized powders have shown smaller particle size as well as narrow size range as compared with other synthesized powders. SEM micrographs of various spinel powders synthesized are given in Fig. 5. As can be seen from Fig. 5, urea combustion synthesized powders show faceted and equiaxed shape, whereas sucrose combustion synthesized powders show a very narrow particle size with uniform distribution. Among the solid state reaction synthesized powders, CSSR powder appears to be irregular in shape whereas MWSSR powder is very fine (<5 μm).

3.2. Sinterability of the powders

B.D,% T.D (theoretical density), A.P and W.A values of various powders sintered at 1625 °C for 2 h are listed in Table 3 along with their crystallite size, and lattice parameter values. The green density (G.D) values of the pressed pellets are also given in Table 3. As can be seen from this table, powders obtained by the different techniques show the following trend in their sinterability: CSCS > CSSR > MWSSR > MWUCS > CUCS. The CSCS material had highest B.D and lowest percentage of A.P and W.A, whereas, CUCS shows the lowest B.D and highest percentage of A.P and W.A when they were sintered at 1625 °C for 2 h.

Though the starting materials for CSSR and MWSSR are same, they showed different sintering behaviour. As can be seen from Table 2, MWSSR powder has higher surface area and lower average particle size values than the CSSR powder. In general, the powder with higher surface area and smaller particle size would exhibit the higher sinterability. However, the different trend observed in the present case can be attributed to the possible apparent differences between these two powders in terms of their spinel content, powder morphology (SEM micrograph Fig. 5) and green density of the pressed pellets (Table 2).

All the sintered pellets exhibited $>99\%$ spinel phase (Fig. 6). According to Tables 1 and 2, the crystallite size of sintered spinels obtained by the different techniques is neither a function of crystallite size nor a particle size of starting powders. The lattice parameter values (Table 2) indicate that combustion synthesized powders show higher degree of stoichiometry as compared to solid-state reaction synthesized powders. The obtained lattice parameter values are well comparable with the reported values.[2,7,19] In order to assess the soundness of sintered spinels, three dense CSCS, CSSR and MWSSR pellets were selected and chemically etched (phosphoric acid at 185±5 °C for 4 min),[2] and examined under SEM. The resultant SEM micrographs are shown in Fig. 7(a)–(c), respectively. The SEM micrographs further confirm the sintering characteristics of the pellets.

4. Conclusions

1. $MgAl_2O_4$ spinel (MWSSR) powder can be produced with $>80\%$ spinel content from the aluminum tri-hydroxide and caustic MgO in the presence of 20% C in a domestic microwave oven (2.45 GHz frequency and 700 W power) within 100 min of duration while 50% C was able to produce 93% spinel containing powder within the same time.
2. In conventional solid state reaction, in order to obtain the powder with the ~93% spinel phase, the same aluminum trihydroxide and caustic MgO raw mix was calcined at 1350 °C for 1 h and the total heating and cooling cycle time was more than 24 h.
3. Among the various powders studied, the MWSSR powder was found to be superior in terms of saving in processing time and power in addition to good sintering characteristics in terms of bulk density, apparent porosity and water absorption.

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