

Research Letter

Influence of Phase Composition on Sintered Microstructure of Combustion Synthesized Oxides

Ibram Ganesh^{1,2} and J. M. F. Ferreira²

¹ Centre for Advanced Ceramics, International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), Hyderabad 500-005, Andhra Pradesh, India

² Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810193 Aveiro, Portugal

Correspondence should be addressed to J. M. F. Ferreira, jmf@cv.ua.pt

Received 5 August 2007; Accepted 31 August 2007

Recommended by Jainagesh A. Sekhar

The effects of powders synthesis methods (urea-combustion synthesis (CS) and conventional solid-state (SS) reaction) on the sintering ability, microstructural features, and mechanical properties of Al_2O_3 , MgAl_2O_4 spinel, and 20 wt.% $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ upon sintering at 1625°C were investigated. X-ray diffraction (XRD), scanning electron microscopy (SEM), relative density (RD), apparent porosity and water absorption capacity, hardness, fracture toughness, and three-point bend test studies revealed the superior sintering ability of CS $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ composite powder as compared with one prepared by SS reaction. In contrast, single-phase powders obtained by SS reaction exhibit superior sintering ability over CS synthesized ones. The reasons for differences observed are discussed along this paper.

Copyright © 2007 I. Ganesh and J. M. F. Ferreira. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

1. INTRODUCTION

Fabrication of fine-grained ceramic products has been the topic of many recent investigations on account of their beneficial properties over coarse-grained ceramics [1–3]. Over the last few decades, a great variety of techniques have been developed to synthesize highly reactive and high-purity materials to fabricate such fine-grained ceramic products. These techniques include hydrothermal synthesis, sol-gel, freeze drying of sulfate solutions, controlled hydrolysis of metal alkoxides, decomposition of organo-metallic compounds in supercritical fluids, and aerosol methods [4, 5]. Most of these techniques involve expensive raw materials and are associated with cumbersome processing steps. Recently, the so-called combustion synthesis (also known as self-propagating high-temperature synthesis) has emerged as an effective powder synthesis route as it is a simple and economic process and yields high-purity powders with excellent homogeneity and fine particle sizes [6–8]. However, the influence of phase composition on the consolidation behavior and microstructure development of urea-combustion synthesized materials upon sintering under normal atmospheric pressure has not been studied so far thoroughly [1–5]. In this study, $\alpha\text{-Al}_2\text{O}_3$

and MgAl_2O_4 spinel (single-phase materials) and 20 wt.% $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ (a multiphase material) have been synthesized following urea-combustion synthesis route and by the conventional solid-state reaction route, processed and sintered at 1625°C for 2–3 hours, as these materials have shown their efficacy in many applications. For example, MgAl_2O_4 has been employed for various applications including refractories, humidity sensors, transparent ceramic materials, and as anode material in aluminum electrolytic cells [9]. The reason for selecting $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ system was that the equilibrium phase diagram of these materials predicts little miscibility between the constituent phases [10]. The sintered materials have been thoroughly characterized using different types of spectroscopic and nonspectroscopic techniques and thus the obtained results are presented and discussed.

2. EXPERIMENTAL PROCEDURE

Commercial aluminum trihydroxide (NALCO, NSPH-10, India), caustic MgO (Birla Periclase, India), $\alpha\text{-Al}_2\text{O}_3$ (HP Grade, ACC India Limited, India), and baddeleyite (Pooja Enterprises, Mumbai, India) materials were used in the SS

TABLE 1: Physical properties and chemical composition of raw materials.^a

Composition & property	Al(OH) ₃	Caustic MgO	Al ₂ O ₃	Baddeleyite [†]
Al ₂ O ₃ (wt.%)	64.5	—	99.9	—
MgO (wt.%)	—	82.86	< 0.02	—
ZrO ₂ (wt.%)	—	—	—	93.69
Na ₂ O (wt.%)	0.3	0.093	< 0.06	4.074
CaO (wt.%)	0.03	0.908	< 0.015	0.112
SiO ₂ (wt.%)	0.009	0.97	< 0.0225	0.909
Fe ₂ O ₃ (wt.%)	0.007	0.106	< 0.02	0.226
Sulphate (wt.%)	—	—	—	0.605
LOI (RT-1000°C)	34.5	15.5	< 1	2
Specific gravity (g/cm ³)	2.42	3.58	3.98	—
Average particle size (μm)	85	5.22	0.6	2.6
Phase	γ-Al ₂ O ₃ & α-Al ₂ O ₃	Periclase	Corundum	Monoclinic ZrO ₂

^a Chemical compositions were provided by the suppliers.

[†] Chemical composition as determined by XRF analysis.

reaction route. Their physicochemical properties as given by the suppliers are presented in Table 1. To synthesize the MgAl₂O₄ by CS method, crystalline Al(NO₃)₃ · 9H₂O (total valencies -15) and Mg(NO₃)₂ · 6H₂O (total valencies -10) can be taken as Al and Mg sources, respectively. Direct use of propellant chemistry criterion, with the metal precursors in a 1 : 2 molar proportion, to determine the urea required to balance the total oxidizing and reducing valencies in the mixture, leads to $1(-10) + 2(-15) + n(+6) = 0$. The stoichiometric redox mixture of the metal nitrates and urea, to release the maximum energy for the spinel reaction would require that $n = 6.66$ moles [11]. In a typical experiment, aqueous solutions containing requisite quantities of nitrate/s (and zirconyl chloride) and urea to yield 500 g of each Al₂O₃, MgAl₂O₄ spinel and 20 wt.% ZrO₂-MgAl₂O₄ powders were put in a Pyrex dish and held for 5 minutes at 500°C in an electric muffle furnace, which was rapidly heated to the required temperature. After cooling, the resulting foamy materials were collected. In the case of SS reaction, a stoichiometric mixture of aluminum trihydroxide and caustic MgO was ground in a steel jar for 3-4 hours. The ground mixture was then made into nodules using 5 wt.% polyvinyl alcohol (PVA) solution, followed by oven drying at ~125°C overnight and then calcined at 1300°C for 1 hour [11]. All the prepared powders were ground separately in a planetary ball mill (Fritsch Pulverisette 5, GmbH, Germany), granulated using 5 wt.% PVA solution and then compacted (200 MPa) in the form pellets (30 mm diameter and 10 mm height) in a metal-die and sintered at 1625°C for 2-3 hours in an electric furnace. The relative density (RD), apparent porosity (AP), and water absorption (WA) capacity of the sintered materials were measured by the Archimedes principle. Phase analysis, and crystallite size of the samples was carried out by XRD (Bruker D8 advanced system, Karlsruhe Germany) using Cu K_α radiation as reported before [12]. The microstructure of sintered materials was examined by SEM (JSM-5410, JEOL, Japan). The flexural strength was measured using the 3-point bend test (JIS-R1601). Sintered samples (1625°C for 3 hours) were cut into rectangular specimens (60 × 4 ×

3 mm) for flexural strength measurements. Fracture toughness, K_{Ic} ($K_{Ic} = H a^{1/2} \times 0.203(C/a)^{-3/2}$), was calculated on the basis of the indentation method. Here, $2a$ represents Vickers indent diagonal length, $2C$ the resulted crack length, and H a Vickers hardness ($H_V = K_g/\text{mm}^2 = 10$ MPa).

3. RESULTS AND DISCUSSION

Table 2 lists the codes, BET surface areas, XRD phases, crystallite sizes, and average particle sizes of various powders used in this study along with green density (GD) of their corresponding compacts, and RD, AP, WA, and XRD phases of the bodies sintered at 1625°C for 2-3 hours. The particles size range of the synthesized CSA powder (5–35 μm) was reduced to an average particle size of 7.2 μm after planetary ball milling for about 1 hour (Table 2). Despite the presence of ~1 wt.% MgO (as a grain growth inhibitor/sintering aid) and the higher GD of its compact, CSA exhibited poor densification ability upon sintering at 1625°C for 2 hours. In contrast, the compact made of SSA powder achieved a relative density of ~95% upon the same sintering schedule. This enhanced sintering ability can be attributed to its finer average particle size (1.1 μm) and higher specific surface area (8.0 m²/g). Figures 1(a) and 1(b) show that the sintered microstructures of both samples consist of closely packed equiaxed grains, but of different sizes (5–15 μm, CSA) and (1–4 μm, SSA). The estimated crystallite sizes of the starting CSA and SSA powders were 98 and 86 nm, respectively (Table 2). This means that the different sintering abilities do not derive from the crystallite size. The state of agglomeration of the primary particles should play a main role. From the data available in Tables 1 and 2 and Figure 1, it is also apparent that the grain growth associated with the sintering of Al₂O₃ powder is more influenced by the particle/agglomerate size of the starting powder rather than by the amount of the doping material (MgO) present. These results are in good agreement with the literature reports [3].

In line to Al₂O₃, MgAl₂O₄ spinel powders exhibited similar sintering behaviors. The SSS powder achieved a higher

TABLE 2: Different materials and their sintered properties.^a

Powder	Code	BET SA (m ² /g)	Crystallite size (nm)	XRD phases [§]		Average particle Size (μm)	GD (g/cm ³)	RD (%)	AP (%)	WA (%)	XRD Phases [#]
				Major	Minor						
Al ₂ O ₃	CSA	4.3	98	C	—	7.2	2.38	87.3	1.71	0.49	C
Al ₂ O ₃	SSA	8.0	86	C	—	1.1	2.05	94.9	1.23	0.33	C
MgAl ₂ O ₄	CSS	8.1	43.51	S	—	14.2	2.11	67.2	13.84	67.1	S
MgAl ₂ O ₄ [‡]	SSS	8.1	44.73	S	< 10% C, P	8.0	2.10	94	1.76	0.51	S
*20 wt% ZrO ₂ - MgAl ₂ O ₄	CSZS	9.2	18.0	S	< 20% t-ZrO ₂	4.4	1.93	95	0	0	S, t-ZrO ₂ & m-ZrO ₂
*20 wt% ZrO ₂ - MgAl ₂ O ₄ [†]	SSZS	7.8	11.0	S	< 20% C, P & m-ZrO ₂	7.6	1.93	93.3	2.417	0.64	S, C, P, t-ZrO ₂ & m-ZrO ₂

^a The values were obtained as described in the experimental section.

* Sintered at 1625°C for 3 hours; the rest were sintered at 1625°C for 2 hours.

[‡] Obtained by calcining Al(OH)₃ and caustic MgO at 1300°C for 1 hour.

[†] Obtained by calcining Al(OH)₃, caustic MgO, and baddeleyite at 1000°C for 3 hours.

[§] Phases present in the powders prior to sintering.

[#] Phases after sintering: C, α-Al₂O₃ (corundum); S, MgAl₂O₄ (spinel); P, MgO (periclase); t-ZrO₂, tetragonal zirconia; m-ZrO₂, monoclinic zirconia.

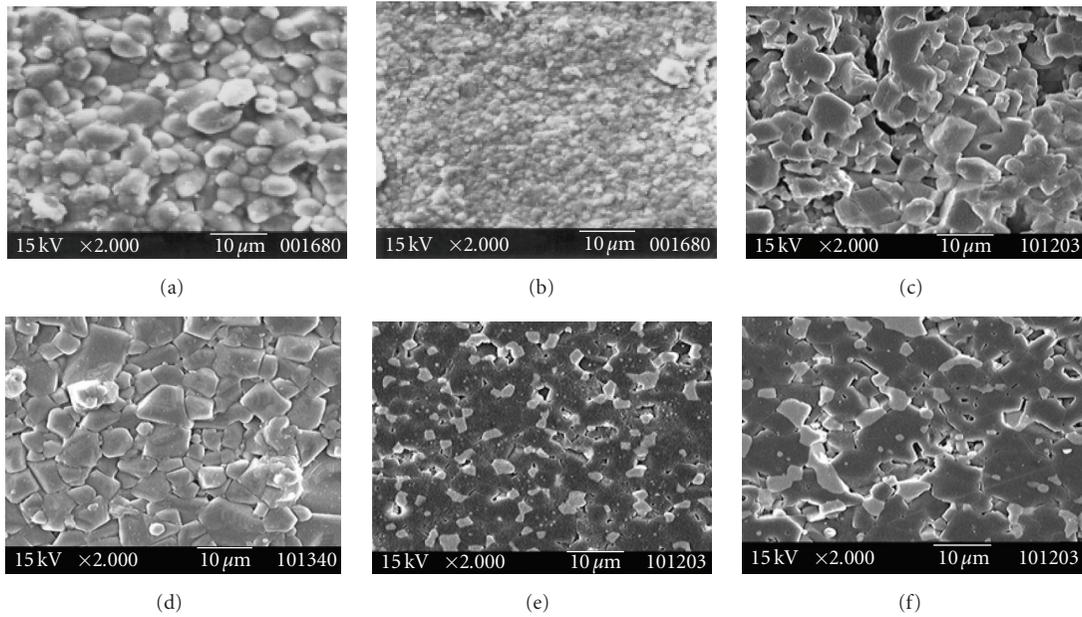


FIGURE 1: SEM micrographs of the materials sintered at 1625°C for 2 hours (samples (a) to (d)) and for 3 hours (samples (e)-(f)): (a) CSA; (b) SSA; (c) CSS; (d) SSS; (e) CSZS; (f) SSZS.

sintered density as compared CSS upon sintering at 1625°C for 2 hours. It has been well documented in literature [11] that partially spinelized (80–90%) powders have enhanced sintering ability in comparison to fully spinelized due to the higher calcination temperature required for full spinelization leading to the formation of hard agglomerates and less reactive powders. Because of this, the use of partially spinelized powders is usually preferred. The same reasoning applies to the CSS powders that were fully converted into spinel due to the intimate mixing of precursor reagents at the molecular scale and to the high combustion temperature experienced, explaining its poorer sintering ability. On the other hand, the uncalcined powders cannot be sintered into dense

bodies because of the volume expansion associated with the spinel phase formation [13]. The reason for higher densification behavior of SSS powder as compared to its CSS counterpart could be related to its lower degree of agglomeration and to the presence of some small amounts of unreacted corundum and periclase, since the average particle size, crystallite size, and the surface area of the powders are comparable. The SEM micrographs of sintered CSS and SSS samples (Figures 1(c) and 1(d), resp.) show similar-sized grains but different porosity fractions, supporting the sintering data.

In contrast to Al₂O₃ and MgAl₂O₄ spinel powders, the composite 20 wt.% ZrO₂-MgAl₂O₄ powder prepared by CS (CSZS) showed enhanced sintering ability in comparison to

TABLE 3: Mechanical properties of 20 wt.% ZrO₂-MgAl₂O₄ composites sintered at 1625°C for 3 hours.^a

Sample	RD (%)	Bending strength (MPa)	Hardness (H _V)	Linear shrinkage (%)	Fracture toughness (MPa.m ^{1/2})
CSZS	95.0	269 ± 4	1355 ± 5	25	5.96 ± 0.3
SSZS	93.3	98 ± 2	1009 ± 3	21	3.30 ± 0.2

^a The values were obtained as described in the experimental section.

that obtained by conventional SS reaction (SSZS) upon sintering at 1625°C for 3 hours (Table 2). Although containing small amounts of unreacted periclase and alumina as SSS powder, the SSZS could not be as easily densified as SSS powder. Literature reports [2, 5–7, 11] usually convey that urea CS powders are less sinterable in comparison to those prepared by SS reaction despite the former being a soft-solution technique granting a molecular level mixing of the precursors in comparison to the high diffusion paths involved in SS reaction process. However, the CSZS powder exhibited superior sintering ability over SSZS upon pressureless sintering under air atmosphere at 1625°C for 3 hours achieving RD > 95%. The micrographs of sintered CSZS and SSZS samples presented in Figures 1(e) and 1(f), respectively, show that the CSZS sample consists of very fine ZrO₂ grains uniformly distributed and embedded in closely packed MgAl₂O₄ grains (Figure 1(e)), while the SSZS consists of coarse and non-uniformly distributed ZrO₂ grains in a coarse MgAl₂O₄ matrix. From these entire results, one can conclude that in the case of composite materials consisting of immiscible phases the CS offers advantages over the SS reaction method since immiscibility hinders the grains of each phase to grow within the short synthesis time frame. Similar observations were also reported by Bhaduri et al. [3, 5] in their recent studies of combustion synthesized (single-phase) alumina [3] and (multiphase) alumina-zirconia [5] systems. A relative density of ~99% for an urea CS Al₂O₃-ZrO₂ composite (1 : 1 molar ratio) powder consolidated by cold isostatic pressing (495 MPa), heat-treating at 1200°C for 2 hours, followed by hot isostatic pressing at the same temperature for further 1 hour under 247 MPa Ar pressure was reported [5]. For a CS alumina powder, the relative density achieved upon hot isostatic pressing was < 95% [3]. From all of these results, it can be concluded that powders derived from CS can exhibit high or poor sintering ability depending being composite powders or single-phase materials, respectively.

The three-point bending strength, indentation hardness and fracture toughness values of both SSZS and CSZS materials sintered at 1625°C for 3 hours are presented in Table 3. The influence of powder synthesis route on the mechanical properties of materials can be clearly realized from this data. The higher linear shrinkages associated with the CSZS material upon sintering further confirm its superior sintering ability over its SS reaction counterpart. The sintered CSZS exhibits a bending strength of 269 MPa, a hardness of 1355 kg/mm², and a fracture toughness of 5.96 MPa.m^{1/2} as compared to SSZS, which shows only 98 MPa, 1009 kg/mm² and 3.30 MPa.m^{1/2}, respectively. The uniformly distributed fine ZrO₂ grains in the sample CSZS restrict the grain growth of MgAl₂O₄ matrix upon sintering leading to a

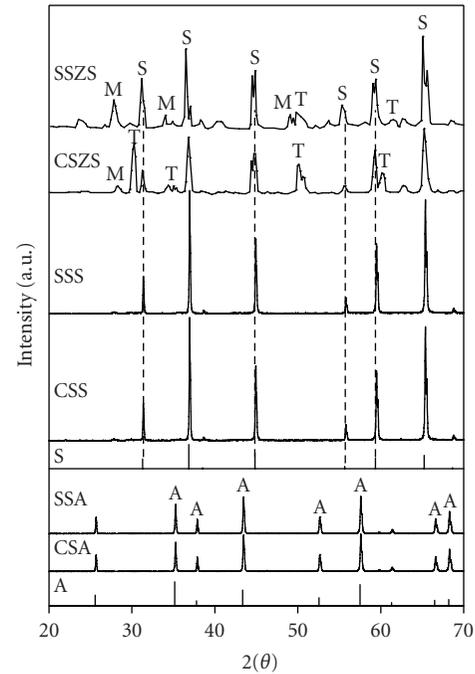


FIGURE 2: XRD patterns of the materials sintered at 1625°C for 2 hours (samples CSA, SSA, CSS, and SSS) and for 3 hours (samples CSZS and SSZS): A- α -Al₂O₃ (corundum), ICDD File no. 00-046-1212; S-MgAl₂O₄ spinel, ICDD File no. 00-021-1152; M-monoclinic ZrO₂; T-tetragonal ZrO₂.

denser and tougher composite. Further, when zirconia exists as metastable tetragonal crystals (t-ZrO₂) finely dispersed in a ceramic matrix at room temperature, it transforms to monoclinic (m-ZrO₂) phase under stress during fracture (stress-induced transformation). This tetragonal-monoclinic transformation is accompanied by a volume expansion, which nucleates microcracks in the surrounding material and restrains the crack propagation. The observed differences in the mechanical properties of CSZS and SSZS could therefore be attributed not only to the different developed microstructures but also to the presence of ZrO₂ particles of different phases. From the XRD data of sintered materials (Figure 2), it is clear that some amount of tetragonal zirconia was transformed into monoclinic phase upon sintering the powders due to the loss of symmetry upon sintering/densification [10], with the extent of t-ZrO₂ → m-ZrO₂ transformation being higher in the SSZS sample. For comparison purposes, the ICDD files of corundum and MgAl₂O₄ spinel are also presented in Figure 2.

4. CONCLUSIONS

Single-phase well-crystalline α -Al₂O₃ and MgAl₂O₄ spinel powders and multiphase uniformly distributed ZrO₂-MgAl₂O₄ composite powders can be synthesized by CS. Single-phase powders obtained by SS reaction exhibit superior sintering ability over urea-combustion synthesized (CS) ones. Contrarily, CS multiphase 20 wt.% ZrO₂-MgAl₂O₄ powders exhibit higher sintering ability due to the presence of immiscible fine and uniformly distributed t-ZrO₂ that restricts the grain growth of spinel upon sintering leading to denser and tougher composite in comparison to that prepared from SS reaction powders. The enhanced sintering ability of CS 20 wt.% ZrO₂-MgAl₂O₄ powder results in a significantly stronger composite material after sintering at 1625°C for 3 hours.

ACKNOWLEDGMENTS

I. Ganesh thanks SERC-DST (Government of India) for awarding BOYSCAST fellowship (SR/BY/E-04/06). The financial support of CICECO is also acknowledged.

REFERENCES

- [1] J. Karch, R. Birringer, and H. Gleiter, "Ceramics ductile at low temperature," *Nature*, vol. 330, no. 6148, pp. 556–558, 1987.
- [2] H. Gleiter, "Nanocrystalline materials," *Progress in Materials Science*, vol. 33, no. 4, pp. 223–315, 1989.
- [3] S. Bhaduri, E. Zhou, and S. B. Bhaduri, "Auto ignition processing of nanocrystalline α -Al₂O₃," *Nanostructured Materials*, vol. 7, no. 5, pp. 487–496, 1996.
- [4] M. Kumagai and G. L. Messing, "Enhanced densification of boehmite sol-gels by α -alumina seeding," *Journal of the American Ceramic Society*, vol. 67, no. 11, pp. c230–c231, 1984.
- [5] S. Bhaduri, S. B. Bhaduri, and E. Zhou, "Auto ignition synthesis and consolidation of Al₂O₃-ZrO₂ nano/nano composite powders," *Journal of Materials Research*, vol. 13, no. 1, pp. 156–165, 1998.
- [6] A. G. Merzhanov, "Self-propagating high-temperature synthesis: twenty years of search and findings," in *Combustion and Plasma Synthesis of High-Temperature Materials*, Z. A. Munir and J. B. Holt, Eds., p. 1, VCH, New York, NY, USA, 1990.
- [7] K. C. Patil, S. T. Aruna, and S. Ekambaram, "Combustion synthesis," *Current Opinion in Solid State and Materials Science*, vol. 2, no. 2, pp. 158–165, 1997.
- [8] S. R. Jain, K. C. Adiga, and V. R. Pai Verneker, "A new approach to thermochemical calculations of condensed fuel-oxidizer mixtures," *Combustion and Flame*, vol. 40, no. 1, pp. 71–79, 1981.
- [9] I. Ganesh, K. A. Teja, N. Thiyagarajan, R. Johnson, and B. M. Reddy, "Formation and densification behavior of magnesium aluminate spinel: the influence of CaO and moisture in the precursors," *Journal of the American Ceramic Society*, vol. 88, no. 10, pp. 2752–2761, 2005.
- [10] R. Guinebretière, Z. Oudjedi, and A. Dauter, "Orthorhombic zirconia phase in ZrO₂-MgAl₂O₄ composite material," *Scripta Materialia*, vol. 34, no. 7, pp. 1039–1044, 1996.
- [11] I. Ganesh, B. Srinivas, R. Johnson, B. P. Saha, and Y. R. Mahajan, "Effect of fuel type on morphology and reactivity of combustion synthesised MgAl₂O₄ powders," *British Ceramic Transactions*, vol. 101, no. 6, pp. 247–254, 2002.
- [12] H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, John Wiley & Sons, New York, NY, USA, 2nd edition, 1974.
- [13] Z. E. Nakagawa, N. Enomoto, I. S. Yi, and K. Asano, "Effect of corundum/periclase sizes on the expansion behavior during synthesis of spinel," in *Proceedings of UNITECER Congress*, pp. 379–386, Tokyo, Japan, 1995.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

