Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 36 (2010) 1211–1215
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Co-precipitated $ZnAl_2O_4$ spinel precursor as potential sintering aid for pure alumina system

T.K. Parya [a,*], R.K. Bhattacharyya [a], S. Banerjee [a], U.B. Adhikari [b]

[a] Department of Chemical Technology, Calcutta University, 92 A.P.C. Road, Kolkata 700 009, India
[b] Central Glass & Ceramic Research Institute, 196 Raja S.C. Mullick Road, Kolkata 700 032, India

Received 14 May 2009; received in revised form 10 September 2009; accepted 12 December 2009

Abstract

Ultra-fine $ZnAl_2O_4$ spinel hydrogel precursor synthesized from mixed salt solutions of Zn^{2+} and Al^{3+} ions using ammonium hydroxide–hexamethylenetetramine as basic media for co-precipitation was used as bonding material and sintering aid for pure alumina system. The hydrogel powder exhibited some well-defined $ZnAl_2O_4$ spinel phases at 800 °C. Alumina compacts were fabricated by incorporating small proportions of the precursor in alumina powder and firing at different temperatures (1350–1500 °C). The degree of densification was studied by measurement of fired shrinkage, apparent porosity, bulk density and cold crushing strength. Phase compositions and microstructural features of sintered samples were evaluated by XRD and SEM respectively. Addition of 0.2% hydrogel powder to alumina exhibited remarkable influence on development of high mechanical strength. The *in situ* formed $ZnAl_2O_4$ spinel dopant acted as a grain growth inhibitor in the alumina system.

Keywords: $ZnAl_2O_4$ precursor; Consolidation; Alumina–spinel composites

1. Introduction

Direct bonded or spinel bonded high purity alumina has attracted special attention of ceramists as one of the prime structural ceramic materials. It finds extensive applications in multifunctional fields like electronics, membrane, catalyst carrier, engine components, grinding media, electrical insulator and computer tape guides because of its excellent combination of enhanced properties such as high mechanical strength, high abrasion resistance, good thermal conductivity, significant electrical resistivity with low dielectric losses. However, fundamental studies of solid-state sintering of alumina are highly complicated due to the presence of two microstructural features:

(i) liquid phases at grain boundary from impurities of starting materials and
(ii) existence of pores due to agglomeration of starting powders.

This necessitates a very high temperature to the tune of 1700 °C to achieve the densification of pure alumina. So, the recent researches towards the generation of superior alumina ceramic products with desired characteristics largely hubs around the proper selection of high purity alumina and its crystal form as well as on the choice of prospective sintering aids for controlling the densification, phase transformation and microstructural aspects of sintered alumina compact. Ayadi and Lukin [1] studied the sintering of alumina consisting of highly dispersed α-Al_2O_3 prepared by the plasma-chemical method. They reported that introduction of MgO improved sinterability and the addition of partially stabilized zirconia enhanced the ultimate strength of alumina ceramics. Nordahl and Messing [2] demonstrated that the seeding of nano-crystalline transition alumina powders was a viable option for producing high quality alumina based ceramics. Bodur [3] investigated the pressureless sintering of an MgO-doped gelcast alumina ceramic at 1600 °C in air with different soaking times. Shui et al. [4] studied origin of shape deformation during sintering of alumina grains. They prepared alumina compacts by uniaxial pressing followed by cold isostatic pressing and their structures were examined to clarify the origin of deformation during sintering. Kosmos et al. [5] developed suitable coarse grained alumina ceramic materials for metal–ceramic seals used in high vacuum technology. Goldsby [6] prepared sintered alumina materials

---

* Corresponding author. Tel.: +91 33 2350 8386; fax: +91 33 2351 9755.
E-mail address: tapanparya@yahoo.co.in (T.K. Parya).

0272-8842/$36.00 © 2010 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2010.01.013

using commercial methods from mechanically mixed powders of nano- and micro-alumina. The powders were consolidated at 1500 and 1600 °C in argon. Kim et al. [7] investigated the reaction sintering and microstructural development of alumina with addition of 1–25 mol.% AlN by heating under 1-atm nitrogen gas at 1600–1800 °C. Cutler et al. [8] demonstrated that the sintering temperature of 96% alumina bodies can be reduced to 1300–1400 °C range with bulk densities above 3.80 g cm^{-3} by using combinations of oxides and nanosized particle. It is proposed that this low temperature sintering would result from the formation of liquid phase.

Since the efficiency of a chemically bonded ceramic material depends largely on the effect of heat on chemical bond and the removal of porosity during sintering, there is immense scope on the sintering study of alumina bodies using reactive co-precipitates of spinel precursors as potential sintering aids. Active ultra-fine $ZnAl_2O_4$ precursor synthesized by co-precipitation or sol–gel route may be a prospective entrant for this purpose due to their high purity, homogeneity and large surface area with active sites. *In situ* derived $ZnAl_2O_4$ spinel formed on thermal treatment of active ultra-fine $ZnAl_2O_4$ hydrogel could play the role of a good sintering aid for pure alumina.

So the goal of present investigation is to study the effect of *in situ* formed $ZnAl_2O_4$ spinel precursor on the densification behavior and microstructural aspects of pure alumina system during sintering at lower temperature (1350–1500 °C). Since large additions of sintering aid may adversely affect the end product properties, the addition of the spinel precursor was restricted to a lower range.

2. Experimental

The starting materials for the present investigation were commercial alumina (ALCOA, 99.67%) as matrix, aluminum nitrate nonahydrate crystal ([$Al(NO_3)_3{\cdot}9H_2O$], Merck, Extra Pure [$Al(NO_3)_3{\cdot}9H_2O$] $\geq$ 95%), zinc nitrate hexahydrate ([$Zn(NO_3)_2{\cdot}6H_2O$], Merck, Purified [$Zn(NO_3)_2{\cdot}6H_2O$] 96–103%) as precursors and ammonia solution (30% GR grade, sp. gr. 0.90 Merck) and hexamethylenetetramine ([$(CH_2)_6N_4$], Merck, Pure [$(CH_2)_6N_4$] $\geq$ 99%) as precipitating agents. Zinc aluminate hydrogel powder in a molar ratio of 1:1 was synthesized from a mixed salt solution of Zn^{2+} and Al^{3+} ions by interaction with ammonia solution and hexamethylenetetramine as basic media for gel formation [9]. The dried hydrogel powder was added to the alumina powder in the proportion of 0.1, 0.2, and 0.3 wt% respectively with 2.5 wt% moisture and thoroughly mixed in an electrically operated mixer. Each batch mixture was then pressed into cylindrical compacts in a hydraulic press at a pressure of 1000 kg cm^{-2}. Alumina compact without any additive was also prepared following the same procedure for comparative study. All the compacts were dried in air at 110 °C and then fired for 2 h at different temperatures between 1350 and 1500 °C in an electrically operated furnace.

The magnitude of sintering was then studied by measurement of shrinkage on firing, apparent porosities, bulk densities and cold crushing strengths of the compacts following standard methods while crystalline phase analysis and microstructural aspects were evaluated by XRD and SEM techniques, respectively.

Table 1
Physico-chemical properties of alumina powder.

Chemical composition	Value
%Al_2O_3	99.67
%Na_2O	0.31
%SiO_2	Trace
%LOI	0.30
Morphological parameters	
Mean particle diameter	1.01 μm
Specific surface area	5.1 m^2 g^{-1}
Crystalline variety	α-Al_2O_3

3. Results and discussion

Physico-chemical properties of Al_2O_3 powder used in the study are shown in Table 1 while Table 2 indicates properties of co-precipitated $ZnO–Al_2O_3$ hydrogel powder used as sintering aid for alumina powder compacts.

After drying, the hydrogel containing samples showed sufficient green strength (around 125 kg cm^{-2}) suitable for safe handling. The samples were fired in an oxidizing atmosphere due to absence of any redox system in the composition. Firing temperatures were kept relatively low (1350–1500 °C) considering the higher reactivity of *in situ* formed $ZnO:Al_2O_3$ spinel. The fired color of the samples of the sintered compacts was perfectly white without formation of any crack or visible defects.

The magnitude of sintering was studied by the measurement of firing shrinkage, apparent porosity, bulk density and cold crushing strength of the compacts. Variation of these properties as a function of additive contents and sintering temperatures are graphically represented in Figs. 1–4.

3.1. Volume shrinkage

From Fig. 1 it is evident that the fired volume shrinkage increased in a regular manner with increase in hydrogel content for a given temperature of firing. During firing at 1500 °C, maximum shrinkage was observed for 0.2% addition of hydrogel. The shrinkage value of the compacts improved steadily with increasing firing temperature up to 1500 °C

Table 2
Properties of $ZnO–Al_2O_3$ hydrogel powder [9].

Molar ratio, $ZnO:Al_2O_3$	1:1
DTA peak temperatures (endo), °C	100, 290, 500
XRD of powdered sample heat treated at 800 °C	
Crystalline phase	$ZnAl_2O_4$
SEM micrograph of powdered sample heat treated at 800 °C	
Shape of particles	Spherical
Size of particles, dia.	0.12–0.28 μm

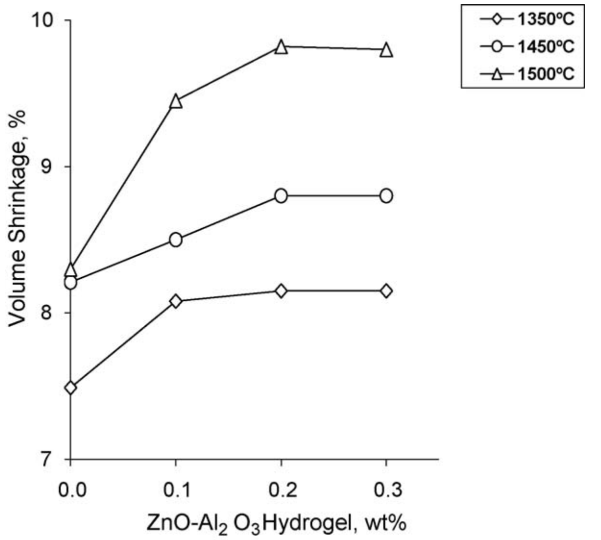

Fig. 1. Variation of volume shrinkage (%) of Al_2O_3–$ZnAl_2O_4$ compacts on firing.

indicating rapid elimination of pores by material interaction and transportation caused by higher thermal activation. In all cases, neither cracks nor distortion were noticed in any sample.

3.2. Apparent porosity

The degree of densification in a system is generally manifested through the magnitude of apparent porosity. Fig. 2 represents variation of apparent porosity of Al_2O_3–$ZnAl_2O_4$ compacts with hydrogel content on firing. Apparent porosity curves declined gradually with increasing content of hydrogel at all firing temperatures up to 0.2% addition and then exhibited a slight ascending trend. In this particular system, intensive interaction of *in situ* formed microfine spinel with α-alumina particles might have occurred to cause close particle to particle bonding among the crystallites and also alignment of particles leading to elimination of pores.

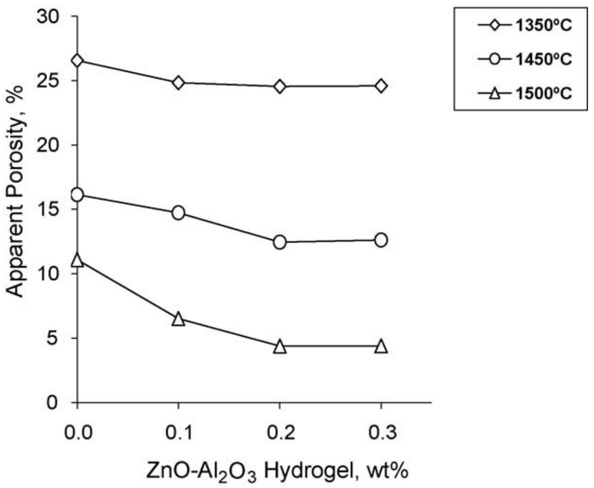

Fig. 2. Variation of apparent porosity (%) of Al_2O_3–$ZnAl_2O_4$ compacts on firing.

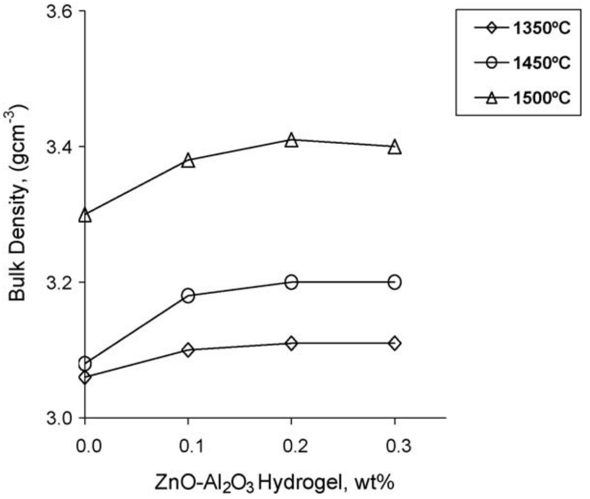

Fig. 3. Variation of bulk density (g cm^{-3}) of Al_2O_3–$ZnAl_2O_4$ compacts on firing.

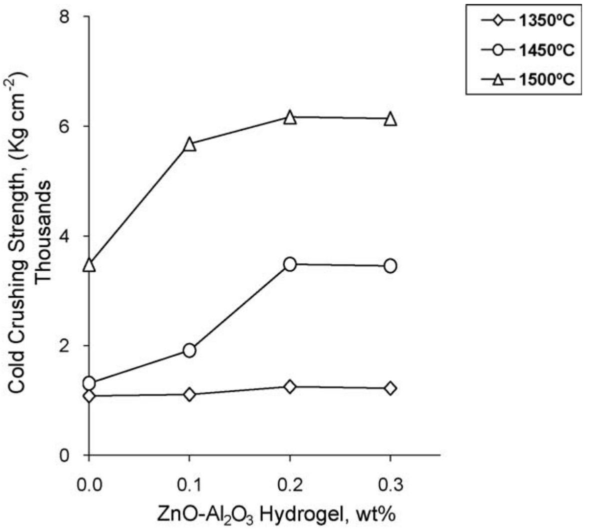

Fig. 4. Variation of cold crushing strength (kg cm^{-2}) of Al_2O_3–$ZnAl_2O_4$ compacts on firing.

Fig. 2 also reflects the predominance of firing temperature on apparent porosity of a sample with fixed amount of dopant. Apparent porosity decreased sharply for all the compacts with increase in firing temperature. Sample containing 0.2% dopant yielded dense compact with lowest porosity (4.40%) during sintering at 1500 °C. The drastic reduction of apparent porosity of the samples during firing at 1500 °C may be attributed to the mineralizing action of *in situ* formed reactive $ZnAl_2O_4$ spinel phase.

This was also evident from the much higher values of apparent porosity exhibited by the dopant free compacts at all firing temperatures.

3.3. Bulk density

As the pure alumina systems investigated contained only minor additions of dopant, they may be considered as a single phase system with slight possibility of formation of a liquid phase at the grain boundary due to release of minor amount of alkali present in the alumina powder. Bulk density results of sintered products correlated the magnitude of densification to a great extent as evident from Fig. 3. Compacts with dopant had comparatively higher bulk density values than that without it at all temperatures. Compact with 0.2% addition attained maximum bulk density of 3.41 g cm^{-3} at 1500 °C which is 86% of theoretical density of pure alumina.

As evident from Fig. 3, the rate of increase of bulk density with temperature was slow upto 1450 °C followed by a rapid increase at 1500 °C. The trend was true for all the set of compacts irrespective of dopant content. The temperature of 1500 °C may be correlated to the rapid increase of the sintering rate due to the formation of a minor liquid phase either in the Na_2O–Al_2O_3 or Na_2O–$ZnO{\cdot}Al_2O_3$ system.

3.4. Cold crushing strength

Cold crushing strength plays a significant role in the structural application of ceramic materials. Compressive strength values of the samples are shown in Fig. 4 against dopant content which demonstrates that cold crushing strength increased radically with temperature up to 1500 °C for all the compacts with or without dopant. Dopant free compact had much less cold crushing strength compared to those with addition of dopant. Maximum cold crushing strength value (6168 kg cm^{-2}) was obtained for compact with 0.2% addition of dopant at a firing temperature of 1500 °C.

Thus, achievement of appreciably high strength (6168 kg cm^{-2}), approach of bulk density to nearly 86% of theoretical density with a value of 3.41 g cm^{-3} and substantially low apparent porosity (around 4.4% only) for alumina compact with 0.2% addition of $ZnAl_2O_4$ spinel fired at 1500 °C indicates excellent sintering action of the spinel.

3.5. Crystalline phase identification

The X-ray diffraction pattern of compacts containing 0 and 0.2% $ZnAl_2O_4$ spinel precursor sintered at 1500 °C (Fig. 5) indicates that α-alumina was the only one stable crystalline phase in both the compacts. However, no characteristic peak for $ZnAl_2O_4$ spinel was detected in dopant containing compact probably due to formation of mixed secondary phase not crystalline but amorphous. But the slight shift of certain peaks towards lower 2θ values and relatively higher intensity of the peaks of the dopant containing compact in comparison to that of undoped compact may be attributed to formation of a solid solution between $ZnAl_2O_4$ and Al_2O_3.

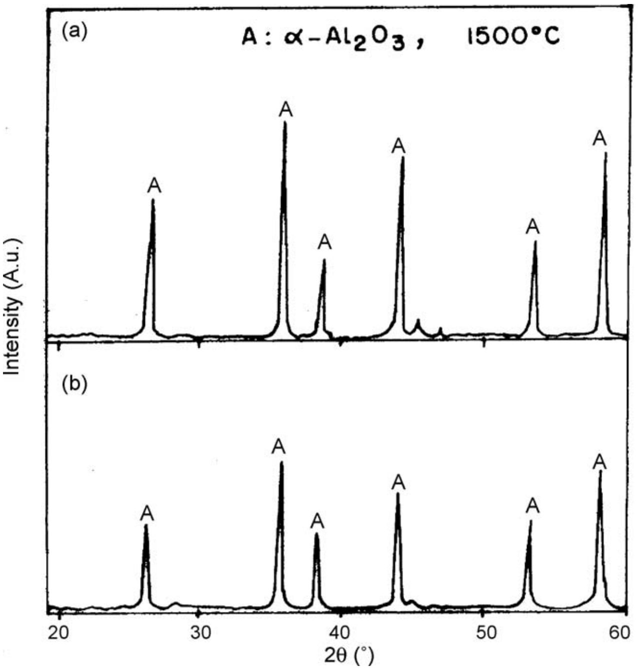

Fig. 5. XRD pattern of compacts sintered at 1500 °C. (a) Compact with 0.2% $ZnAl_2O_4$ spinel precursor and (b) pure alumina compact.

3.6. Microstructure by SEM

The microstructural observation of sintered alumina specimens with and without the presence of *in situ* $ZnAl_2O_4$ spinel fired at 1500 °C is exhibited in Figs. 6 and 7, respectively. The microstructural features were somewhat different in nature. Few trans-angular fractures through grain boundaries and a number of entrapped pores were noticed in the undoped specimen having acicular grains with a size range varying from 0.8 to 1.1 μm. SEM micrograph of alumina compact with 0.2% $ZnAl_2O_4$ hydrogel indicated the presence of fine sub-rounded grains of α-alumina crystals having size range of 0.7–0.8 μm which are homogeneously distributed in the alumina matrix leading to the development of a well-sintered interlocked alumina compact. Thus *in situ* formed $ZnAl_2O_4$ spinel dopant acted as a grain growth inhibitor in the alumina system.

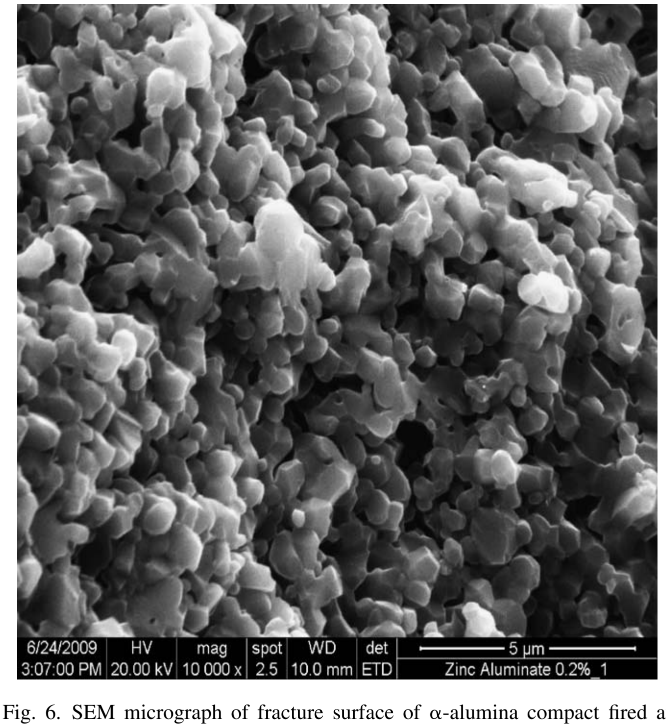

Fig. 6. SEM micrograph of fracture surface of α-alumina compact fired at 1500 °C with 0.2% $ZnAl_2O_4$ spinel precursor.

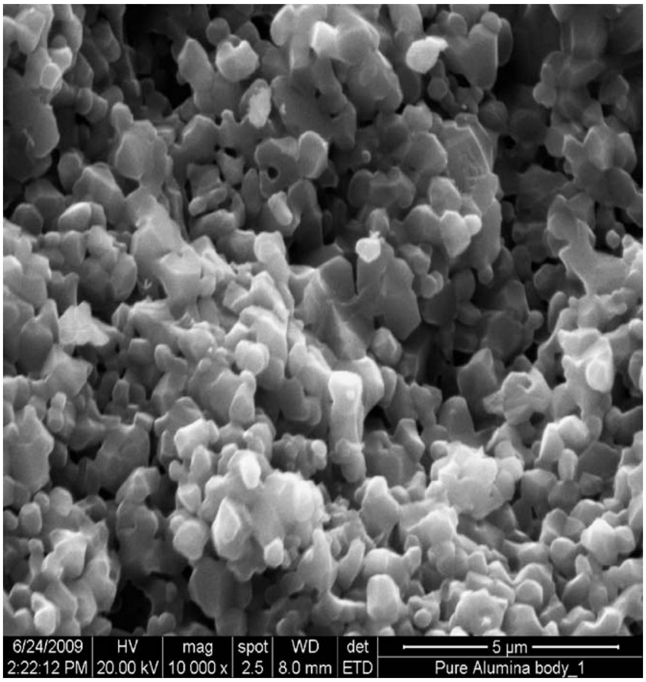

Fig. 7. SEM micrograph of fractured surface of α-alumina fired at 1500 °C without precursor.

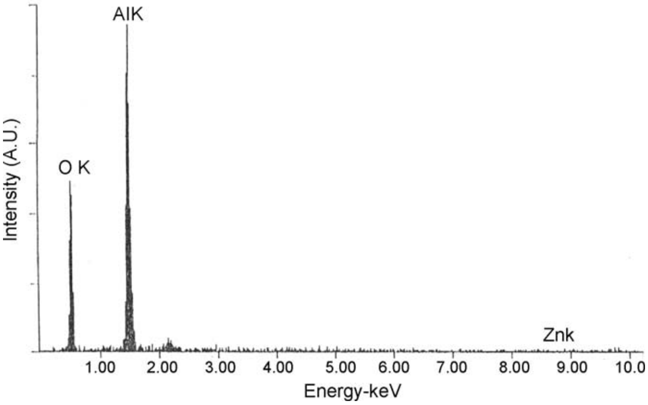

Fig. 8. EDAX analysis of α-alumina compact fired at 1500 °C with 0.2% $ZnAl_2O_4$ spinel precursor.

From the EDAX analysis of alumina compact with 0.2% $ZnAl_2O_4$ hydrogel (Fig. 8), no secondary phase could be detected. This might be due to the formation of a solid solution between $ZnAl_2O_4$ spinel and Al_2O_3 as corroborated by XRD observations.

4. Conclusions

From the present investigation on the densification study of alumina compacts in presence of *in situ* microfine $ZnAl_2O_4$ spinel precursor, following conclusions may be drawn:

1. $ZnAl_2O_4$ spinel precursor functioned as a prospective non-conventional sintering aid for pure α-Al_2O_3 system.
2. Minor addition of $ZnAl_2O_4$ hydrogel could be distributed uniformly throughout α-Al_2O_3 powder mass during fabrication resulting in moderate green strength at 110 °C.
3. Enhanced densification of alumina bodies occurred with minor presence of *in situ* $ZnAl_2O_4$ spinel precursor (0.2%) during firing at 1500 °C. The $ZnAl_2O_4$ spinel formed intense solid solutions with α-Al_2O_3 grains leading to a well-sintered Al_2O_3 compact body. Na_2O from alumina might have formed very little secondary liquid phase with either alumina or spinel.
4. The SEM micrographs of sintered alumina compacts with $ZnAl_2O_4$ spinel addition exhibited no excessive grain growth of α-Al_2O_3 indicating that $ZnAl_2O_4$ spinel precursor acts as crystal growth inhibitor in pure alumina system.

References

[1] M.B. Ayadi, E.S. Lukin, Corundum ceramics based on aluminium oxide obtained by plasma chemical method, Glass Ceram. 55 (1–2) (1998) 57–58.

[2] C.S. Nordahl, G.L. Messing, Sintering of α-Al_2O_3-seeded nanocrystalline γ-Al_2O_3 powders, J. Eur. Ceram. Soc. 22 (4) (2002) 415–422.

[3] C.T. Bodur, Pressurless sintering of a gelcast alumina ceramic, Ceram. Eng. Soc. Proc. 22 (4) (2001) 75–82.

[4] S. Shui, Y. Zhang, N. Uchida, K. Uematsu, Origin of shape deformation during sintering of alumina compacts, J. Ceram. Soc. Jpn. 106 (9) (1998) 873–876.

[5] A. Kosmos, D. Susnik, D. Kolar, Parameters influencing the preparation of coarse grained Al_2O_3 ceramics, Eur. Ceram. V Part 2 (1997) 912–915.

[6] J.C. Goldsby, High temperature mechanical behaviour of polycrystalline alumina from mixed nanometer and micrometer powders, Ceram. Int. 27 (6) (2001) 701–703.

[7] Y.W. Kim, H.C. Park, Y.B. Lee, K.D. Oh, R. Stevens, Reaction sintering and microstructural development in the system Al_2O_3–AlN, J. Eur. Ceram. Soc. 21 (13) (2001) 2383–2391.

[8] I.B. Cutler, C. Bradshaw, C.J. Christensen, E.P. Hyatt, Sintering of alumina at temperatures of 1400 °C and below, J. Am. Ceram. Soc. 40 (1957) 134–139.

[9] U.B. Adhikari, M.B. Saha, T.K. Parya, Synthesis and characterization of ZnA_2lO_4 precursor in relation to different basic media, J. Indian Chem. Soc. 81 (2004) 674–679.