SINTERING BEHAVIOR AND MICROSTRUCTURAL EVALUATION OF MgO-DOPED α-Al_2O_3

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Abstract

There have been widespread interests in recent decades in porous ceramics owing to their specific properties, such as low bulk density, low specific heat, low thermal conductivity and high specific surface area. Alumina has been one of the first developed advanced ceramics to be used in load bearing applications as orthopedic implants. The properties of α-Al_2O_3 can be modified by introducing a second suitable metal oxide to form a composite oxide. Among various metal oxides MgO is considered as a promising metal oxide which can modify the properties of alumina in the α-Al_2O_3-MgO mixed oxides by grain growth inhibition due to the strong basic characteristics of MgO. In this work, porous α-Al_2O_3 – MgO alumina-based ceramics were fabricated by a tape casting method and powder metallurgy technique. MgO-doped α-Al_2O_3 ceramics sintered at 1400°C for 2-4-6 h in air atmosphere. The effect of sintering time on the porosity, density and shrinkage properties of samples were investigated. The sintering behavior, surface morphology, elemental distribution and phase evaluation of the composite ceramics were evaluated by SEM-EDX and XRD, respectively.

Key words: *α-Al_2O_3, porous ceramics, SEM-EDX, grain growth inhibition*

1. INTRODUCTION

There are currently widespread interests in porous ceramics owing to their specific properties, such as low bulk density, low specific heat, low thermal conductivity and high specific surface area (Carn 2004; Sepulveda 1997; Colombo 2003; Liu 1998; Mear 2007; Zou 2005; Zampieri 2004). Bioceramic materials have attracted a great deal of interest, for numerous applications by scientists, physicians and engineers for the last four decades. In general, bioceramic materials are classified into three broad categories that include bioinert (such as alumina, zirconia), bioresorbable (such as tricalcium phosphate, TCP) and bioactive (such as Hap bioactive glasses, glass-ceramics). A bioinert material is nontoxic but biologically inactive, whereas a bioactive material is one that elicits a specific biological response at the interface of the biological part and the material, which results in the formation of a bond between and tissues and the material (Ashiku 1997; Gross 1988). Alumina can be sintered to a high density when small amounts of MgO are added. It is thought that the MgO is segregated to the grain boundaries and inhibits grain growth (Jorgensen 1964; Brook 1969), either by second-phase pinning (Jorgansen 1967) or by a solid-solution-impurity drag mechanism (Brook 1968). In the present investigation, sintering and production of MgO-doped porous alumina has been studied in two typical fabrication methods. In this work, we produced porous α-Al_2O_3 – MgO ceramics through a powder metallurgical technique and tape casting method. The effect of sintering time on the porosity, density and microstructural properties of samples were investigated.

2. EXPERIMENTAL STUDY

Powder metallurgy technique; The composition of the samples examined in this study is high-purity α-Al_2O_3 - 0.5 wt. % MgO. High-purity Al_2O_3 and MgO powders were supplied by Alumina Refinery. The raw materials were weighed in weight proportion and ball milled with ethanol for 6 days using zirconia balls at 250 r.p.m. The Al_2O_3- MgO ceramic slurry mixture was well homogenized with 1 mol% Darvan ® 821A was added as a binder to ultra-fine powder (≤ 1 μm) to give sufficient strength to the green compact. Darvan ® 821A is a highly effective dispersing agent used to lower the viscosity of particulate slurries and to inhibit the settling of particulate solids. Mixture was dried overnight at 80 °C and then dried and shifted through a 38 μm sieve for granulation. The powders were pressed

hydrostatically at 300 MPa and the green density of each pellet was maintained at 60 % of theoretical density. The isothermal sintering was carried out at 1400°C for 2-4-6h. in static air in a closed alumina crucible and cooled to room temperature (5 ˚C/min).

Tape casting method; An azeotropic mixture of acetone/2-propanol (66/34 w/w) were used as solvent. Poly vinylbutyral (Butvar, B-98, Sigma Aldrich, CAS: 63148-65-2, USA), was used as binder, and polyethylene glycol (PEG 400, Merck, CAS: 25322-68-3, Germany) was used as dispersant for all the slips prepared for the tape casting. Butylbenzyl-phtalate (BBP, Merck, CAS: 85-68-7, Germany) was used as plasticizer. The formulation of the tape casting slurries is shown in Table 1. The tape casting compositions were prepared for Al_2O_3 with 0.5 wt. % MgO. To obtain binder for slurries, Butvar B-98 was dissolved in the acetone and di-propanol azeotropic mixture. After obtaining binder, the plasticizer and dispersing agent were added. Milled composition was placed on a magnetic stirrer for the removal of the solvent in powder-binder mixture. Tape casting was performed using a laboratory tape casting bench with a stationary double blade system. Slurries were tape casted onto a glass where the device was moved at a constant speed of 10 cm/s. The drying of the tapes was carried on at room temperature for 24 h. The dried tapes were cut into 15 mm x 20 mm rectangles and laminated with a pressure of 300 MPa. The isothermal sintering was carried out at the same condition as in powder metallurgy technique.

Table 1. Formulation of Al_2O_3-MgO slurries for tape casting

Materials	**Function**	**wt.%**
Al_2O_3- MgO	Powder	41
PVB	Binder	4
PEG	Dispersant	0.5
BBP	Plasticizer	4.5
Acetone/2-Propanol	Solvent	50

The following techniques were employed to characterize the produced sintered α-Al_2O_3 – MgO ceramics. The relative density, open porosity and water absorption of the sintered materials were determined using Archimedes' water displacement method, as specified by European Standard EN 99 (ISO 10545-3, 1991) (Acchar 2008). The vacuum method (ISO 10545-3) was used in the laboratory to determine water absorption with greater precision. The vacuum method allows all open pores to be filled and the vacuum process was conducted in a chamber in which the air pressure was lowered to a value of 10^{-3} mbar and held at that value for 30 minutes. The crystal structure of the samples was determined from X-ray diffraction (XRD) data. An X-ray Diffractometer (Rigaku D/MAX/2200/PC) with a monochromatic Cu-K_α radiation (λ= 1.5408 Å) was used over a 2θ angle from 20° to 80° to characterize the crystal structure of the sintered compacts. The surface-fracture morphology and elemental analysis of the ceramics was examined by using a scanning electron microscope (SEM, Model JEOL-JSM 6060-LV, Japan) and energy-dispersive X-ray spectroscopy (EDS).

3. RESULTS AND DISCUSSION

3.1. Physical Properties and Densification

Figure 1a, 1b and Figure 2a, 2b presents the relative density versus open porosity and water absorption in samples sintered at 1400°C for 2-4-6 h. produced by tape casting method and powder metallurgy technique respectively. Values were determined according to equation (1)

The foregoing formulas contain the following magnitudes, all expressed in grams (g):

$$E_v = \frac{m_{2v} - m_1}{m_1} \times 100(\%) \quad (1)$$

m_1: mass of the dry sample

m_{2v}: mass of the sample impregnated with water after the vacuum process and weighing, also under vacuum.

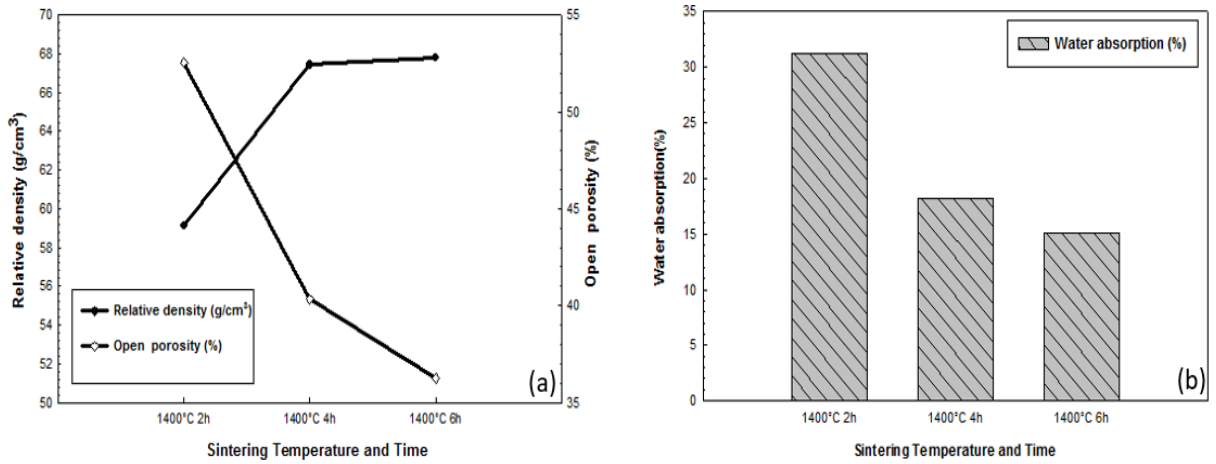


Figure 1. (a) Variations in relative density - open porosity and (b) water absorption in α-Al_2O_3 – MgO ceramics sintered at different sintering time produced by tape casting method.

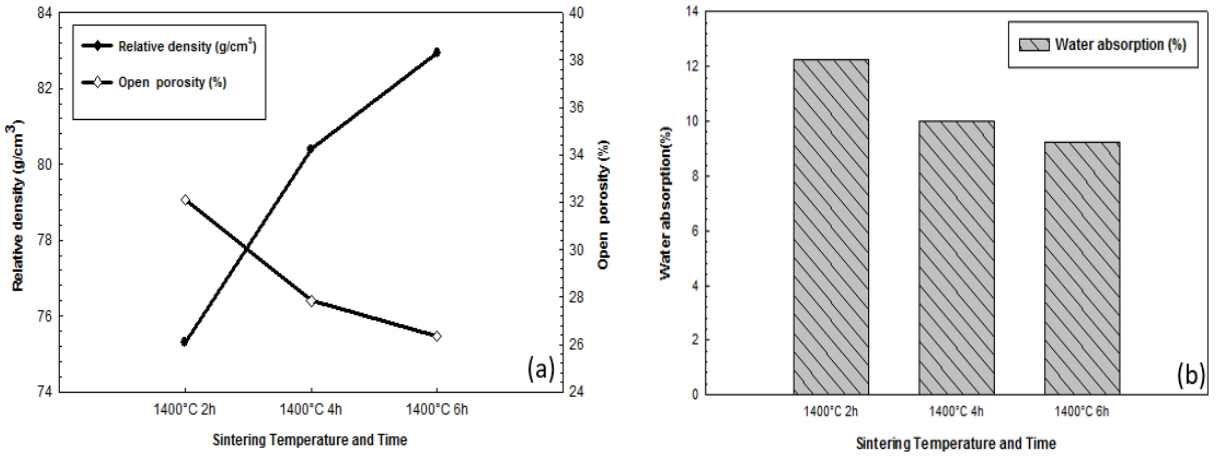


Figure 2. (a) Variations in relative density - open porosity and (b) water absorption in α-Al_2O_3 – MgO ceramics sintered at different sintering time produced by powder metallurgy technique.

In this study, the relative densities of sintered α-Al_2O_3 – MgO ceramics produced by tape casting method were found as % 67.8 at 1400°C 6h whereas the relative densities of α-Al_2O_3 – MgO ceramics produced by powder metallurgy technique were found as % 80.9 at 1400°C 6h depending on the production method. Figure 1a, 1b and Figure 2a, 2b reveals that the increasing sintering time increases the bulk density of the composites. It can be seen that for all samples, the sintering time has a positive impact on the sintered density, where longer sintering time gives higher density. This may be attributed to reduction in the amount of porosities during sintering which leads more dense materials. Open porosity values (%) of sintered ceramics which are produced by powder metallurgy technique at

1400°C 6h was found to be 26.34%±0.11, whereas for ceramics which are produced by the tape casting method at the same conditions was 36.24%±0.09. Minimum water absorption (9.22%) value was obtained at 1400°C 6h sintered α-Al_2O_3 – MgO ceramics produced by powder metallurgy technique.

3.2. XRD Analysis

The results of the crystallographic analysis of the produced samples and powders, carried out with X-ray diffraction, are summarized in Figure 3. In all cases, the diffractograms have predominantly registered the corundum phase – (Al_2O_3), matched for every sample (ICSD card no. 71-1128) due to the dissolution of MgO and reacts with Al_2O_3 in the ceramic composite. Figure 3a shows the X-ray diffraction patterns of the original powder mixture after ball milling. After 6 days of milling, the peaks become increasingly broader with long milling time and a number of new broadened peaks appear. As the sintering is occurred, the peaks are sharpened suggesting the increase in the crystallite size (Figure 3b and 3c). In order to realize the sub-micron microstructure in the sintered ceramics, it is essential to have the nanocrystalline powders as starting milled powders. The figure proves that the Al_2O_3-MgO composites are successfully produced without noticeable undesirable phases. X-ray diffraction patterns of Al_2O_3-MgO composite powders show that the peaks correspond to corundum phases, confirming that MgO is effectively incorporated into the Al_2O_3 matrix by forming corundum. The X-ray diffraction patterns of sintered ceramics (Figure 3b) which are produced by the tape casting method lead to the low crystallinity in comparison to the other production method. As very well-known from crystallographic theory, the more the element in a lattice, the more the visible peaks but in lower intensity.

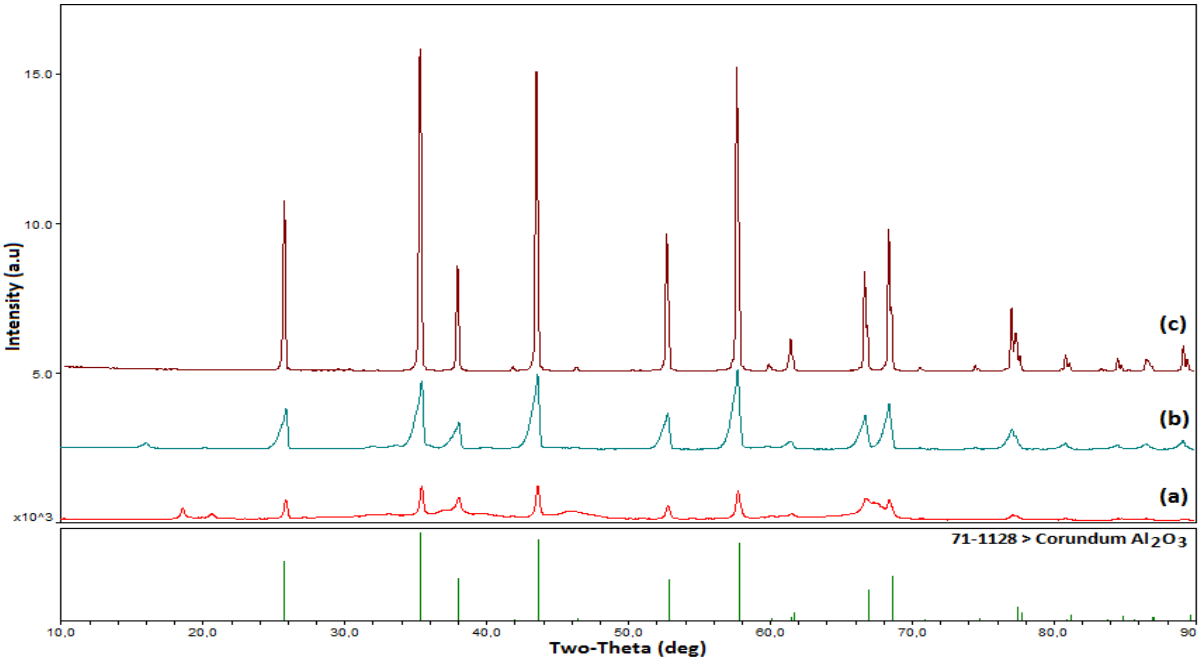


Figure 3. (a) X-ray diffraction of the initial powders after ball milling for 6 days. (b) X-ray diffraction of the sintered sample at 1400°C 6h obtained by tape casting method. (c) X-ray diffraction of the sintered sample at 1400°C 6h obtained by powder metallurgy technique.

3.3. SEM and EDS Analyses

The surface morphology of the MgO doped alumina-based ceramics was examined by scanning electron microscopy (SEM), equipped with an energy dispersive spectrometer (EDS, INCA IE 350, 207 and U.K.). The EDS spectra were observed with an image analyzing program. The samples were fixed on aluminum stubs and pre-coated with gold/palladium thin film for 5 min under argon atmosphere using a Technics Hummer II sputter coater. The SEM samples were examined at an accelerating voltage of 20 kV. EDS was used to determine their surface composition with ≈1 μm^2 resolution and source energy of 10 keV. Three runs were repeated and averaged for the surface elemental analysis of each specimen. SEM images of the sintered ceramics after polishing and thermal etching of the surfaces were presented in Figure 4 (a- f). SEM images (a-f) in Figure 4 reveal that the homogenous morphology and different grain size distribution were obtained for all compositions after sintering.

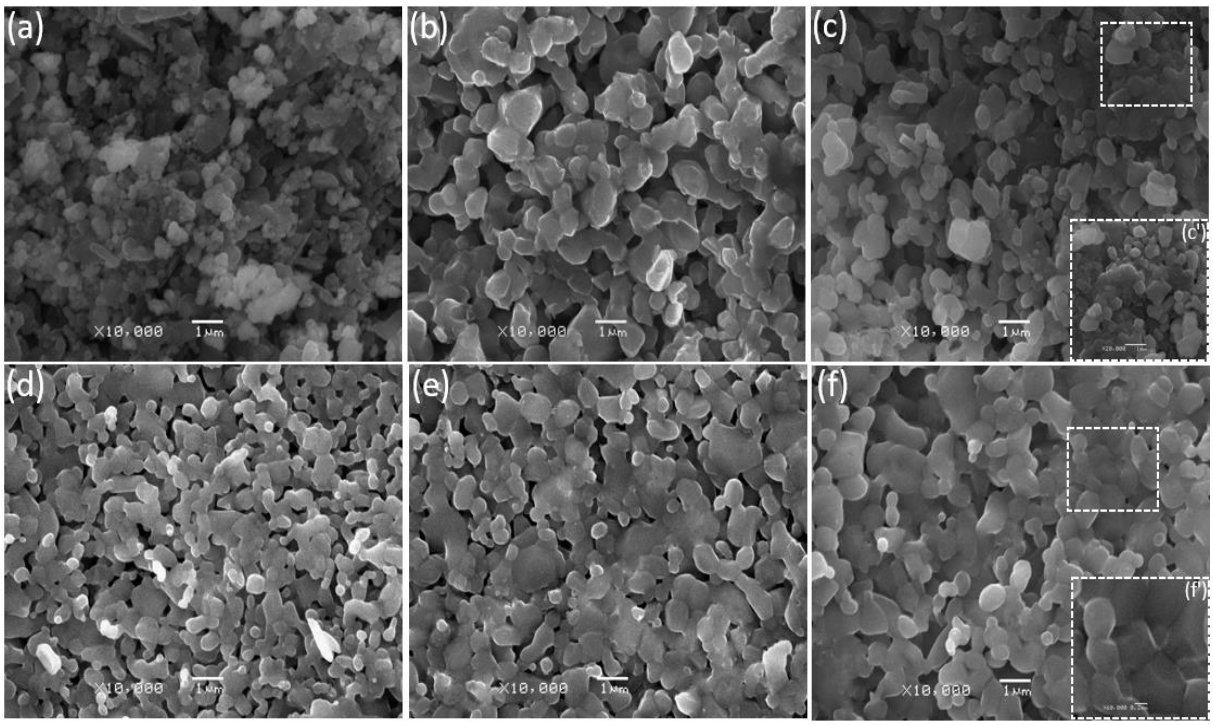


Figure 4. SEM images of the α-Al_2O_3 – MgO ceramics sintered at 1400°C (a) 2h, (b) 4h and (c-c') 6h. obtained by tape casting method. SEM images of the α-Al_2O_3 – MgO ceramics sintered at 1400°C (d)2h, (e) 4h and (f-f') 6h. obtained by powder metallurgy technique.

Figure 4 (from d, e to f) also represents the surface morphology of samples become more smooth by increasing sintering time and production method. As observed, especially in Figure 4 (f and f '), the increasing glassy phase and MgO may contribute to the smoothness of the surface and more particles seem to be embedded to the matrix structure. It is found that the average grain size has a slight increase as the sintering time increases for both production methods. Energy dispersive X-ray spectroscopy (SEM/EDS) were involved to explore the morphology and elemental composition of the ceramic samples after sintering at 1400°C 6h. EDS elemental analysis results were obtained by the aerial elemental analysis for each sample surface. The SEM images with EDS spectra of the surfaces of the ceramics are shown in Figure 5(a)-(d). The energy peaks corresponding to Al and O from EDS analysis are very strong for all compositions (Figure 5. (a)-(d) while the magnesium element can be detected for both ceramic composites.

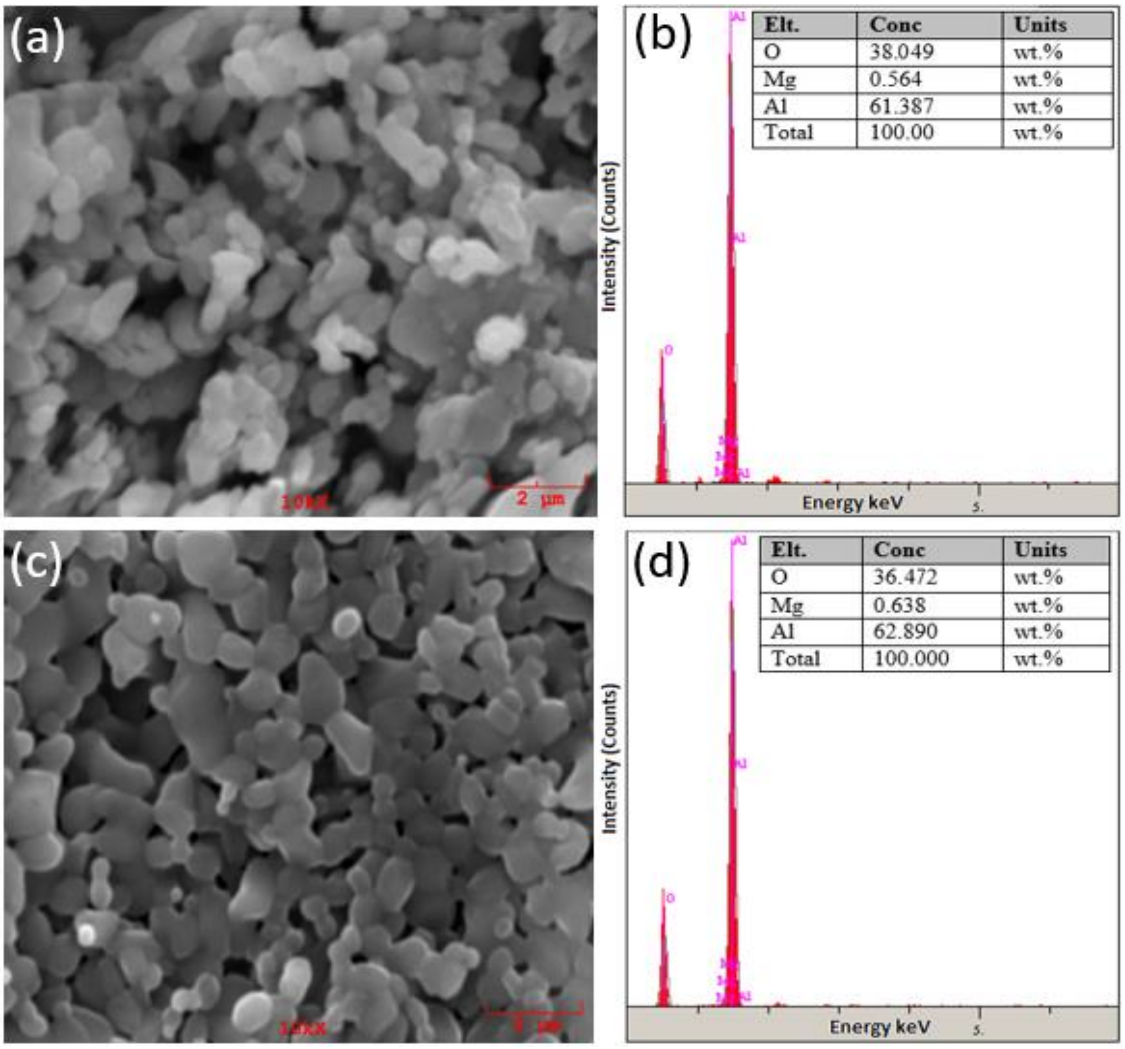


Figure 5. (a)-(c) SEM images of the ceramic composites sintered at 1400°C 6h obtained by tape casting method and powder metallurgy technique respectively. Fig. 5 (b)-(d) The EDS spectra of the surfaces ceramic composites sintered at 1400°C 6h obtained by tape casting method and powder metallurgy technique respectively.

4. CONCLUSIONS

The present investigation suggests two different aspects of production method α-Al_2O_3 – MgO ceramics. The effects of sintering time on the phase composition, densification and microstructure of MgO doped Al_2O_3 ceramic composites were studied. The main phase of the sintered ceramic composites was corundum (Al_2O_3) which are known biocompatible. It has been shown that different production method influences the morphological evaluation and the physical properties of sintered alumina based ceramics. The preferable technique for desired porous ceramics should be achieved by tape casting method, while the dense ceramics should be obtained by powder metallurgy technique. Bioceramics must have properties of osteointegration by means of vein growth in the structure for better scaffold and tissue interaction.

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