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Al_2O_3 Ceramics with Graded Porosity Produced from Natural and Artificial Pore Formers

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ABSTRACT

Al_2O_3 ceramics with graded porosity were produced by using corn starch and PMMA sphere as pore former additives (PFA). Graded porosity was obtained by uniaxially pressing the stacks of Al_2O_3 mixtures with and without PFA together. Pressed samples were heat-treated to remove PFAs at 600^{o}C and sintered at 1540^{o}C. Final porosity of graded ceramics produced from starch and PMMA were measured as 12 and 16%, obtained median pore size were 3 and 11 µm, respectively. The elastic moduli of the samples were measured by pulse-echo method and results showed that moduli values of the samples varied significantly depending on the PFA type. PMMA added samples had lower elastic moduli values than starch added ceramics as a result of higher pore size and interconnected pore structure. By using the pulse-echo method, the elastic properties of the graded samples couldn't be measured effectively.

Keywords: Graded porosity, alumina, pore former.

ÖZ

Aşamalı gözeneğe sahip Al_2O_3 seramikleri, gözenek oluşturucu ilave (GOİ) olarak nişasta ve PMMA kürelerin kullanılmasıyla üretilmiştir. Aşamalı gözenek, GOİ içeren ve içermeyen Al_2O_3 karışımlardan hazırlanan yığınların, tek eksenli preste birlikte preslenmesiyle elde edilmiştir. Preslenen numuneler, ilk olarak 600^{o}C'de ısıl işleme tabi tutularak GOİ'lerin uzaklaştırılması sağlanmış ardından 1540^{o}C'de sinterlenmiştir. Aşamalı gözeneğe sahip seramiklerin gözenek miktarı nişasta ve PMMA kullanılan seramikler için sırasıyla %12 ve 16 olarak ölçülmüştür. Gözenek boyutu yine sırasıyla 3 ve 11 µm olarak elde edilmiştir. Numunelerin elastik modülleri darbe-yankı yöntemi kullanılarak ölçülmüş ve sonuçlar GOİ türüne bağlı olarak modül değerlerinde önemli bir değişimin olduğunu göstermiştir. PMMA ilaveli numuneler, nişasta eklenen numunelere kıyasla, daha büyük gözenek boyutu ve bağlantılı gözenek yapısı nedeniyle daha düşük elastik modül değerlerine sahip olmuşlardır. Darbe-yankı yöntemi kullanılarak aşamalı gözeneğe sahip numunelerin elastik özellikleri verimli bir şekilde ölçülememiştir.

Anahtar Kelimeler: Aşamalı gözenek, alümina, gözenek oluşturucu.

1. INTRODUCTION

Porosity in the ceramic materials had been accepted as one of the main sources for the failure until it was discovered that they presented unique properties for some specific applications such as filters, membranes, substrates, insulators, biomaterials and drug delivery systems. Several techniques have been preferred to produce porous ceramics. Among these techniques pore former addition enables to control both pore size and pore volume of the final ceramic. Natural-artificial, organic-inorganic additives with low burning or pyrolysis temperature have been used for pore formation. PVC-PS-PMMA beads, starch, seed, naphthalene, salts and ceramic-metallic particles are the well-known examples. Thermal treatment, dissolution or leaching process can be used to remove PFAs from the ceramic body [1].

Graded porosity can be obtained by either changing the pore size or pore volume through the cross section of the ceramic sample. This pore structure provides a porous surface (higher porosity and/or larger pore size) and higher surface area for filter, membrane and substrate applications while dense base gives sufficient strength to the porous ceramics. The graded structure is also beneficial for bio-ceramics that have been used for osteoimplant application, as well. The porous upper part contributes the bone regeneration and dense lower part increases the mechanical properties of the bioceramic [2-3].

Several processes have been used to fabricate graded porosity; pressing, tape casting and slip casting. Li et al. used pressing process; they filled the die with powders with different stearic acid ratios layer by layer and compacted them [4]. Werner et al. produced multi-layer hydroxyapatite by multiple tape casting process instead of individual tape casting of the slurries and further stacking-laminating steps. In multiple tape casting, slurries with different pore former type and amount were cast one layer on top of the other after 24 hour drying step of the cast layer [5].

Wave motion measurement is one of the effective methods to obtain the elastic properties of ceramics besides stress-strain measurements. Transmission and reflection of the pulses are measured in pulse-echo method and this is a very convenient method the fact that small samples are used [6]. Pulse-echo method has been preferred to measure the elastic moduli of porous Al_2O_3 in several studies [7-8].

The study aims to achieve Al_2O_3 ceramics with graded porosity by dry pressing which is very common and simple method used for shaping ceramics and to characterize the produced ceramics for further potential applications.

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2. EXPERIMENTAL PROCEDURE

Al_2O_3 powder (Almatis, CT 3000 SG, d_{50}=0.5 μm), corn starch (d_{50}=21.9 μm) and PMMA spheres (d_{50}=44.9 μm) were used in this study. The particle size of Al_2O_3 powder and PFAs was measured by laser diffraction technique (Malvern, MasterSizer 2000). The amount of PFAs used was either 5 or 15 wt.% and the powder mixtures prepared via dry method by using mixer (Speed Mixer, DAC 150.1 FVZ) at 500 rpm for 1 minute. Prepared mixtures were firstly pressed solely, then graded samples were produced by filling the die with the stacks of pure Al_2O_3 powder, 5 wt.% of starch or PMMA and 15 wt.% of starch or PMMA. Pressing all layers was carried out at 50 MPa. The prepared compositions for the study are given in Table1.

Table 1. Prepared compositions

Composition	Al_2O_3 content (wt%)	PFA type and content (wt%)
A	100	-
A-S5	95	Corn starch, 5
A-S15	85	Corn starch,15
A-SG	93	Corn starch
A-P5	95	PMMA sphere, 5
A-P15	85	PMMA sphere, 15
A-PG	93	PMMA sphere

Controlled Pulser/Receiver) based on transmission and reflection of pulses throughout the samples. The details of the measurement are described in a previous study [9]. The velocity of the waves through the thickness of the samples was determined by Equation (1) [10].

$$\nu=(2d)/t \quad (1)$$

where d is the sample thickness (mm), t the ultrasonic wave's propagation time (ns) and ν the velocity of the wave (m/s). Standard velocity-elasticity relationships can be used to calculate the elastic and bulk moduli according to Equations (2) and (3).

$$E= [\nu_l^2\rho(1+ \sigma)(1-2\sigma)]/(1- \sigma) \quad (2)$$

$$K=E/[3(1-2\sigma)] \quad (3)$$

where ν_l is the longitudinal wave velocity (m/s), ν_s the shear wave velocity (m/s), E the Elastic modulus (pascals), K the bulk modulus (pascals), ρ the density (kg/m^3), σ the Poisson's ratio. Poisson's ratio was calculated from the relationship $\sigma=(1-2b^2)/(2-2b^2)$ where b equals to ν_s/ν_l [11].

3. RESULTS AND DISCUSSIONS

The optical microscopy images of PMMA sphere and corn starch are given in Fig. 1(a) and (b), respectively. According to images, PMMA sphere consists of ellipsoid grains and their size changes between 25-50 μm while starch has angular-like particles with a particle size around 15-25 μm.

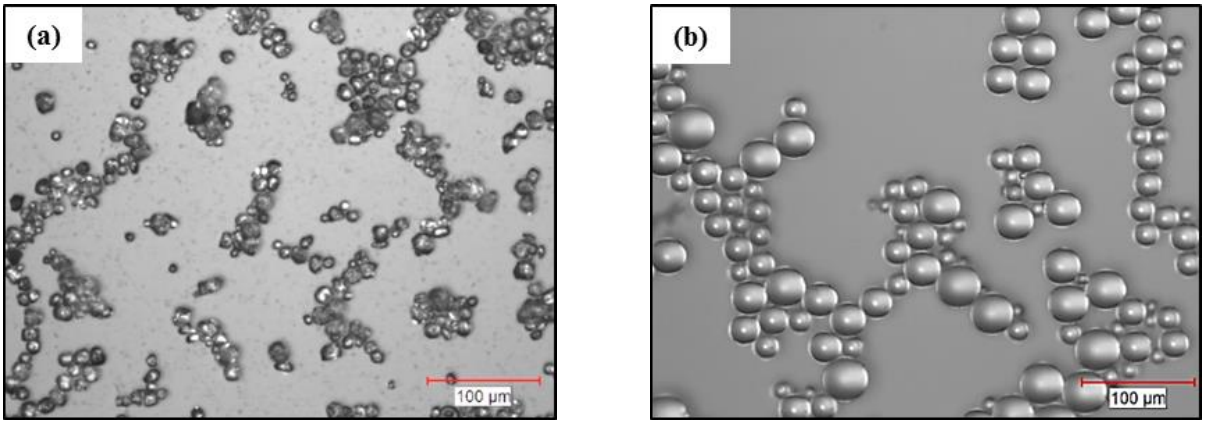

Figure 1. Optical microscopy images of (a) corn starch and (b) PMMA sphere

PFAs were removed by a heat treatment process at 600ºC for 1h and sintering was carried out at 1540ºC for 1h. Density of all samples was measured via Archimedes displacement method.

Mercury intrusion porosimetry (MIP) (Micromeritics, AutoPore IV 9500) was performed to characterize pore size and distribution of the graded samples. Starting powders and fracture surface of the samples were investigated by optical microscopy (Nikon, Eclipse) and scanning electron microscopy (SEM) (Zeiss Evo 50 EP).

Elastic properties were characterized via pulse-echo method (Olympus Panametrics, Model 5800 Computer

As seen from Fig. 2, nearly full densification was obtained for composition A, while porosity increased gradually with increasing PFA content for the other compositions. The porosity values of compositions with PMMA were higher than the compositions with starch since the PMMA spheres occupy larger volume compared to starch particles of equal weight. This is due to the lower density of PMMA compared to corn starch. The relative density of A-P15 was measured as 70.96% while it was 76.37% for A-S15. The obtained densities of graded samples were very close to the estimated values (the estimated density of A-SG was 3.46 and that of A-PG was 3.35 g/cm^3 as calculated from rules of mixtures).

The firing shrinkage values of the graded samples of A-SG and A-PG were measured as 16.8 %and 16.4%, respectively.

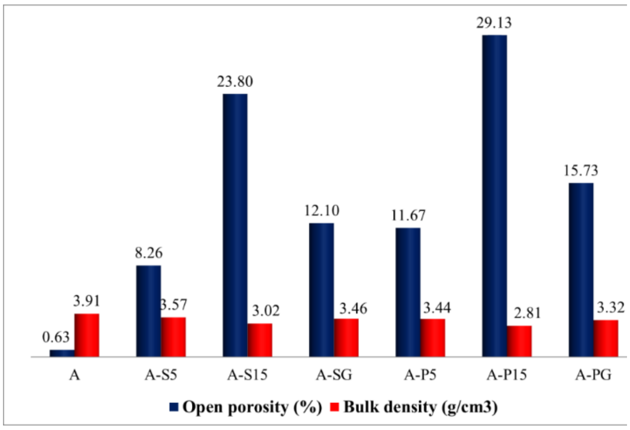

Figure 2. Open porosity and bulk density values of the Al_2O_3 ceramics

Pore size and its distribution for graded samples are given in Figure 3. Both of the samples had a bimodal pore size distribution and showing that two types of pores formed in the ceramics. Large pores (from 10 to 200 µm) were generated by the removal of PFAs and small pores (from 0.2 to10 µm) were produced between the primary Al_2O_3 particles. Median pore size was measured for A-SG as 3 µm and for A-SP as 11µm. Despite the coarser particle size of PFAs, measured pore size was smaller due to the measurement principle of mercury intrusion porosimetry (MIP). During the measurement, the actual pore size cannot be measured. The technique determines the size of throat or pore channels where the mercury intrusion begins. Therefore, smaller size is obtained by MIP than optical microscopy or SEM images.

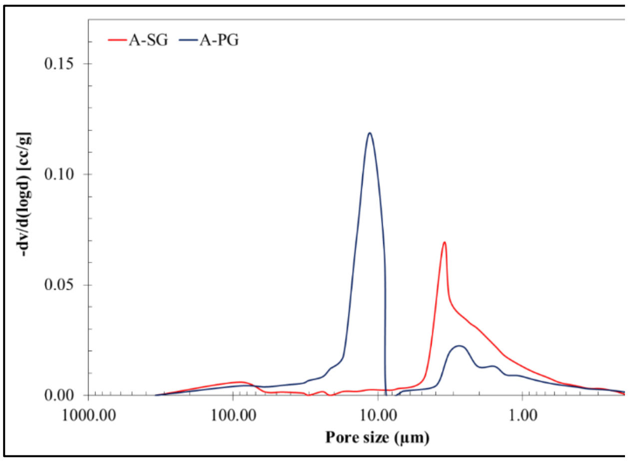

Figure 3. Pore size and distribution of graded samples

The microstructures of A-SG and A-PG are given in Fig. 4 (a)-(b) and the graded structures of both samples can be seen clearly. The porosity increases gradually from the lowest to the upmost layer. Porous part of the samples still contains dense regions (marked by arrows), non-uniform distributions of PFAs were obtained in spite of high mixing rate applied during the mixing process. The microstructure of A-PG has more porous regions than that of A-SG, since the volume of PMMA added was higher than that of starch, as mentioned before.

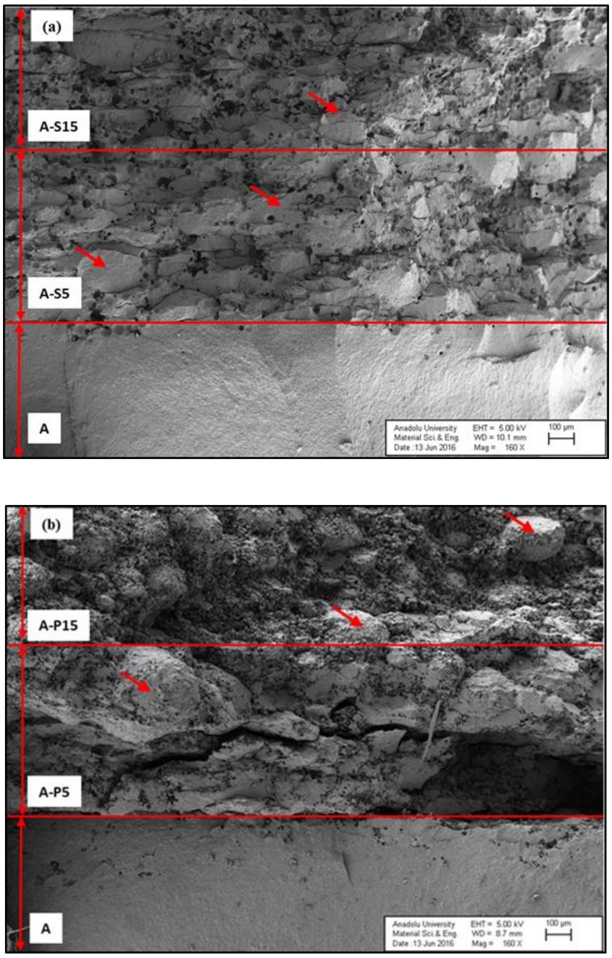

Figure 4. Microstructures of graded samples (a) A-SG and (b) A-PG

The elastic and bulk moduli of the samples as a function of porosity are given in Figure 5. The dashed lines represent starch added samples while solid lines represent PMMA added samples. The elastic and bulk moduli values of sample A were 350 GPa and 140 GPa, respectively. The values are comparable with those in previous studies. Deng et al. used pulse-echo method to measure the elastic modulus of dense and porous Al_2O_3 ceramics and elastic modulus value of dense sample was 390 GPa [8]. Elastic moduli of PMMA added samples showed a very abrupt decrease compare to the starch added samples. For A-S5 the elastic modulus was measured as 190 MPa, for A-P5 the value reduced to 30 MPa. Even though the porosity values of these two samples were almost same, the elastic modulus of A-P5 was lower as a consequence of the larger pore size and interconnected pore structure of the latter. Also, the pore shape had an important contribution to the properties. Starch produced isolated pores, while PMMA produced pores that tended to be connected and this might be the reason for the reduction in moduli values. Deng et al. measured the elastic modulus of the Al_2O_3 with 20% porosity as 200 GPa, Asmani et al. achieved elastic modulus values of about 220 GPa for Al_2O_3 ceramics having 18% porosity. The elastic values of starch added samples were close to those obtained in previous studies.

For graded samples, the echo signal could not be detected during measurements. Hence, elastic and bulk moduli of graded samples could not be measured.

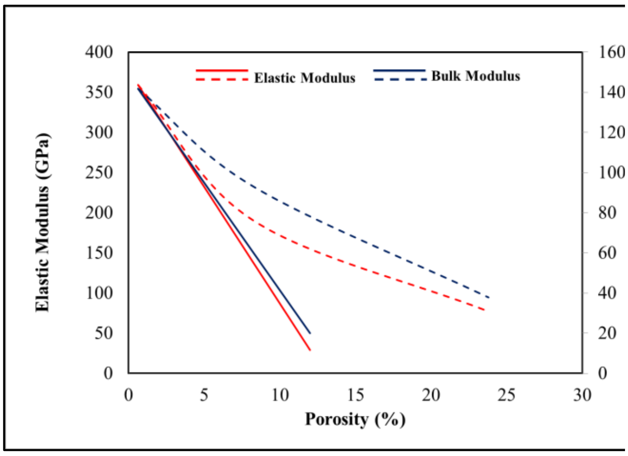

Figure 5. Elastic and bulk moduli of Al_2O_3 ceramics as a function of porosity (dashed lines represent starch added and solid lines represent PMMA added samples)

4. CONCLUSIONS

Porous alumina ceramics with graded porosity were produced by using starch and PMMA as PFAs. Gradient porosity was successfully obtained for both PFA type. The porosity values of the graded samples were 12 and 16% for A-SG and A-PG samples, respectively. Pulse-echo method was used to measure the elastic and bulk moduli of the porous samples. Depending on the PFA type, these properties showed significant differences. By using starch, an isolated pore structure of smaller pore size was obtained. The properties of starch containing samples showed relatively good agreement with those published in the literature. Pulse-echo method presented consistent results for the non-graded samples but it's not a feasible method for the graded samples.

5. REFERENCES

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