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EFFECT OF PARTICLE SIZE OF ALUMINUM ON THE DEVELOPMENT OF CLINOPTILOLITE BASED POROUS CERAMIC FILTERS

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ABSTRACT

This paper reports the effect of particle size of Al-metal powder addition on the development of clinoptilolite based porous ceramic filters. The clinoptilolite particles was mixed with 10 wt.% of Al-powder and the three different clinoptilolite-metal powder mixture samples were prepared namely: (i) coarse sample (used large size of Al-powder by mixing in dry ball mill for 5 min.), (ii) moderate sample (using fine size of Al-powder) and (iii) fine sample (planetary milling of the moderate sample in an aqueous medium for 1 hour). The mixtures were shaped by uniaxial pressing at 50 MPa and later sintered at the temperatures of 1200°C for 1 hour under air atmosphere. The microstructure and phase evolution were investigated by SEM and XRD, respectively. The coarse sample indicated corundum crystallization with silicon (Si) and with poor cristobalite crystallization. The cristobalite crystallization is prodominantly for the fine and moderate samples. Except the planetery milled sample (fine) the porosities of the samples were good enough (~28%) but the pore sizes were different; the coarse sample showed large pores up to 150 μm in size, the moderate sample produced relatively fine and narrow pore size distribution (4-65 μm). The results indicated that the moderate sample leads to production of ceramic filter with high selectivity during filtration.

Key words*:* *Porous ceramics, clinoptilolite, Al-metal powder, oxidation, corundum.*

KLİNOPTİLOLİT TABANLI SERAMİK FİLTRELERİN ÜRETİMİNDE ALÜMİNYUM TANE BOYUTU ETKİLERİ

ÖZ

Bu makalede, klinoptilolit tabanlı seramik filtrelerin üretiminde tane boyutu etkileri araştırılmıştır. Burada klinoptilolit tozları ağırlıkça % 10 Al tozu ile karıştırılmış ve üç farklı klinoptilolit-metal toz karışımı örneği hazırlanmıştır: (i) iri taneli numune (iri boyutlu Al tozları kuru olarak bilyalı değirmende 5 dakika boyunca karıştırılmıştır), (ii) orta taneli numune (ince boyutlu Al-tozu kullanılmıştır), ve (iii) ince taneli numune (orta taneli numune planetary değirmende 1 saat öğütülmesi ile hazırlanmıştır). Karışımlar, 50 MPa basınç değerinde tek eksenli presle şekillendirilmiş ve daha sonra oksijen atmosferde 1200°C'de 1 saat süre ile sinterlenmiştir. Mikroyapı ve faz gelişimi SEM ve XRD analizleri ile araştırılmıştır. İri taneli numunede, korundum, silisyum (Si) ve düşük oranda kristobalit fazında kristalleşme elde edilmiştir. İnce ve orta taneli numunelerde ağırlıklı kristallenme kristobalittir. Planetary değirmende öğütülmüş numunede gözeneklilik düşüş gösterirken iri ve orta boyutlu tanelerin kullanıldığı numunelerde gözeneklilik ~%28 oranındadır, ancak gözenek boyut dağılımları farklılık göstermiş ve iri boyutlu tanelerin kullanıldığı numunede 150 μm'ye kadar büyük gözenekler gözlenmiştir. Orta boyutlu tanelerin kullanıldığı numunelerde nispeten küçük ve dar bir aralıkta gözenek dağılımı elde edilmiştir (4-65 μm). Sonuçlar, orta boyutlu tanelerin kullanıldığı numunenin filtrasyon sırasında yüksek seçiciliğe sahip seramik filtrenin üretimine imkan sağladığını göstermektedir.

Anahtar kelimeler: *Gözenekli seramikler, klinoptilolit, Al-metal tozu, oksidasyon, korundum.*

1. INTRODUCTION

Interaction between some metal oxides and Al-metal powder during milling and sintering is well known processes where the reaction-bonded alumina process involves milling of a mixture of Al metal and various ceramic oxide powders followed by heat-treating of the compacted powders in air such that the metal is oxidised to small Al_2O_3 particles which sinter and thereby bond the large ceramic powder. [1-2]. Reaction sintering process leads to production of alumina based ceramics which are of high strength and hardness with high chemical stability. The fabrication of porous ceramics has been extensively studied with different ceramic powders such as the zirconium-aluminum powder [3], clay with Al and Mg powder [4], kaolin with Al-powder mixtures [5-6], kyanite-aluminum metal [7] and andulisite rich schist with aluminium powder [8].

The powder processing of the metal-ceramic powder mixture greatly determined the reaction efficiency as well as the properties of the final product. The mixture powders were prepared by dry-mixing [4, 6] or wet-milling [5, 7, 9]. The wet milling leads to hydrolysis or amorphization of the metal component, so as a nonpolar medium was preferred [10]. Besides the type of aqueous medium, the amount of metal additive, the milling time and sintering temperature in an air or inert atmosphere are the parameters to investigate. The amount of Al-powder additive used was generally up to 16 wt. %. The high aluminium ratio leads to a material with high open porosity and with highly improved hydrophilic nature [6]. The longer milling applied to the kaolin-aluminum powder leads to new phases such as; quartz, silicon and nacrite. On the other hand, the sample shaped and sintered at high temperature had less porosity due to the formation of glassy phase [5]. The applied sintering temperature greatly determined the microstructure as well as phase evaluation. Adding aluminum metal powder to kaolinite and hot processing in oxidizing atmosphere and with rapidly quenching in air to room temperature was studied for different temperatures. Significant corundum phase appeared at about the temperature up to 1000°C and gradually increased at 1200°C. High temperature led to mullite formation. The bodies obtained by reactive sintering at 1550°C had a high open porosity initiated during the oxidation of aluminum powder. The porosity increased when a small amount of magnesium powder was added. In spite of this high porosity the sintered bodies had a good mechanical cohesion. [4]. Attrition milling in an aqueous medium led to significant particle size reduction and developed homogeneity of the kyanite-aluminum powder mixture. Nearly half of the aluminum powder was oxidized during milling. During sintering up to 1600°C, the aluminum completely oxidized to alumina through both solid-state and liquid-state oxidation of the milled aluminum metal. This highly reactive alumina combined with the silica that was expelled during the decomposition of the kyanite. A dense, equiaxed fine-grain-size mullite was produced [7].

Natural zeolite are abundant raw materials in many countries, and was shown to gain interesting ceramic properties solely through high temperature (~1150ºC) phase transformations [4]. It is also known that ceramic powders may be produced from mineral powders through heat treatment in powder form so that they can be subsequently sintered into ceramic forms [5]. In light of these, it is the aim of this investigation to show how it is possible to obtain ceramic powders from the mixture of pure quartz and natural zeolite through heat treatment in powder form so that the ceramic powders can be advantageously used for fabricating microporous ceramic bodies which may have potential for filter applications. The composition of clinoptilolite contained high alkaline and alkaline earth metal cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and thus it has been used as a flux material for ceramic fabrication [11-13]. In this study, the fabrication of alumina based porous ceramic for solid-liquid separation is investigated from the mixture of clinoptilolite-Al-metal powders. The microstructure is studied for different size of Al-metal powder.

2. EXPERIMENTAL

The starting materials of this study were clinoptilolite-type natural zeolite (Manisa–Gördes–Turkey) and commercial pure aluminum. The composition of the zeolite was analyzed by X–ray fluorescence and listed in Table 1. The size of clinoptilolite was determined using a laser size analyzer (Malvern). The size of zeolite powder was of finer than 43 μm. Two different sizes of laboratory pure aluminum powders was provided by Aldrich such as fine size (δ_{90}=58 μm and δ_{10}=16 μm) and coarse size (δ_{90}=142 μm and δ_{10}=27 μm).

Table 1. The chemical composition of the zeolite (clinoptilolite) material and aluminium* (% wt.).

SiO_2	Al_2O_3	CaO	K_2O	MgO	Na_2O	Fe_2O_3	TiO_2	SO_3	P_2O_5	MnO
72.28	11.85	3.97	2.46	1.74	2.71	1.63	0.14	0.09	0.06	0.04

* high purity: 99 % wt.

The clinoptilolite powder was mixed with 10 wt.% of Al-powder and the three different clinoptilolite-metal powder mixtures were prepared namely: (i) coarse sample (used large size of Al-powder by mixing in dry ball mill for 5 min.), (ii) moderate sample (using fine size of Al-powder) and (iii) fine sample (planetary milling of the moderate sample in an aqueous medium for 1 hour). The milling was achieved using a RETSCH planetary ball-mill (PM 200) at 280 rpm and the slurry obtained was then dried at 100°C for 24 h. The samples were formed into a green body by uniaxial pressing in a cylindrical steel mould of 30 mm in diameter under a pressure of 50 MPa. Afterwards, the samples were sintered at 1200°C for 1 hour in air. The heating rates of the furnace were 10°C/min.

The crystalline phases of all the sintered samples were identified by X-ray diffraction (XRD) analysis using Rigaku Miniflex powder diffractometer. The measuring rate was of 2 °/min. and the interval was of 10°-70°. The microstructure of the samples was investigated by Nova NanoSEM 650 scanning electron microscope (SEM). Apparent porosity was measured by water immersion technique according to Archimedes' principle. Pore size distribution was measured by mercury porosimetry (Quantachrome pore master).

3. RESULTS AND DISCUSSION

In our previous study [13] it was found out that the clinoptilolite sintered at 1200°C indicated very poor formation of cristobalite and it was largely converted to an X-ray-amorphous material. In this study, the clinoptilolite with Al-metal powder mixture sintered at the same temperature showed different crystallization. It was determined that the crystallization was thermodynamically stable hexagonal closed-packed α–Al_2O_3 (corundum). However, the crystallization was greatly determined by the size of the Al-powder used. Figure 1 shows XRD spectra of the three different clinoptilolite-metal powder mixture samples which are namely the coarse sample (the large size of Al-powder to used), the moderate sample (being the fine size of Al-powder), and the fine sample (planetary milling of the moderate sample). The coarse sample indicated corundum crystallization and the fine and moderate samples showed predominantly the cristobalite crystallization. The secondary phase was Si and its crystallization was higher with the large size Al-powder. The results indicated that the process of Al-powder oxidation within the clinoptilolite matrix was greatly determined by the size of the metal powder and its crystallization. It is obvious that the milling in an aqueous medium led to oxidation of the metal powder [4]. Herein, the phases were similar for the fine and moderate samples. So it can be said that the fine size of Al-powder was good enough for the oxidation during sintering to produce silicate based material. The reaction between the Al powder and the clinoptolite was hindered with the size of the metal powder and thus the crystallization of the aluminium as corundum phase was higher.

The amount of apparent porosity for the samples was measured by Archimedes' technique. The apparent porosities were determined to be 28.00%, 28.13% and 17.05% for coarse, moderate and fine samples, respectively. Relatively low porosity was obtained with the fine sample. The use of fine size aluminium leads to a low porosity [6].

Figure 2 shows the SEM micrograph of the fracture surface of the coarse sample after pressing. The observed large sizes of particles are the Al-metal powders. Figure 3a-b show the SEM micrograph of a typical fracture surface of the sintered ceramic bodies is given where the samples formed from moderate sample (a) and coarse sample (b). According to the images, the oxidation and crystallization of the metal powder leads to open porosity [1]. The open pores can be seen in Figure 4a-b for the sample namely moderate (a) and coarse (b). It is obvious that the samples have no cracking in spite of the cristobalite crystallization (Fig. 1). It is known that the quartz and cristobalite have different thermal expansion coefficients. The cristobalite also shows a polymorphic transformation; the temperature at about 200°C instantaneously increased the volume by about 5%. The volume change creates microcracks and the mechanical strength of the materials is decreased [14-16].

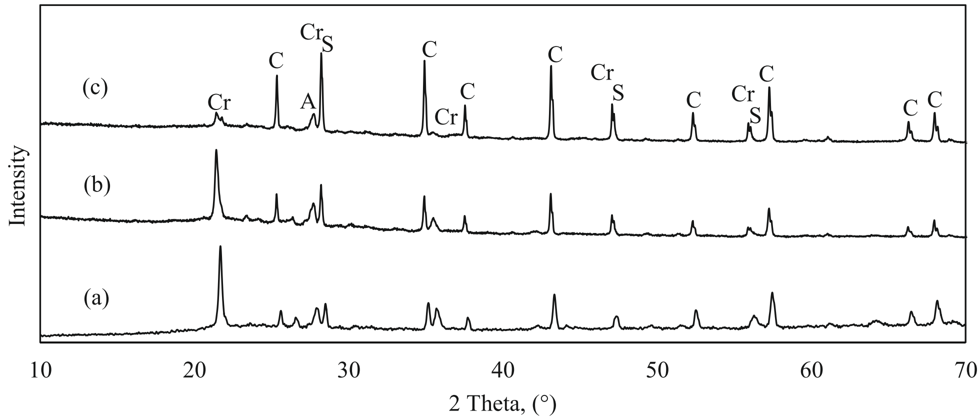


Figure 1. Representative XRD spectra of the clinoptilolite-Al-metal powder mixtures: a) fine sample, b) moderate sample and c) coarse sample [C: Corundum, Cr: Cristobalite, S: Silicon, A: Anorthite].

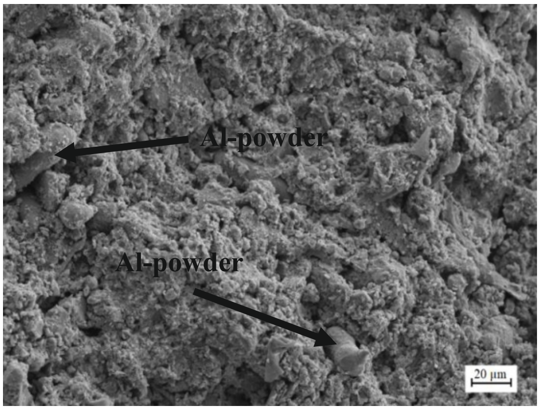


Figure 2. SEM image from the fracture surface of coarse sample-green body.

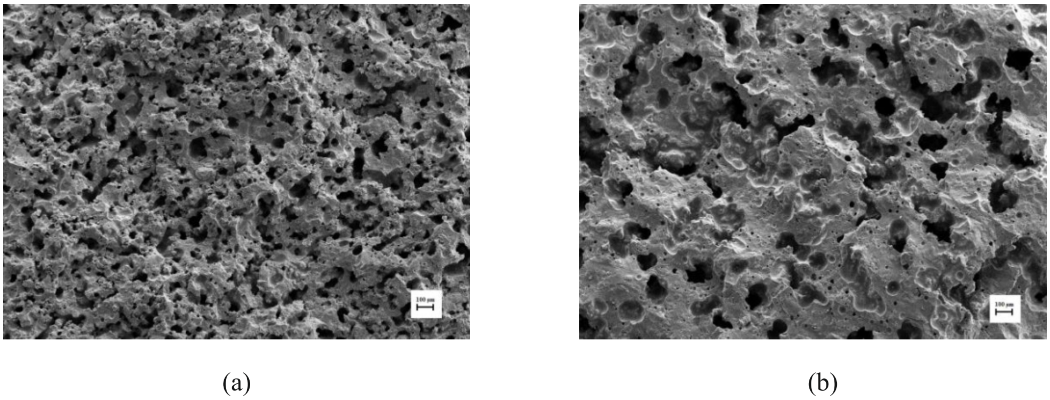
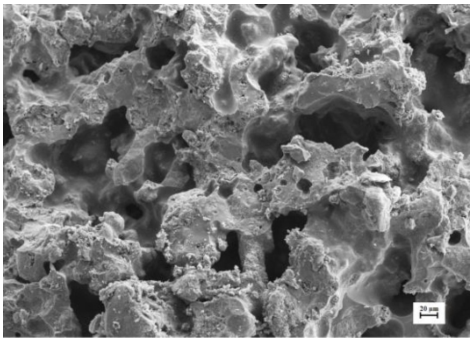
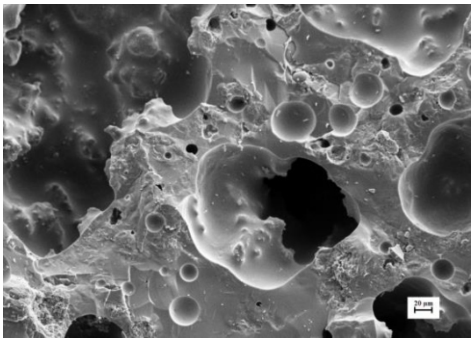


Figure 3. Representative SEM micrograph of a typical fracture edge of the ceramic bodies formed from a) moderate and b) coarse samples sintered at 1200°C.



(a)



(b)

Figure 4. Higher magnifications of the porous ceramics produced from a) moderate sample and b) coarse samples sintered at 1200°C.

Figure 5 shows the pore size distribution of the materials with coarse porosity (coarse pore size), moderate porosity (fine pore size) and fine porosity (relatively finer pore size). Mean pore sizes were about 50, 35 μm and 15 μm for the coarse, moderate and fine samples, respectively. All the samples displayed a monomodal pore-size distribution corresponding to macropores with very fine pores up to 5 μm which were located near the large pores produced due to the crystallization (Fig. 4).

It is well known that aluminium oxide film always present on the Al-particle surface and prevents the particles for furthermore oxidation. The thickness of the oxide film could be increased by milling of the Al-particles in an aqueous medium or applied heat treatment [4, 13]. The current study focused on the heat treatment of the Al-particles within the ceramic powder matrix such as clinoptilolite; the ceramic additive may increase the melting point of the Al-powder as well as the density of surface layer (Al_2O_3) formed by the oxidation [13]. The current results showed that the size of Al-metal powder was the basic parameter for achieving the crystallization as alumina based (corundum) or cristobalite as well as to produce a porous microstructure. The cristobalite based sample contained secondary phase as Si and corundum leads to production of preserving structure integrity.

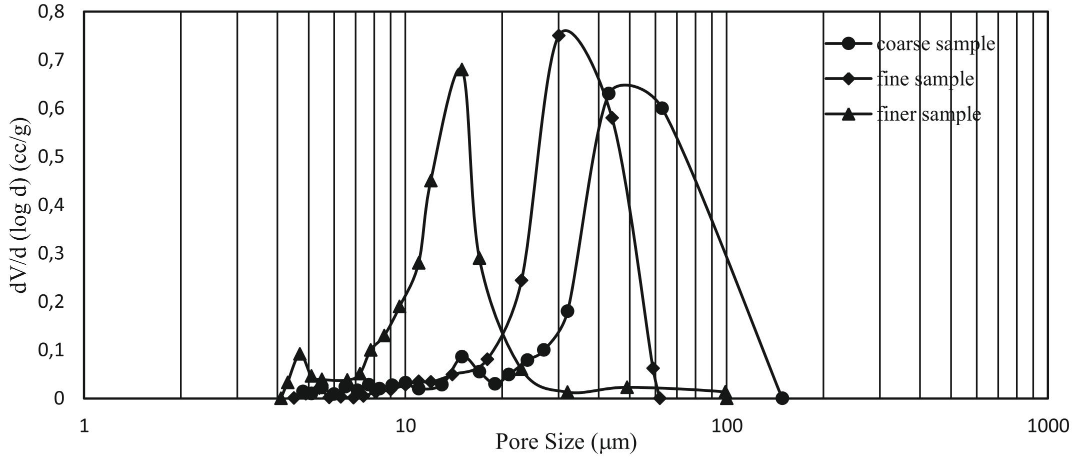


Figure 5. Pore size distribution of the porous ceramic prepared with a) coarse sample, b) moderate sample and c) fine sample.

4. CONCLUSIONS

Production of high performance porous ceramic filter was investigated from the mixture of silicate based ceramic powder (clinoptilolite) and 10 wt. % of Al-metal powder. The zeolite having high specific surface and it makes the material as high reactive during sintering and thus obtained Si component. The cristobalite-corundum and Si composition produced porous ceramic with no cracks. The size of aluminium powder determined the crystallization as well as pore size and distribution. High porosities (~28%) could be obtained with coarse and moderate samples but the moderate sample achieved high selectivity filter material for solid-liquid separation where relatively fine and narrow pore size distribution (4-65 μm) was obtained.

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