Preparation and Investigation of Alumina-Zeolite Composite Materials

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Abstract. In this research, alumina-zeolite composite materials were synthesised by mechanical activation and oxidation sintering technique. A comprehensive examination of the microstructure of the starting raw materials and the sintered ceramic specimens have been studied via X-ray diffraction (XRD) and scanning electron microscopy (SEM). Moreover, several properties were investigated such as volume shrinkage, density, porosity, weight loss and water absorption based on the compositions of the composite specimens, sintering temperature, and microstructure. The authors have found that the raw material compositions and the sintering temperature have great influence in the microstructure and the characteristic of the final prepared ceramic specimens.

Keywords: Ceramic composites, Zeolite, Alumina, Mechanical activation

1. Introduction

Generally, the research topics in ceramics and particularly in ceramic matrix composite have drawn a great deal of interest in recent years [1-34], due to the possibility of producing technical ceramic with fascinating properties and excellent performance compared with monolithic polycrystalline ceramics which suffer from inferior mechanical properties like a brittle fracture. Many studies have been done regarding ceramics strengthen ceramic-matrix composites (CMCs) which show not only enhanced mechanical characteristics like fracture toughness [35-36], mechanical strength [37-39], creep resistance [40] and wear resistance [41-42] but also exhibit better functional properties such as heat conductivity [43-44], optical behaviour [45] and magnetic characteristic [46-47]. Among CMCs, Ceramic strengthened alumina matrix composite has outstanding mechanical, thermal, and chemical properties. These interesting properties make alumina matrix composite material of preference for many applications, for instance, electronic substrate, refractories, wear resistance materials, bio-ceramic material, catalyst, and armour [48-49]. Although large studies have been conducted regarding alumina matrix composite only view are done concerning ceramic reinforced alumina matrix composite. Addition of zeolite as reinforcing element to alumina matrix could be interesting due to the special characteristics of the zeolites such as their large surface area, their high ions exchange capacity, good adsorption efficiency and their capability to host a secondary phase in their structure. These behaviours are attributed to the unique porous structure of the zeolites [50-51]. This work aims at preparation of alumina-zeolite ceramic composite materials via mechanical activation and oxidation sintering method.
The microstructure investigation of the raw materials and the final specimens have been performed using X-ray diffraction (XRD) and scanning electron microscopy (SEM), furthermore, the influence of raw materials composition, sintering temperature on the shrinkage, density, weight loss and porosity was examined. Preparation of these kinds of materials using available and relatively cheap raw materials could lead to the production of economically cost-effect materials with better characteristics.

2. Experimental methods

$\text{Al}_2\text{O}_3$ powder (98 %; MOTIM) and natural zeolite powder from Tokaj area (Hungary) were used as basic raw materials without any purification. Stichometric amount of these raw materials were properly mixed according to Table 1, the prepared mixture was milled using Retsch PM 400 planetary ball miller operated at 150 rpm for 20 minutes. The milled powders were pressed uniaxially via mechanical pressing using a pressure of 101.91 MPa to produce green ceramic discs with 25 mm in diameters and 10 mm in width. The prepared green discs were then sintered in a programmable electric furnace in a temperature range of 1100-1250 °C for a residence time of 3 hours and heat loading rate of 60 °C/h.

| Alumina % | Zeolite % |
|-----------|-----------|
| 90        | 10        |
| 80        | 20        |
| 70        | 30        |
| 60        | 40        |
| 50        | 50        |

2.1. Instrumental analysis

XRD investigation is done using Rigaku Miniflex II X-ray diffractometer designed in Bragg-Brentano geometry equipped with copper X-ray tube, operated using CuKα radiation (λ= 1.54184 Å) with scanning range of 20 between 0-70° and scanning rate of 1°/min with step size of 0.01016°, DIFFRACT measurement software was used for the computer-based examination. The mineralogical constituents, chemical composition and loss on ignition (LOI) of the natural zeolite resulted from XRD is shown in Table 2.

3. Results and discussion

3.1. XRD analysis

Figure 1 shows XRD diffractogram of the zeolite before and after milling, the difference in the intensities of the graphs is assigned to the difference in the shape and size of the particles of zeolite before and after mechanical milling. Table 2 exhibits the percentage of the composition and loss on ignition (LOI) of the zeolite in wt% resulted from XRD analysis. The largest amount of the mineral in zeolite was found to be silica (cristobalite) with 50% and then montmorillonite with 30% after that the other minerals with 20% of the total amount.

![Figure 1. XRD diffractogram of the naturally occurring zeolite](image)
Table 2. Mineralogical constituents and the chemical composition of the natural zeolite

|        | wt % | CaO | SiO₂ | Al₂O₃ | MgO | Na₂O | CO₂  | H₂O | Loss on ignition |
|--------|------|-----|------|-------|-----|------|------|-----|-----------------|
| Quartz | 8.00 | 8.00| 0.00 |       |     |      |      |     |                 |
| Cristobalite | 50.00 | 50.00| 0.00 |       |     |      |      |     |                 |
| Montmorillonite | 30.00 | 19.13 | 4.06 | 3.21 | 0.74 | 2.87 | 2.87 |     |                 |
| Calcite | 2.00 | 1.12| 0.88 |       |     |      |      |     |                 |
| Clinoptilolite | 10.00 | 5.79 | 1.89 | 0.57 | 0.88 | 2.87 | 1.75 |     |                 |
| Total   | 100.00 | 1.12 | 82.92 | 5.95 | 3.21 | 0.88 | 2.87 | 5.50 |                 |

A close investigation reveals that sintering at different temperatures produces ceramic specimens with different shrinkages and colours (Figure 2). This could be explained by recrystallization of zeolite which starts with dehydration that intensively occurs at about 450 °C and resulted in some physicochemical reactions which can noticeably change the microstructure.

![Figure 2](image-url)  
**Figure 2.** Samples with different composition sintered at (1100 °C, 1150 °C, 1200 °C and 1250 °C)

3.2. **SEM** investigation of the raw materials

The microstructures of the naturally occurring zeolite from Tokaj area (Hungary) and alumina are shown in Figure 3, zeolite has smaller grain size in the range of 0.5-25 µm compared to alumina which has a grain size varying from 0.5-50 µm [52].

![Figure 3](image-url)  
(a) (b)  
**Figure 3.** Secondary electron images of a) natural zeolite and b) alumina powder
Figure 4 demonstrates the fractured surface of the prepared ceramics specimens (50% zeolite-50% alumina) sintered at variable temperatures (1100 °C, 1150 °C, 1200 °C and 1250 °C), it can be clearly seen that sintering at higher temperature decreases the size of the pores of the prepared specimens, therefore, increase the density.

![Figure 4 SEM images](image)

**Figure 4.** SEM images of the fractured surface of 50% alumina-50% zeolite-sintered a) at 1100°C, b) at 1150°C, c) at 1200°C and d) at 1250°C

Figure 5. a exhibit the density measurements of the variable compositions of the alumina-zeolite samples sintered at varying temperatures. As the amount of alumina increased in the sample the density is gradually increased and this happening because alumina has higher density compared with zeolite. Moreover, increasing the sintering temperature leads to increase the density due to the decomposition of zeolite which normally happens above 1100 °C and leads to some physico-chemical reaction that closes the pores and therefore increase the density. The connection between the alumina composition and the shrinkage is illustrated in Figure 5. b, where the shrinkage is highly decreased as the alumina composition is increased and this could be attributed to the fact that alumina is stable even at higher temperature than 1300 °C and only zeolite is decomposing and recrystallizing below 1300 °C which make the specimens shrink. Figure 6. c and 6. d demonstrate apparent porosity and water absorption respectively, the two figures are quite similar to each other. They both show increasing in their value as the alumina composition increase, and decrease in their values as the sintering temperature increase and this because of the crystal growth of alumina requires higher temperature. The correlation between weight loss and alumina composition is shown in Figure 5. e. The weight loss is dramatically decreasing as the amount of alumina in the samples are increasing this because the largest amount of the weight loss is coming from zeolite which contains CO₂ and H₂O which evaporate at a relatively lower temperature.
Figure 5. The correlation between a) density, b) shrinkage, c) apparent porosity, d) water absorption and e) weight loss of prepared ceramic specimens based on alumina composition of the samples sintered at variable temperatures

4. Conclusion
To summarize, the properties of the final product are highly affected by the composition percentages and sintering temperatures. A remarkable change is observed in density, porosity, shrinkage, weight loss and colour of the produced specimens, this change in the characteristics of the different samples can be assigned to the physicochemical reactions which take place at relatively high temperature thanking to formation of mullite from zeolite-alumina mixture which should be confirmed later using XRD. The
data examined in this study could be used to control the microstructure and, hence, the properties of pre-sintered ceramic materials.

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