Mechanical properties of mullite reinforced ceramics composite produced from kaolin and corn starch

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Abstract

In this research, the authors have prepared mullite-containing ceramics by mixing Sedleky ml kaolin, Nabalox 315 alumina and corn starch as a bio-origin additive. Pellets were prepared from the mixtures using an uniaxial compression process. The pressed samples were pre-sintered at 1250 °C using oxidation and reduction atmospheres and then sintered at a temperature above 1400 °C in nitrogen gas. In this way, the typical carbothermal reduction and nitridation processes of clay minerals were performed, reinforced mullite ceramics were prepared and their main mechanical properties were investigated. Based on the obtained results, sintering in nitrogen gas resulted in a more wear-resistant surface layer.

Keywords: kaolinite, mullite, nitridation, reduction, wear resistance

Kulcsszavak: kaolinit, mullit, nitridálás, redukálás, kopásállóság

1. Introduction

The microstructure, properties and applications of the technical ceramics are greatly influenced by the production techniques [1-3]. Starting with the raw materials, relatively inexpensive natural materials can be used to achieve cost-benefit relationship, but the main drawback is the existence of some quantity of impurities in these raw materials [4-6]. Therefore, during the manufacturing of some high-tech ceramics and composite, high purity synthetic materials are usually used. The produced materials are normally made under special circumstances, for example, preparation of barium-titanate nanopowders through sol-gel method [7-9]. After the starting raw materials are selected, the next step is the formation and sintering process, then finishing the product. The main properties of the ceramics are significantly influenced by the applied temperatures and conditions of the heat treatment [10-12].

Mullite or mullite-containing ceramics can be made from different raw materials. The cost-effective way to produce the mullite phase is through thermal decomposition of kaolin or other aluminosilicates [13-15]. Mullite-based ceramics or high purity mullite ceramics can be formed by the reaction of free SiO₂ and Al₂O₃ [16-19]. By controlling the reaction conditions and heat treatment, a high-tech ceramic powder or products can be prepared from kaolin clay minerals. For example,

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through the carbothermal reduction reaction (CRR) or the carbothermal reduction and nitridation process (CRN). Using CRR or CRN method, silicon carbide (SiC), silicon oxynitride (Si₂ON₂), silicon nitride (Si₃N₄), SiAlONs and also aluminum nitride AlN can be prepared. In the CRN method, a mixture of various aluminosilicates, like kaolinite and active carbon or carbon black, as a carbon source is sintered at high temperature (1400-1650 °C) using flowing nitrogen gas to create the new crystalline or amorphous phases in the material [20-27]. These new phases and their microstructure can improve the mechanical properties of the mullite-based ceramics.

This research aims to produce mullite-containing ceramics with a reinforced structure during the sintering of kaolin-based ceramics using nitrogen gas above 1400 °C.

2. Materials and experiments

In this research, the authors prepared mullite-containing ceramics by mixing Sedleky ml kaolin, Nabalox 315 alumina and corn starch as a bio-origin carbon source additive. The kaolin was the main raw material. For making the mixtures, 10 wt.% alumina and other 0, 10, 20, 30 and 40 wt.% corn starch were added to the ceramic powders. The measured powders were milled and homogenized in a planetary ball mill, then cylindrical samples with a diameter of 25 mm were prepared by the uniaxial powder compression process. The pressed samples were pre-sintered at 1250 °C using oxidation (OX) and reduction (RED) atmosphere and then sintered at a temperature above 1400 °C using nitrogen gas (OX-NIT, RED-NIT).

Fig. 1 The abrasion wear resistance tester
1. ábra A kopásállóságmérő

In this way, partly the typical carbothermal reduction and nitridation processes of clay minerals were performed and mullite-based ceramic samples were prepared with a silicon nitride and SiAlON-reinforced surface layer. To compare the properties, a part of the samples was sintered in an oxidation

atmosphere at a temperature above 1400 °C (14 OX). The phase compositions of the sintered ceramics were determined by an X-ray diffractometer. Thereafter the mechanical properties of the samples such as micro-Vickers hardness (HV 0,1), abrasion resistance, compressive strength were investigated. During the abrasive wear test (Fig. 1), the sample was pressed to the rotating wheel by using a weight on the load arm. The role of the weight is to control the contact pressure. During the test, quartz sand was fed between the rotating wheel and the test sample through a feeder. After the specified times (5, 25 minutes), the sample was removed. The amount of material removed can be determined using the following formula:

$$V_{\text{worn}} = \frac{m_1 - m_2}{\rho_{\text{sample}}} \cdot 1000 \quad (1)$$

where V_{worn} is the worn volume loss [mm³], m_1 is the original weight of the sample [g], m_2 is the weight after the test [g], ρ_{sample} is the density of the sample [g/cm³] [28].

3. Results and discussions

The distinctive properties of the samples have changed after the different heat treatments. Fig. 2 shows how the color of samples is changed depending on the used sintering processes.

Fig. 2 The pressed samples after the pre-sintering and sintering processes
2. ábra A préselt minták az elő-szinterelési és szinterelési folyamatok után

The phase compositions of prepared samples were determined by using powder samples which were taken from the pressed samples after their heat treatment. The pre-sintered samples made without corn additive, were found to contain 43% mullite, 25% cristobalite, 1% quartz, 9% corundum and 22% X-ray amorphous based on the XRD analysis. Usually, increasing the amount of vegetable additive increase the amount of X-ray amorphous phase and decreases the amount of corundum and cristobalite phases. Using higher sintering temperature, the mullite crystal structure is changed and the amount of it increases from 43% to 70% because the Al_2O_3 from the corundum phase and the free SiO_2 which was formed during the thermal decomposition of kaolin will create more secondary mullite crystals. After the phase composition analysis of the powders, no significant difference was found between the compositions of the samples made with different production methods. But when the XRD analysis were done just on the surface of the sintered samples, some new crystalline phases (Fig. 3) can be found. After the reduction pre-sintering, the test samples have hercynite and SiC phases while during the nitridation sintering process, nitrogen-containing phases are formed like Si_2ON_2 and Si_3N_4 . The RED and RED-NIT type samples are containing 20-44% X-ray amorphous phases, which may hide additional nitrogen-containing nanocrystals. This is due to the fact that after the second heat treatment, the quantity of the measured X-ray amorphous phase is increased.

The amount of cristobalite phases was decreased when the added amount of corn additive increased. Therefore, the ceramics made with corn additive can contain higher amounts of nitrogen-containing phases.

Fig. 3 The phase composition on the surface of the sintered samples made with 40 wt.% corn additive

3. ábra A 40 tömeg% kukorica-adalékkal készített szinterezett minták felszínének fázisösszetétele

During the research work, three characteristic mechanical properties of the samples were investigated after each sintering method. Based on the results, the mechanical properties of the ceramic samples have been carried out after the nitridation sintering. Fig. 4 shows the micro-Vickers hardness of the ceramic samples as a function of their porosity which was determined through Archimedes water absorption test. Different colors indicate the type of the sintering methods in the Figure: black – oxidation, red – reduction pre-sintering, blue – oxidation pre-sintering and nitridation sintering, green – reduction pre-sintering and nitridation sintering and finally turquoise – oxidation sintering. Generally, the micro-hardness of sintered mullite ceramics is twice the hardness of the original pre-sintered sample. Samples pre-sintered in the oxidation atmosphere have the lowest hardness. During the reduction pre-sintering, carbon-containing phases like SiC particles have formed. These SiC particles increase the micro hardness of the ceramic samples. The micro hardness value of the samples sintered at 1450°C (14 OX) is lower than that obtained after the nitridation sintering.

Fig. 4 The micro-Vickers hardness as function of porosity of the ceramic samples

4. ábra A mikro-Vickers keménység a kerámi minták porozitásának függvényében

Fig. 5 shows the worn material volume after different abrasion time (5 and 25 minutes) as function of the porosity

of the sintered samples. As the value of porosity increases, the volume of material worn per unit time increases. Especially in the case of reduction pre-sintering, the wear of ceramic samples increases dramatically. However, there is a significant improvement, thanks to the nitridation sintering. With a longer wear time, the same amount of wear can be measured for example, in the case of oxidation pre-sintering, the volume of material worn during 5 minutes of wear is the same as in the case of nitridation sintering after 25 minutes. In the case of reduction pre-sintering and nitridation sintering, the difference is even greater due to the high wear of the pre-sintered samples. As a result of nitridation sintering, the authors were able to produce mullite-based ceramic samples with higher wear resistance characteristics.

Fig. 5 The worn material volume of the ceramic samples after 5- and 25-minutes abrasion time

5. ábra A kerámi minták kopott anyagmennyisége 5 és 25 perces koptatási idő után

Fig. 6 shows the change in compressive strength according to the change in porosity. An increase in porosity (less dense ceramic sample) has a negative effect on the mechanical strength. The compressive strength values of the samples prepared by the oxidation pre-sintering method are almost independent of the amount of corn additive. In comparison, the reduction pre-sintering significantly increases the compressive strength of the prepared ceramic samples, but with increasing the porosity of samples, their strength will decrease. For the specimens made without corn, the average strength of the

ceramics increased from 63 MPa (OX) to 215 MPa (RED). This improvement in strength is due to a new microstructure created by sintering in the reduction atmosphere. As a result of nitridation sintering, there is a further improvement in compressive strength.

Fig. 6 The compressive strength of the ceramic samples
6. ábra A kerámiaminták nyomószilárdsága

4. Conclusions

Pre-sintering in the reduction atmosphere has formed carbides (SiC) in the structure of the mullite ceramics; because of this, the ceramics have higher micro hardness (HV 0,1) and strength. During the high-temperature nitridation sintering the mullite crystal structure has changed and different nitrogen-containing phases are formed on the surface of the mullite-based ceramic samples depending on the quantity of the corn additive. The properties of the pre-sintered ceramic specimens have significantly improved after the sintering in nitrogen gas. Based on the results, the authors have successfully produced mullite ceramics with a mechanically wear resistant surface layer which are containing silicon nitride, by using high temperature (> 1400 °C) sintering in nitrogen gas.

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