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EFFECT OF MECHANICAL ACTIVATION ON MULLITE FORMATION IN AN ALUMINA-QUARTZ CERAMICS SYSTEM

VPLIV MEHANSKE AKTIVACIJE NA NASTANEK MULLITA V KERAMIČNEM SISTEMU GLINICA-KREMEN

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Powder mixtures of alumina and quartz were being mechanically activated in a planetary mill for 2 h. Both non-activated and activated samples were sintered at different temperatures (1250, 1300, 1325, 1350 and 1375) °C for (1, 2, 3 and 5) h and the formation of a mullite phase was examined with an X-ray diffraction analysis. It was determined that the mechanical activation increased the quantity of the mullite phase.

Keywords: mullite, mechanical activation, amorphization, X-ray diffraction, alumina, quartz

Mešanice prahov glinice in kremena so bile 2 h mehansko aktivirane v planetarnem mlinu. Neaktivirani in aktivirani vzorci so bili sintrani (1, 2, 3 in 5) h pri različnih temperaturah (1250, 1300, 1325, 1350 in 1375) °C), z rentgensko difrakcijsko analizo pa je bil preiskovan nastanek mullitne faze. Ugotovljeno je bilo, da mehanska aktivacija poveča količino mullitne faze.

Ključne besede: mullit, mehanska aktivacija, amorfizacija, rentgenska difrakcija, glinica, kremen

1 INTRODUCTION

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is an important ceramic phase in conventional ceramics (such as tableware, construction ceramics and refractories), advanced high-temperature structural materials, heat exchangers, catalysator convertors, filters, optical devices and electronic packaging materials. However, mullite suffers from its relatively low fracture toughness which limits its application in industrial use. The conventional route for the preparation of mullite is the solid-state reaction between alumina and silica, which is controlled with diffusion. The mullite formation with this method takes place at a relatively high temperature (>1500 °C). The mullitization temperature and the morphology of mullite particles depend on the particle size of the initial raw materials and the preparation of the precursors before sintering. Mullite has been synthesized in many ways like simple sintering of alumina and silica powders, sol-gel method, co-precipitation, hydrothermal and chemical-vapor-deposition processes. The mullitization temperature is as high as 1600 °C for the conventional fabrication method, i.e., the solid-state reaction of high-purity alumina and quartz.[1–3]

Mechanical activation of starting materials is a promising method for a precursor preparation. The particle-size reduction, which increases the contact surfaces between the particles, is a direct consequence of milling. Also, the energy of the system increases resulting in a decrease in the reaction temperature.[4] Different processes can remarkably influence the reactivity of the solids. Particularly, the mechanical treatments are important as long as they can help to produce the changes in the texture and structure of the solids. In many cases, these alterations in the structure cause certain modifications in the phases formed with a thermal treatment of the solids that were mechanochemically treated.[5,6]

In this work, the effects of mechanical activation on structural disordering (amorphization) in an alumina and quartz ceramics system and a formation of mullite were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2 EXPERIMENTAL METHODS

Alumina and quartz were supplied from the Çelvit Ceramic Company, Turkey. The chemical composition of alumina is 99.425 % Al_2O_3, 0.52 % SiO_2 and 0.055 % Na_2O. The composition of quartz is 99.1 % SiO_2, 0.28 % Al_2O_3, 0.16 % CaO + MgO, 0.17 % K_2O + Na_2O, 0.05 % Fe_2O_3, 0.05 % TiO_2 and 0.19 % LOI. Alumina and quartz were mixed to obtain the appropriate stoichiometric ratio according to the chemical formula of mullite ($3Al_2O_3 \cdot 2SiO_2$) in ashless rubber-lined ceramic jars for 2 h using zirconia balls and distilled water as the milling media. After drying, the mixture was made in a high-energy planetary ball mill (Fristch) with a rotation speed of 600 r/min. The ball-to-powder weight ratio was adjusted to 20. The precursor milling was carried out for 2 h. An

X-ray diffraction analysis was performed using a Rigaku Ultima X-ray diffractometer and CuKα radiation. A Joel 6060 LV scanning electron microscope was used for the morphological analysis of non-activated and activated mixed powders. The degree of amorphization (A/%) of the mechanically activated powder was calculated from equation (1):[7,8]

$$\%A = \left[1 - \frac{B_0 I_x}{B_x I_0}\right] \times 100 \quad (1)$$

where I_o is the integral intensity of the diffraction peak for the non-activated mixture, B_o is the background of the diffraction peak for the non-activated mixture and I_x and B_x are the equivalent values for the mechanically activated mixture. After the activation, both non-activated and activated powders were sintered in an electrical furnace with a heating rate of 10 °C/min at (1250, 1300, 1325, 1350 and 1375) °C for (1, 2, 3 and 5) h and the formulation of the mullite phase was examined with XRD. In addition, the degree of mullite crystallization (C/%) of non-activated and activated powders at different firing temperatures and times was calculated from equation (2):

$$\%C = \left[\frac{B_0 I_x}{B_x I_0}\right] \times 100 \quad (2)$$

where I_o is the integral intensity of the diffraction peak for the reference mullite powders, B_o is the background of the diffraction peak for the non-activated mixture and I_x and B_x are the equivalent values for the mullite crystallization (the reference mullite is Nabaltec mullite and the JCPDS card number is 01–079–1454). The integrated intensity of the (121) XRD reflection (2θ from 40.5° to 41.5°) was measured to determine to content of the mullite phase.

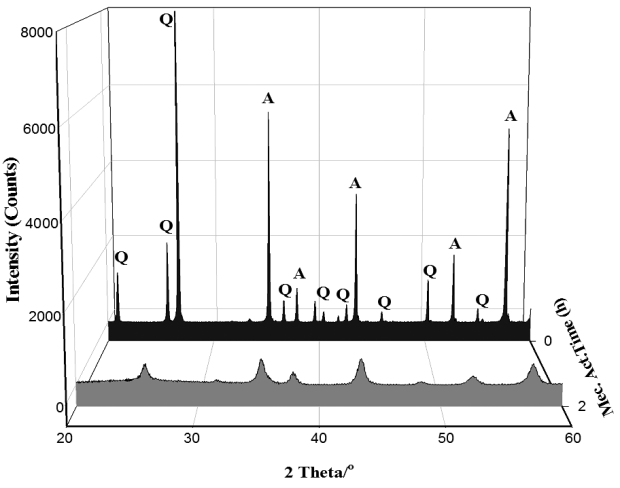

Figure 1: XRD patterns of non-activated and activated alumina-quartz powders (A: alumina, Q: quartz)

Slika 1: XRD-posnetek neaktiviranega in aktiviranega prahu glinica-kremen (A: glinica, Q: kremen)

3 RESULTS

3.1 Structural changes in the activated alumina-quartz mixture powders

The X-ray diffraction analysis of non-activated and activated mixture powders is given in **Figure 1**. A comparison of the peaks from the two diffraction patterns shows that all the diffraction peaks get shorter after a mechanically activation. This reflects the partial amorphization and structural disordering in alumina and quartz. Mechanical activation has already been reported to amorphize materials.[8]

The scanning electron micrographs (SEM) of non-activated and activated alumina and quartz mixture powders can be observed in **Figure 2a**, **b**. The particle size in the non-activated mixture is over 5 μm (**Figure 2a**). After the mechanical activation, the mixture of the powders is agglomerated. The degrees of amorphization of alumina and quartz were founded to be approximately 70 % and 85 %, respectively.

3.2 Mullite formation

Figure 3a, **b** shows the XRD patterns of non-activated and activated quartz-alumina mixture powders fired at 1250 °C and 1375 °C for 60 min. It is found that the intensity of the mullite phase in the activated sample increases. **Figure 4a**, **b** shows the mullite content of the non-activated and activated quartz-alumina mixture powders sintered at 1250–1375 °C for different times. In the samples sintered at 1250 °C for 60 min, the mullite content gradually increased from mass fraction 8.13 % to 45 % during the activation. On the other hand, when they

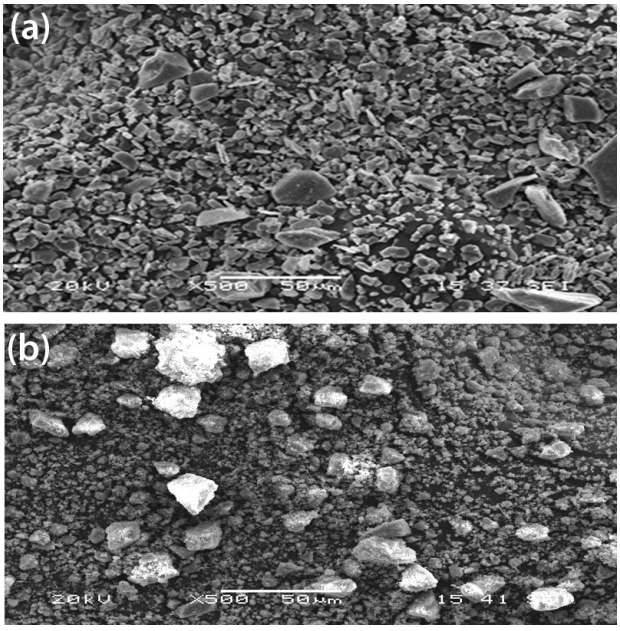

Figure 2: SEM micrographs of: a) non-activated and b) activated alumina-quartz powders

Slika 2: SEM-posnetek: a) neaktiviranega in b) aktiviranega prahu glinica-kremen

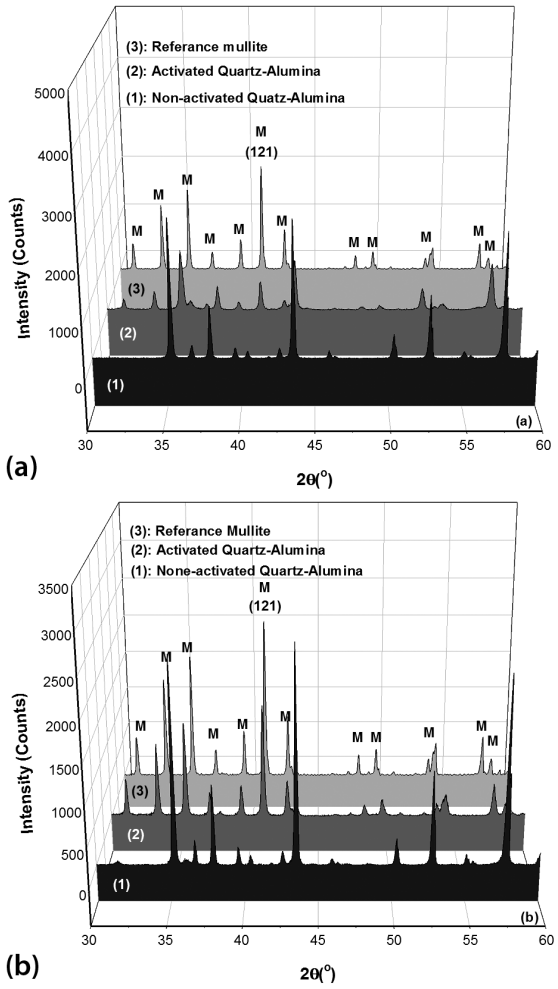

Figure 3: Comparison of the XRD patterns for the reference mullite with the XRD patterns for non-activated and activated quartz-alumina mixtures fired at: a) 1250 °C for 60 min and b) 1375 °C for 60 min

Slika 3: Primerjava XRD-posnetkov referenčnega mullita z XRD-posnetki neaktivirane in aktivirane mešanice kremena in glinice: a) 60 min segrevanega na 1250 °C in b) 60 min segrevanega na 1375 °C

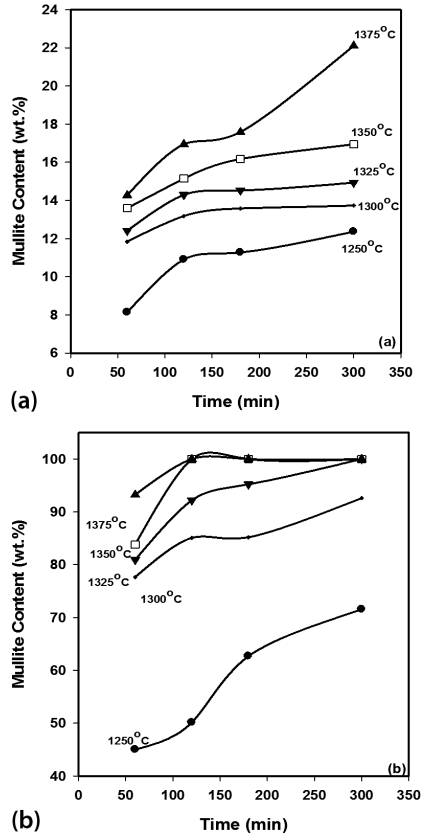

Figure 4: Mass fractions of the mullite content in: a) non-activated and b) activated sintered samples

Slika 4: Masni deleži mullita v: a) neaktiviranih in b) aktiviranih sintranih vzorcih

were sintered at 1375 °C for 60 min, the mullite content increased from 14.2 % to 92.3 % during the activation.

Mechanical treatment in a high-energy mill generates a stress field within the solids. Stress relaxation can occur via several mechanisms: (1) heat release, (2) development of a surface area as a result of the brittle fracture of the particles, (3) generation of various sorts of structural defects and (4) stimulation of chemical reactions within the solids. All of the relaxation channels cause changes in the reactivity of the solid substance that is under treatment, which is why the resulting action is called mechanical activation.[9] The concentration of the mechanically induced defects and their spatial distribution depend upon the condition of the energy transfer in the mill. The creation of defects enhances the stored energy in the solids and consequently causes a decrease in the activation barrier to further processing of the solids.[10]

4 CONCLUSION

The effect of mechanical activation on mullite formation in a quartz-alumina ceramics system was studied by using XRD and SEM. The mechanical activation caused amorphization and structural disordering of the quartz-alumina mixture. The degree of amorphization of quartz and alumina were found to be approximately 70 % and 85 %, respectively. The application of high-energy milling allowed a dramatic change in the structure and surface performance of alumina and quartz, so the content of mullite was increased with mechanical activation.

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