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EFFECT OF MECHANICAL ACTIVATION ON THE SYNTHESIS OF A MAGNESIUM ALUMINATE SPINEL

VPLIV MEHANSKE AKTIVACIJE NA SINTEZO MAGNEZIJ-ALUMINATNEGA ŠPINELA

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A magnesium aluminate spinel powder (72 % Al_2O_3 & 28 % MgO) was prepared with mechanical activation. Samples were sintered in a temperature range of 1400–1750 °C. The final sintered products were characterized with densification, phase and microstructural analyses and a hardness measurement to evaluate the influence of mechanical activation on the synthesis of a magnesium aluminate spinel.

Keywords: mechanical activation, magnesium aluminate spinel, ceramic, sintering, densification, mechanical properties

Prah magnezij aluminatnega špinela (72 % Al_2O_3 & 28 % MgO) je bil pripravljen z mehansko aktivacijo. Sintranje vzorcev je bilo izvedeno v temperaturnem območju 1400–1750 °C. Na končnih sintranih vzorcih je bila določena zgostitev, opravljena je bila analiza faz in mikrostrukture ter meritev trdote, da bi ocenili vpliv mehanske aktivacije na sintezo magnezij- aluminatnega špinela.

Ključne besede: mehanska aktivacija, magnezij-aluminatni špinel, keramika, sintranje, zgoščevanje, mehanske lastnosti

1 INTRODUCTION

Magnesium aluminate spinel ($MgAl_2O_4$, MA) is a widely used refractory material due to its high-temperature properties, mechanical resistance, thermal-shock resistance and high corrosion resistance to acidic and basic slags.[1,2] MA spinel has a high melting point (2135 °C), high hardness (16.1 GPa), relatively low density (3.58 g/cm^3), high strength (180 MPa) at room and at elevated temperatures, high chemical inertness, a low thermal-expansion coefficient (9×10^{-6}/°C between 30 °C and 1400 °C) and high thermal-shock resistance.[3]Also, MA spinel refractories are very attractive due to their environmental friendliness, contrary to magnesium chromite refractories. However, aspinel formation is accompanied by a 5–7 % volume expansion which does not allow it to densify in a single-stage firing.[4] Therefore, the synthesis of spinel and fabrication of spinel refractories were not feasible with commercial methods due to the difficulty with sintering.[1,2] High-purity spinel was synthesized mostly with hydrothermal techniques, sol-gel, spray plasma, cool drying, controlled hydrolysis, co-precipitation, mechanical activation and the aerosol method.[1]

Mechanical activation is a method, which can induce changes tothe solid-state properties, such as the distortion of the structure, accompanied by the accumulation of energy and the formation of active centers on the newly formed surfaces.[5] Different processes can remarkably influence the reactivity of solids. Mechanical treatments are particularly important as long as they can help to produce changes to the texture and structure of the solids. In many cases, these alterations tothe structure cause certain modifications to the phases formed due to the thermal treatment of the solids, which were mechanochemically treated.[6]

The main aim of this study was to prepare a magnesium aluminate spinel by firing between 1400–1750 °C and to analyze the effect of mechanical activation. Investigations of the phases, crystal morphology and densification of the fired products were carried out. In addition, the hardness values of the samples for different sintering temperatures were studied.

2 EXPERIMENTAL DETAILS

Al_2O_3 (72 % of mass fractions) and MgO (28 % of mass fractions) powders were ball milled with alumina balls in a polyethylene bottle for 1 h. The mixture was made in a high-energy planetary ball mill (Fristch) at a rotation speed of 600 min^{-1}. The ball-to-powder weight ratio was adjusted to 20. Milling of the precursor was carried out for 1 h. Activated and non-activated powders were uniaxially pressed to form pellets at 255 MPa. The pellets were sintered in the temperature range of 1400–1750 °C for 1 h. An X-ray diffraction analysis was performed using a Rigaku Ultima X-ray diffractometer. A Joel 6060 LV scanning electron microscope was used for the morphological analysis of the non-activated and activated powders and sintered samples. The hardness

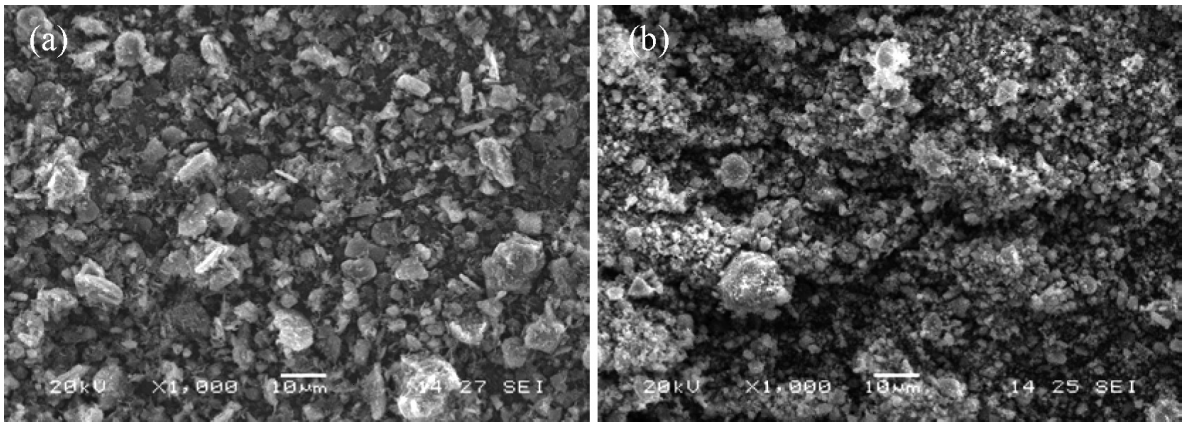

Figure 1: SEM micrographs of powder mixtures: a) non-activated, b) activated for 1 h
Slika 1: SEM-posnetka mešanice prahu: a) neaktiviran, b) aktiviran 1 h

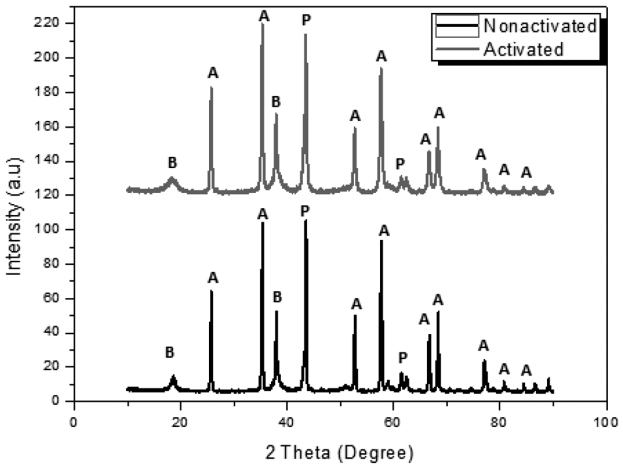

Figure 2: XRD patterns of non-activatedand activated powder mixtures of MgO and Al_2O_3(A: Al_2O_3, B: $Mg(OH)_2$, P: MgO)
Slika 2: Rentgenograma neaktivirane in aktivirane mešanice prahu MgO in Al_2O_3 (A: Al_2O_3, B: $Mg(OH)_2$, P: MgO)

measurements of the samples were done using Leica Microsysteme GmbH. The apparent porosity and bulk density of the sintered samples were measured with the liquid-displacement method using Archimedes'principle. Water absorption was alsoinvestigated.

3 RESULTS AND DISCUSSION

Figure 1 shows SEM micrographs of non-activated and activated powder mixtures. The non-activated powder mixture has well-defined faces and edges. However, the particle size decreases and the particle shape becomes round with mechanical activation.

Figure 2 shows XRD patterns of the non-activated and activated powder mixtures of MgO and Al_2O_3. As a result, $Mg(OH)_2$, Al_2O_3 and MgO peaks are observed.

SEM micrographs of the fractured surfaces of all the samples sintered in the temperature range of 1400–1750 °C for 2 h are shown in **Figure 3**. It can be seen that all the samples appear to be relatively dense

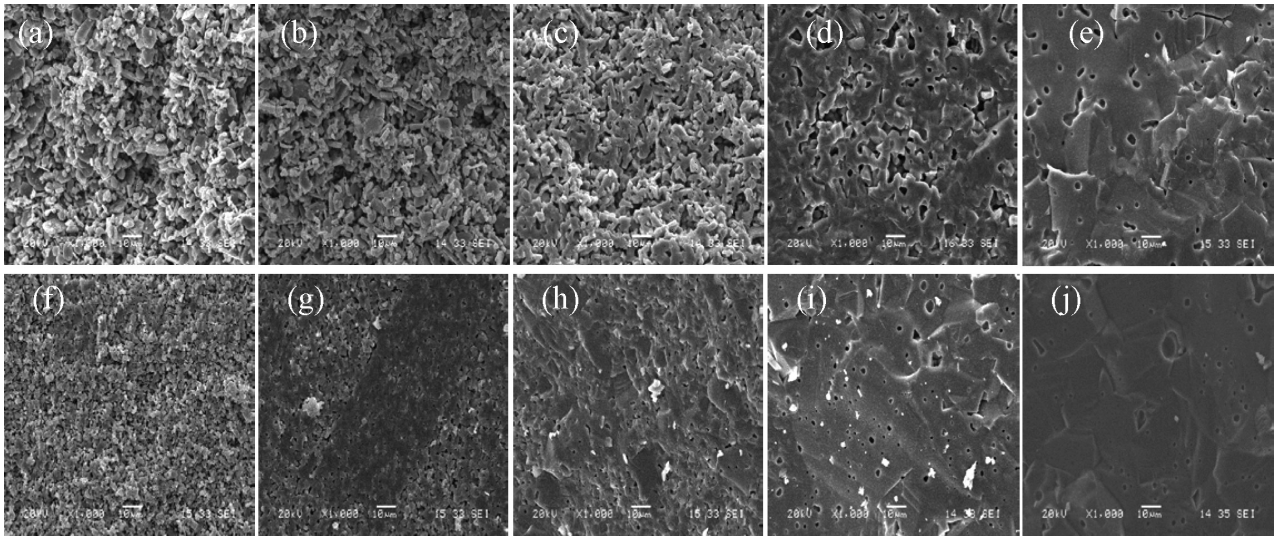

Figure 3: SEM micrographs of all sintered samples prepared from: a), b), c), d), e) non-activated and f), g), h), i), j) activated powder mixtures
Slika 3: SEM-posnetki vseh sintranih vzorcev pripravljenih iz: a), b), c), d) , e) neaktivirana in f), g), h), i), j) aktivirana mešanica prahu

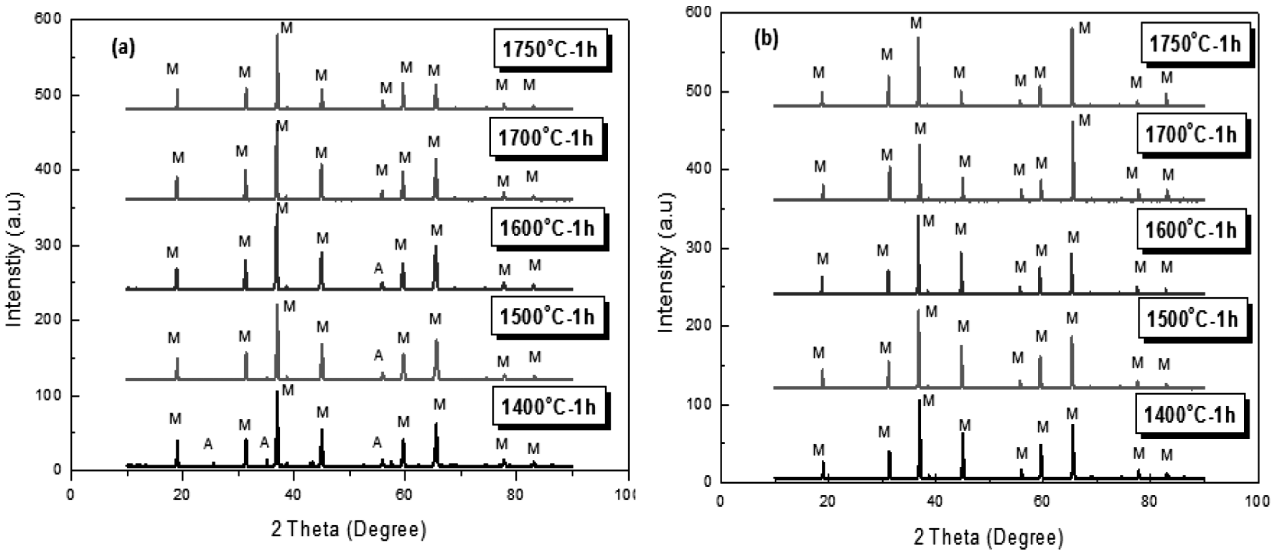

Figure 4: XRD patterns of: a) non-activated and b) activated samples sintered at different temperatures for 2 h(M: $MgAl_2O_4$, A: Al_2O_3)
Slika 4: Rentgenogrami: a) neaktivirani in b) aktivirani vzorci sintrani 2 h na različnih temperaturah (A: Al_2O_3, M: $MgAl_2O_4$)

with the increasing sintering temperature and mechanical activation. After the sintering at 1700 °C, spinel grain growth was found for the non-activated and activated samples. However, porosity levels seem relatively higher for the non-activated samples.

Figure 4 shows the XRD patterns of the non-activated and activated samples after the sintering in the temperature range of 1400–1750 °C for 2 h. These confirm that the Mg-Al spinel is the only phase of the activated samples. However, Al_2O_3 peaks are also present at 1400 °C for the non-activated samples.

Figure 5 summarizes the bulk density and apparent porosity of all the sintered samples. A general trend in the increasing bulk density and decreasing apparent porosity with the increasing sintering temperature was observed. The mechanically activated samples showed relatively higher density values compared to those of the non-activated samples. On the other hand, the mechanically activated samples obtained a lower apparent porosity than the non-activated samples. The sintered bulk density and apparent porosity ofthenon-activated and activated samples are 3.76 g/cm^3 and 3.1 g/cm^3, respectively.

The reduction of the particle size decreases the distance between the vacancy sites (or betweenthegrain boundaries) and enhances the vacancy diffusion to the surface, thus increasing the densification. The reduction of the particle size is obtained with mechanical activation.[7]

Figure 6 shows the water absorption of all the sintered samples. It can be seen that the water absorption decreases with the sintering temperature and mechanical activation. For the activated samples, there is no relative water absorption above 1600 °C.

Figure 7 shows the hardness resultsfor the non-activated and activated samples with respect to the sintering temperature. The highest hardness value of an activated sample is 1623 HV at 1650 °C. Also, the hardness values of the activated samples arehigher than those for the

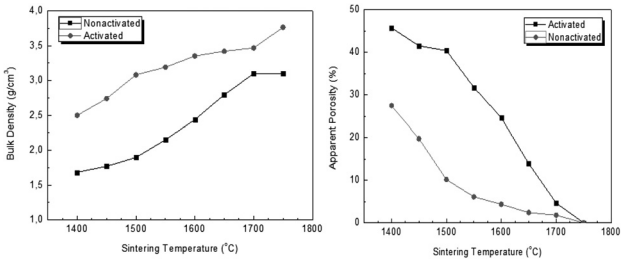

Figure 5: Bulk-density and apparent-porosity plots for all the sintered samples
Slika 5: Diagrama gostote osnove in navidezne poroznosti vseh sintranih vzorcev

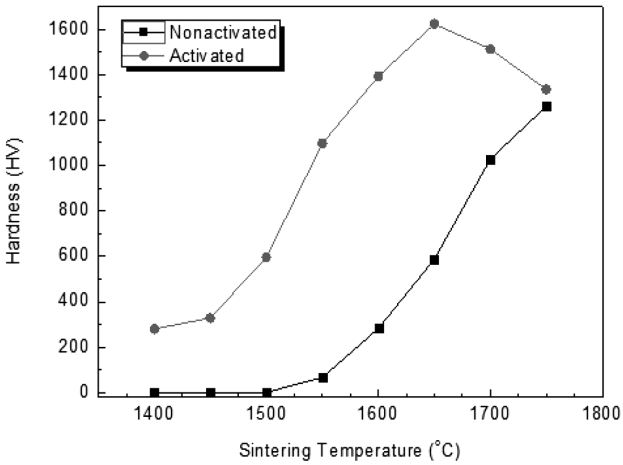

Figure 6: Hardness measurements forall the sintered samples
Slika 6: Meritve trdote vseh sintranih vzorcev

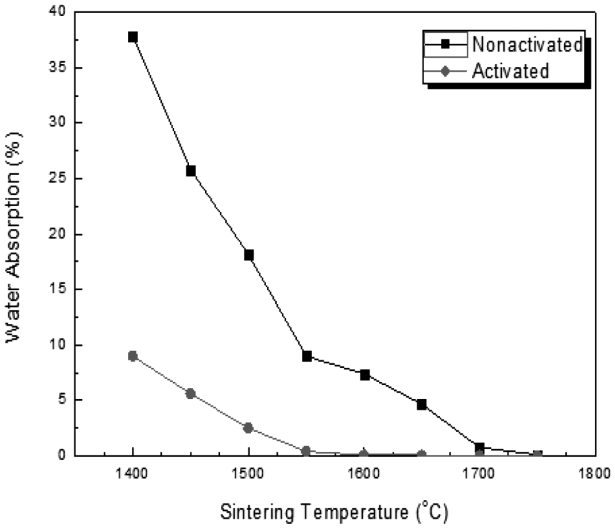

Figure 7: Water absorption of all the sintered samples
Slika 7: Absorpcija vode vseh sintranih vzorcev

non-activated samples. These results arerelated to thedensification and a low porosity level.

4 CONCLUSIONS

Magnesium aluminate spinel samples were synthesized using mechanical activation. The activated samples resulted in higher density and hardness values in comparison with the non-activated samples. In addition, theactivated samples exhibited dense grains and a low porosity. So, mechanical activation can facilitate a single-stage sintering process and greatly influence the costs of the production.

5 REFERENCES

[1] P. Orosco, L. Barbosa, M. C. Ruiz, Synthesis of magnesium aluminate spinel by periclase and alumina chlorination, Materials Research Bulletin, 59 (**2014**), 337–340, doi:10.1016/j.materresbull.2014.07.026

[2] P. G. Lampropoulou, C. G. Katagas, Effects of zirconium silicate and chromite addition on the microstructure and bulk density of magnesia–magnesium aluminate spinel-based refractory materials, Ceramics International, 34 (**2008**), 1247–1252, doi:10.1016/j.ceramint.2007.03.015

[3] I. Ganesh, Fabrication of magnesium aluminate ($MgAl_2O_4$) spinel foams, Ceramics International, 37 (**2011**), 2237–2245, doi:10.1016/j.ceramint.2011.03.068

[4] H. S.Tripathi, B. Mukherjee, S. Das, M. K. Haldar, S. K. Das, A.Ghosh, Synthesis and densification of magnesium aluminate spinel: effect of MgO reactivity, Ceramics International, 29 (**2003**), 915–918, doi:10.1016/S0272-8842(03)00036-1

[5] E. Turianicová, A. Obut, Ľ. Tuček, A. Zorkovská, İ. Girgin, P. Baláž, Interaction of natural and thermally processed vermiculites with gaseous carbon dioxide during mechanical activation, Applied Clay Sci., 88–89 (**2014**), 86–91, doi:10.1016/j.clay.2013.11.005

[6] S. Koç, N. Toplan, K. Yýldız, H. Ö. Toplan, Effects of mechanical activation on the non-isothermal kinetics of mullite formation from kaolinite, J. Therm. Anal. Calorim., 103 (**2010**), 791–796, doi:10.1007/s10973-010-1154-5

[7] R.Sarkar, S.Kumar Das, G.Banerjee, Effect of attritor milling on the densification of magnesium aluminate spinel, Ceramics International, 25 (**1999**), 485–489, doi:10.1016/S0272-8842(98)00065-0