e-ISSN: 2687-6698 **Research Article**

Turkish Journal of Analytical Chemistry
www.turkjac.org
2019

The effects of mechanical activation on corrosion resistance of cordierite ceramics

Can Serkan Keskin[1,2*], Ceren Ayna Çakır[3], Hüseyin Altundağ[1,2], Nil Toplan[4], Hüseyin Özkan Toplan[4]

[1] Sakarya University, Faculty of Sciences, Department of Chemistry, 54050, Sakarya, Türkiye
[2] Sakarya University, Biomedical, Magnetic and Semiconductor Materials Application and Research Center, 54050, Sakarya, Türkiye
[3] Sakarya University, Institute of Natural Sciences, 54050, Sakarya, Türkiye
[4] Sakarya University, Faculty of Engineering, Metallurgy and Materials Engineering, 54050, Sakarya, Türkiye

Abstract

The corrosion degrees of produced non-activated and activated cordierite-based ceramics were investigated in hydrochloric and sulfuric acid solutions. The composition of talc, alumina, and kaolinite powders was mechanically activated in a planetary mill. The concentrations of aluminum, magnesium, silicon, calcium, and potassium leached to the acid solutions from non-activated and activated cordierites were measured using ICP-OES. The amorphization of the structures was examined by XRD analysis. As a result, it has been determined that activated cordierite-based ceramics are more durable, and sulfuric acid solution causes more corrosion than hydrochloric acid.

Keywords: Cordierite, mechanical activation, corrosion resistance

1. Introduction

One of the crucial phases of the triple $MgO\text{-}SiO_2\text{-}Al_2O_3$ ceramic system, along with mullite, forsterite, tridymite, cristobalite, enstatite, and sapphire phases, is the cordierite phase ($2MgO\text{-}2Al_2O_3\text{-}5SiO_2$) [1,2]. These ceramics find substantial usage in circuit boards, filters, thermal insulation materials, catalytic converters, membranes, furnaces, refractories, electrical porcelain, and other applications because they have good thermo-mechanical, chemical, and dielectric qualities [3,4].

The cordierite phase is created using a variety of starting materials. Simple compounds like oxides, hydroxides, and carbonates are the earliest of them. The second is binary compounds, which include clays, talc, and sepiolite; the third is ternary compounds, which include chlorite. Industrial wastes such as magnesite and glass slag are also used in cordierite production [4,5].

Although the kaolin-talk system is suitable for producing cordierite ceramics, the specifications of the produced cordierites vary due to the presence of impurities in different kaolinites. For this reason, selecting the appropriate kaolin is crucial to preparing high-performance cordierite ceramics. The sintering of cordierite ceramics is difficult due to the narrow sintering temperature range (1300 – 1400 °C) [6,7]. It is possible to reduce the production temperature and increase the physical properties of cordierite by using different methods such as co-precipitation, solid-state synthesis, or sol-gel.

Since cordierite-based ceramics dissolve more in acidic solutions [8,9], they are susceptible to acid corrosion. There are few studies on the acid solubility of these ceramics. Kang et al. [10] found that μ-cordierite in the cordierite-based glass ceramics they produced was more resistant to acid solutions (especially H_2SO_4) than α-cordierite. Baitalik and Kaya [11] subjected the cordierite-silica-based porous ceramics they produced to the acid corrosion test at 90 °C using a 20% by-weight HCl solution. According to their corrosion test, it was observed that the cordierite phase was completely dissolved in ten days in an acidic medium.

With the mechanical processes carried out in the solid phase, the phase structure of the solids can be changed, and smaller powder particle sizes can be obtained. Therefore, the powder particles exposed to the

Citation: C.S. Keskin, C.A. Çakır, H. Altundağ, N. Toplan, H.Ö. Toplan, The effects of mechanical activation on corrosion resistance of cordierite ceramics, Turk J Anal Chem, 5(2), 2023, 83–88.
https://doi.org/10.51435/turkjac.1333631

Author of correspondence: ckeskin@sakarya.edu.tr
Tel: +90 (264) 295 60 37
Fax: +90 (264) 295 59 50

Received: July 27, 2023
Accepted: November 06, 2023

mechanical process can react at a lower sintering temperature due to increased surface area [12,13]. Obradović et al. [14] investigated the effect of mechanical activation and two-step sintering on cordierite-based ceramics' structure and electrical properties. The mechanical activation provides better homogeneity of powder mixture and powder activity. Also, the obtained densities increased and led to higher dielectric permittivity. Nath et al. [15] reported the mechanical activation effect on cordierite synthesis at lower temperatures. The cordierite was obtained with better properties, such as a higher quantity of cordierite phase and improved physical properties. Đorđević and Jovanić [16] studied mechanical activation influence on electrical properties of cordierite ceramics. The formation temperature of cordierite was affected by activation time, and no significant changes were observed in electrical properties. Yalamaç and Akkurt [17] analyzed the effect of additives and grinding on the synthesis of cordierite. The synthesis temperature successfully decreased to a lower value using additives and grinding. Wu et al. [18] investigated the corrosion resistance of zircon-modified cordierite–spodumene composite ceramics. The corrosion resistance and mechanical strength were improved with zircon modification. Çıtak et al. [19] studied the corrosion properties of cordierite-based ZrO_2 composite. The resistance was increased with ZrO_2 addition. In the present study, the effects of structural disorder (amorphization) provided by mechanical activation of the ceramic system (talc-kaolinite-alumina) were determined by X-ray diffraction (XRD) analysis. The microstructural change was analyzed using scanning electron microscopy (SEM). The corrosion resistance of the mixed ceramic systems against two strong acids (H_2SO_4 and HCl) that the material may encounter was examined by ICP-OES.

2. Material and methods

In the present study, the used raw materials are alumina, kaolin, and talc for the production of cordierite-based ceramics, which were supplied by Durovit Company from Turkey. Table 1 shows the company's values of the used raw material's chemical compositions.

Table 1. Chemical composition of raw materials

Compounds (wt.%)	Talc	Kaolin	Alumina
SiO_2	63	52.12	0.52
Al_2O_3	0.40	33.83	99.425
Fe_2O_3	0.25	0.55	—
CaO	0.40	0.15	—
K_2O	0.04	0.13	—
Na_2O	0.08	0.01	0.055
MgO	30	0.05	—
TiO_2	—	0.45	—
L.O.I*	4.83	12.45	—

* Loss on ignition, wt: weight

16 wt.% alumina, 43 wt.% kaolin, and 41 wt.% talc were mixed at 110 °C 24h. A high-energy planetary ball mill (600 rpm) (Fritsch) was used for the mechanical activation of the mixture for 1 hour. An X-ray diffraction investigation was carried out by an X-ray diffractometer (Rigaku Ultima) and CuKα radiation. For the morphological examination of mixed powders that had been activated and non-activated, a Joel 6060 LV SEM was employed. Eq. 1 was used to determine the percentage of amorphization (A%) of mechanically activated powders [20, 21].

$$A\% = \left[1 - \frac{B_o . I_x}{B_x . I_o}\right] \times 100 \qquad (1)$$

Where I_o is the diffraction peak's integral intensity, and B_o is the peak's background for the unactivated mixture. B_x and I_x are the same values for the mixture that has been mechanically activated. One axial hydraulic press operating at less than 100 MPa shaped the mixture of activated and non-activated powders. The sintering process of the shaped samples was carried out under atmospheric conditions by keeping them at 1250 °C for 1 hour with a heating rate of 10 °C/min. The cordierite phase formed after sintering was determined by XRD analysis. The microstructural examinations were carried out using SEM. The images were taken from the fractured surface of the samples. For the corrosion tests of the produced cordierite-based ceramics, 2%, 5%, and 10% HCl and H_2SO_4 solutions were prepared. Sintered pellets were kept in acidic solutions with two different acids and three concentrations for 1 and 10 days. Al, Mg, Si, Ca, and K concentrations in leach solutions were measured with a Spectro Arcos model ICP-OES (Spectro Analytical Instruments Dusseldorf, Germany).

3. Results and discussions

Figure 1 shows the XRD patterns of activated and non-activated alumina-talc-kaolinite mixture powders. Most of the crystalline peaks disappeared after mechanical activation due to the amorphization and structural deterioration in the structure of kaolin talc and alumina. The mechanical activation process causes the mineral particles to become amorphous depending on the rotation speed and duration [22]. It means that mechanical activation decreased the grain size and caused amorphization of the mineral particles of the structure [20,22]. The mechanical activation disrupts the crystal structure and makes it unstable. Some reactions occur during operation, and energy consumption is reduced. The grain size decreases, and the surface area increases, which increases the ability to react.

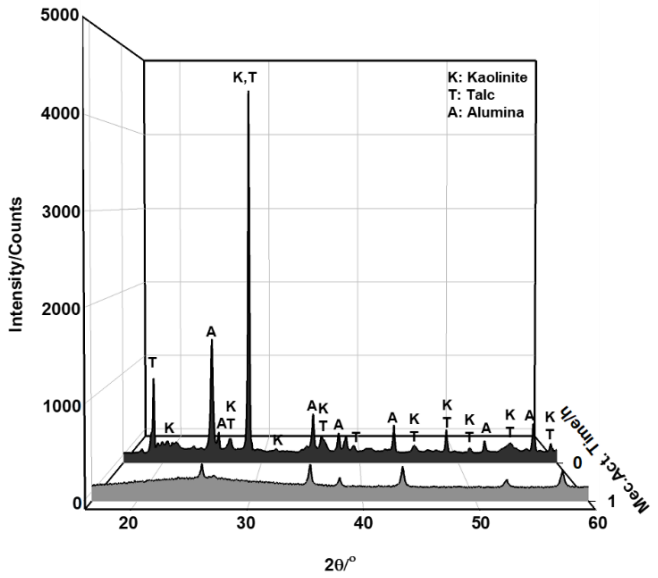

Figure 1. XRD patterns of activated and non-activated alumina-talc-kaolinite–powders

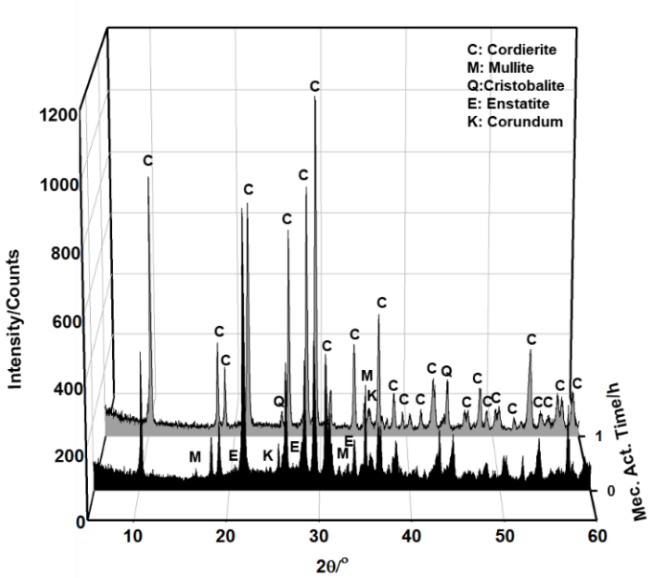

Figure 3. XRD patterns of non-activated and activated samples were sintered at 1250 °C for 1 h.

Thus, solid-solid reactions at high temperatures are carried out at lower temperatures. In two studies, Tromans and Meech [23,24] demonstrated that mechanical activation led to the growth of a significant number of dislocations and the corresponding strain fields, which might result in a general decline in long-range lattice periodicity. The loss of diffraction peaks and line broadening occurred in the X-ray patterns after extensive milling, and this might be seen as forming a metastable "amorphous phase".

Fig. 2a and b show scanning electron micrographs (SEM) of powder mixtures made of talc, kaolinite, and alumina that have been activated and not activated. The non-activated mixture has particles larger than 5 μm in size (Fig. 2a). The powder combination is mechanically activated and then agglomerated. Moreover, Eq. 1 was used to determine the degrees of amorphization of alumina, talc, and kaolinite. Alumina, talc, and kaolinite all had amorphization degrees around 75, 95, and 95%, respectively.

The activated mixture powders are shaped and sintered at 1250 °C for 1h. The mechanical activation caused decreased grain size and increased surface area. Therefore, the sintering temperature was reduced due to the easier powder reaction. Fig. 3 shows the XRD patterns. The XRD pattern of the non-activated sintered sample indicates that cordierite, corundum, enstatite, mullite, and quartz phases are present. The activated sintered samples' diffraction patterns show well-crystallized sharp peaks of cordierite and a small amount of corundum and quartz. The cordierite phase intensity of the activated sample increased. Elmas et al. [25] studied the effect of mechanical activation on the formation of mullite in their study on the Alumina-Quartz system and stated that mechanical activation supports the formation of the mullite phase.

SEM micrographs of activated and non-activated sintered pellets are shown in Fig. 4a and 4b. Non-activated pellets show high porosity between grains (Fig. 4a). However, porosities are smaller in activated pellets (Fig. 4b).

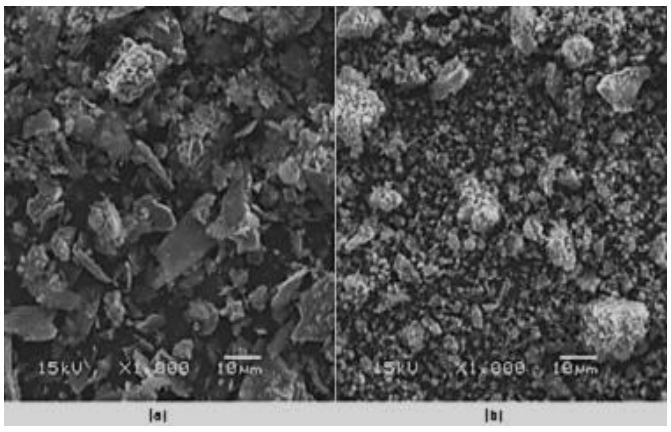

Figure 2. SEM micrographs of non-activated (a) and activated (b) alumina-talc- kaolinite powders

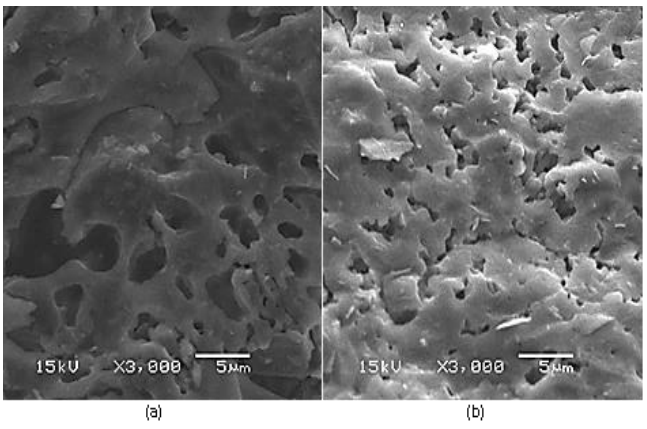

Figure 4. SEM images of (a) non-activated and activated (b) samples sintered at 1250 °C for 1 h.

Based on the SEM images, we can say that mechanical activation has a porosity-reducing effect on the sintering process. Ceramics are porous materials and resistant to acidic corrosion. The amount of porosity was reduced by mechanical activation, and corrosion resistance was increased. Obradovic et al. [1] reported that mechanical activation decreased open porosity and increased density value.

The acidic corrosion rates of activated and non-activated cordierite-based ceramics are shown in Fig. 5. Aluminum was the most dissolved metal in non-activated cordierite-based ceramics. After one day of treatment, the leached Al concentrations from non-activated ceramics in 10% HCl and 10% H_2SO_4 solutions were ~62.0 and ~81.0 mg/L, respectively. In activated ceramics, these concentrations were decreased to ~6.0 mg/L (in HCl solution) and ~8.0 mg/L (in H_2SO_4 solution). The activation process significantly reduced the amount of dissolved Al. Similar results were obtained with Mg and Si except for Ca and K. Although the dissolution of other metals decreased with the activation process, no significant change occurred for Ca. K and Ca were impurities and not parts of the cordierite structure. They were mostly at the grain boundaries [26] and not significantly affected by the activation process. Potassium was affected more than calcium due to binding energy. Also, the bulk densities were measured before and after corrosion, but no difference was observed in the results.

The effect of time on the leached metal concentrations from activated ceramics is shown in Fig. 6. The highest corrosions occurred on the first day, and the concentrations of dissolved metals decreased in ten days. It was observed that after 10 days, there was no Ca, which was found in the grain boundaries, and Mg, which was weakly bound to the structure. Mg was removed easily on the first days of the leaching process and could not be detected in the leaching solution after ten days because it did not remain in the structure. On the first day, the acid dissolved the metals outside the lattice. The concentration of dissolved metals decreased in 10 days because the amount of acid that could enter the lattice was limited.

Fig. 7 demonstrates the effect of acid concentration on the corrosion of activated ceramic. Except for Ca, increased acid concentration increased the concentration of all leached metals as predicted. The leached Ca concentrations were the same in 2% and 10% acids because all Ca were dissolved in 2% HCl and H_2SO_4 solutions. Also, it was concluded that the corrosion strength of H_2SO_4 on activated cordierite-based ceramics was higher than HCl solutions due to the higher acidity of the sulphuric acid.

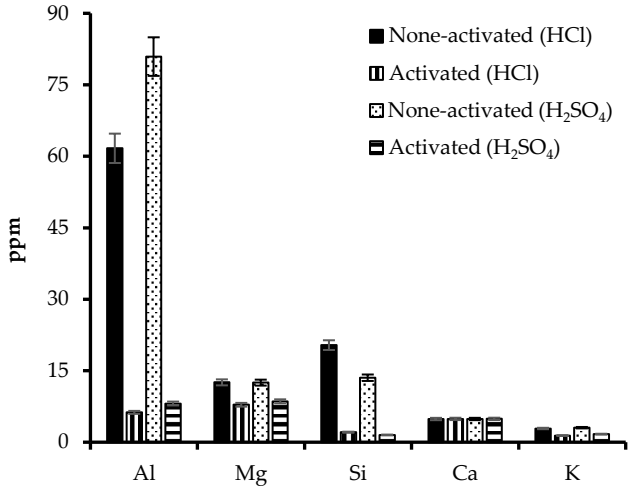

Figure 5. The leached metal concentration of non-activated and activated cordierite-based ceramics (10% acids, 1 day)

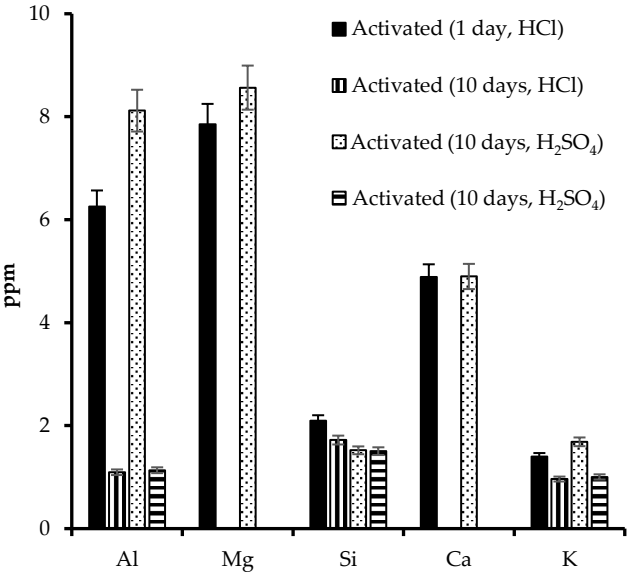

Figure 6. The effect of time on the leached metal concentrations from activated ceramics (10% acids)

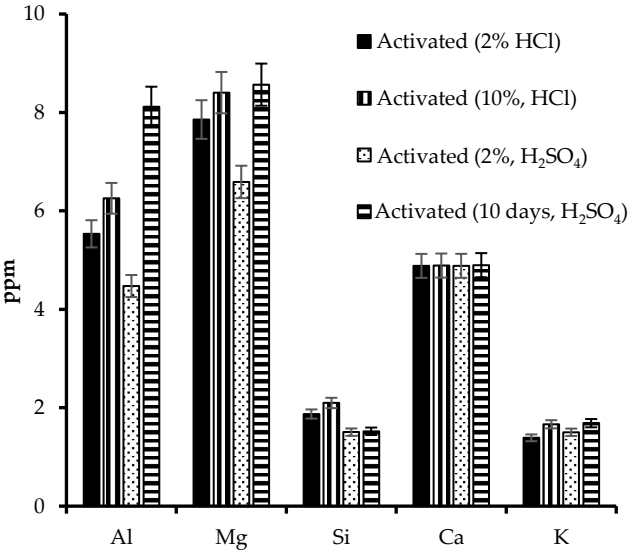

Figure 7. The effect of acid concentration on the leached metal concentrations from activated ceramics (1 day)

4. Conclusions

In the present study, mechanically activated and non-activated cordierite-based ceramics materials were prepared. The amorphization and structural deterioration, microstructure, and corrosion resistance of the bulk materials in HCl and H_2SO_4 were characterized systematically. The most important conclusions are:

1. The mechanical activation in talc, kaolinite, and alumina led to amorphization and structural disordering. Alumina, talc, and kaolinite all had amorphization degrees around 75, 95, and 95%, respectively.

2. The activated and non-activated mixture powders are shaped and sintered at 1250 °C for 1 h. The intensity of the cordierite phase increased in the activated sample.

3. It has been established that mechanical activation lowers open porosity in pellets after sintering.

4. Activated cordierite is approximately 10 times more durable against acidic corrosion than non-activated cordierite. The corrosion degrees are raised by increased acid concentration and strength. The corrosion rates reached a maximum on the first day and then decreased over time due to the limited amount of acid that can enter the lattice.

Acknowledgments

—

Funding

The author (s) has no received any financial support for the research, authorship, or publication of this study.

Authors' contribution

The authors contributed equally to the study.

The declaration of conflict of interest/ common interest

No conflict of interest or common interest has been declared by the authors.

The declaration of ethics committee approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific and ethical rules of the Turkish Journal of Analytical Chemistry. In addition, they declare that this study has not been evaluated in any journal.

References

[1] C.N. Obradovic, N. Dordevic, S. Filipovic, N. Nikolic, D. Kosanovic, M. Mitric, S. Markovic, V. Pavlovic, Influence of mechanochemical activation on the sintering of cordierite ceramics in the presence of Bi_2O_3 as a functional additive, Powder Technol, 218, 2012, 157–161.

[2] J. Liao, G. Qing, B. Zhao, Phase equilibria studies in the CaO-MgO-Al_2O_3-SiO_2 system with Al_2O_3/SiO_2 weight ratio of 0.4, Metals, 13(224), 2023, 2–26.

[3] W. N. Obradović, V. Pavlović, M. Kachlik, K. Maca, D. Olćan, A. Đorđević, A. Thantshapanyan, B. Vlahović, V. Pavlović, Processing and properties of dense cordierite ceramics obtained through solid-state reaction and pressure-less sintering, Adv Appl Ceram, 118(5), 2019, 241–248.

[4] S. Yürüyen, N. Toplan, K. Yıldız, H.Ö. Toplan, The non-isothermal kinetics of cordierite formation in mechanically activated talc–kaolinite–alumina ceramics system, J Therm Anal Calorim, 125(2), 2016, 803–808.

[5] C. Başaran, N. Canikoğlu, H. Ö. Toplan, N. Toplan, The crystallization kinetics of the MgO–Al_2O_3–SiO_2–TiO_2 glass ceramics system produced from industrial waste, J Therm Anal Calorim, 125(2), 2016, 695–701.

[6] A. Peles, N. Đorđevic, N. Obradovic, N. Tadic, V.B. Pavlovic, Influence of prolonged sintering time on density and electrical properties of isothermally sintered cordierite-based ceramics, Sci Sinter, 45(2), 2013, 157–164.

[7] Y. Kobayashi, K. Sumi, E. Kato, Preparation of dense cordierite ceramics from magnesium compounds and kaolinite without additives, Ceram Int, 26(7), 2000, 739–43.

[8] P.Y. Azimov, S.A. Bushmin, Solubility of minerals of metamorphic and metasomatic rocks in hydrothermal solutions of varying acidity: thermodynamic modeling at 400–800 °C and 1–5 kbar, Geochem. Int+, 45(1), 2007, 1210–1234.

[9] A. Harrati, Y. Arkame, A. Manni, A. El Haddar, B. Achiou, A. El Bouari, I. E. A. El Hassani, A. Sdiri, C. Sadik, Cordierite-based refractory ceramics from natural halloysite and peridotite: Insights on technological properties, J Indian Chem Soc, 99(6), 2022, 100496.

[10] J. Kang, J. Wang, X. Zhou, J. Yuan, Y. Hou, S. Qian, S. Li, Y. Yue, Effects of alkali metal oxides on crystallization behavior and acid corrosion resistance of cordierite-based glass-ceramics, J Non-Cryst Solids, 481, 2017, 184–190.

[11] S. Baitalik, N. Kaya, Processing and properties of cordierite-silica bonded porous SiC ceramics, Ceram Int, 43(17), 2018, 14683–14692.

[12] S. Koç¸ N. Toplan, K. Yıldız, H. O. Toplan, Effects of mechanical activation on the non-isothermal kinetics of mullite formation from kaolinite, J Therm Anal Calorim, 103, 2011, 791–796.

[13] J. Ding, J. Wang, H. Yang, Z. Liu, C. Yu, X. Li, C. Deng, H. Zhu, Improvement of mechanical properties of composites with surface modified B_4C for precision machining, Materials, 16(882), 2023, 2–10.

[14] N. Obradović, S. Filipović, N. Đorđević, D. Kosanović, S. Marković, V. Pavlović, D. Olćan, A. Djordjević, M. Kachlik, K.l Maca, Effects of mechanical activation and two-step sintering on

the structure and electrical properties of cordierite-based ceramics, Ceram Int, 42, 2016, 13909–13918.
[15] S.K. Nath, S. Kumar, R. Kumar, Effect of mechanical activation on cordierite synthesis through solid-state sintering method, B Mater Sci, 37(6), 2014, 1221–1226.
[16] N.G. Đorđević, P.B. Jovanić, Influence of mechanical activation on electrical properties of cordierite ceramics, Sci Sinter, 40, 2008, 47–53.
[17] E. Yalamac¸ S. Akkurt, Additive and intensive grinding effects on the synthesis of cordierite, Ceram Int, 32, 2006, 825–832.
[18] J. Wu, C. Hu, C. Ping, X. Xu, W. Xiang, Preparation and corrosion resistance of cordierite–spodumene composite ceramics using zircon as a modifying agent, Ceram Int, 44, 2018, 19590–19596.
[19] B. Çıtak, D. Kırsever, A. Ayday, H. Boussebha, A. Ş. Demirkıran, The corrosion kinetics of cordierite-based ZrO_2 composites obtained from natural zeolite in dilute HCl acid solution, J Compos Mater, 55(20), 2021, 2751–2763.
[20] P. Balaz, Mechanochemistry In Nanoscience And Minerals Engineering (1. edition), 2008, Germany, Springer.
[21] S. Vyazovkin, Isoconversional Kinetics, Handbook of Thermal Analysis and Calorimetry, Editors: M.E. Brown, P.K. Gallagher, 2008, Holland, Elsevier.
[22] J. Wu, C. Lu, X. Xu, D. Wang, Y. Zhang, Y. Zhou, Preparation and characterization of cordierite ceramic from coal series kaolin for electronic application, J Aust Ceram Soc, 55, 2019, 943–952.
[23] D. Tromans, J. A. Meech, Enhanced dissolution of minerals: microtopography and mechanical activation, Miner Eng, 12(6), 1999, 609–625.
[24] D. Tromans, J.A. Meech, Enhanced dissolution of minerals: stored energy, amorphism and mechanical activation, Miner Eng, 14(11), 2001, 1359–1377.
[25] E. Elmas, K. Yıldız, N. Toplan, H.Ö. Toplan, Effect of mechanical activation on mullite formation in an alumına-quartz ceramics system, Mater Technol, 47(4), 2013, 413–416.
[26] L. Curkovic, M.F. Jelaca, Dissolution of alumina ceramics in HCl aqueous solution, Ceram Int, 35(5), 2009, 2041–2045.