

An investigation about the mechanical and corrosion properties of cordierite based ceramic composites

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Abstract

One of the essential phases in the MgO-Al₂O₃-SiO₂ (MAS) system, cordierite, has the chemical formula $2 MgO \cdot 2 Al_2O_3 \cdot 5 SiO_2$. Therefore, cordierite is generally produced from natural raw materials by liquid phase sintering. In this study, dense cordierite and cordierite-based/ZrO₂ ceramic composites were produced economically from natural zeolite at a temperature as low as 1250 °C. Phase analyses with XRD and microstructure examinations with SEM/FESEM were performed. The hot salt corrosion behaviour of ZrSiO₄ crystals in a cordierite matrix was also tested. It was determined that the addition of ZrO₂ to reduce the average grain size had a positive effect on wear and corrosion resistance. Density, porosity, hardness, flexural strength and wear behaviour of the cordierite-based/ZrO₂ ceramic composites were determined. In addition, the hardness values of the zirconia free sample, the samples containing 10 and 20 wt.% zirconia were measured as 11.29, 12.60 and 12.91 GPa, respectively, while the specific wear rates were identified as 5.097 × 10⁻³, 6.302 × 10⁻⁶ and 3.393 × 10⁻⁷ mm³/Nm, respectively. The hardness increased and the wear resistance changed with the addition of zirconia.

Keywords: cordierite, composites, zirconia, wear resistance, corrosion

I. Introduction

Cordierite containing 13.8% MgO, 34.8% Al_2O_3 and 51.4% SiO_2 (wt.%) is an important industrial ceramics due to its superior thermal shock resistance resulting from its low coefficient of thermal expansion and good chemical and thermal stability at high temperatures [1–4]. The main usage areas of cordierite are: refractory material, catalyst carrier in automotive exhaust systems, filter for molten metals, rack for industrial furnaces, holder for electric heaters, heat exchanger for gas, turbine engines, refractory coatings for metals etc. [5–8].

Cordierite can be produced in form of ceramics, glass or glass-ceramics by solid-state sintering, liquid phase sintering and melting [2,9]. Generally, single-

phase cordierite ceramics are preferred in industrial applications due to their homogeneous properties. However, single-phase cordierite ceramics production requires expensive methods or high temperatures. The most common manufacturing process for the singlephase cordierite is solid state sintering at high temperatures of a mixture of SiO₂, Al₂O₃ and MgO prepared according to cordierite stoichiometry [10]. However, cordierite ceramics are difficult to produce by solidstate sintering [1,2,4,11] because cordierite is a phase occurring in a very narrow region surrounded by other phases such as enstatite and mullite, which are sensitive to SiO₂ content, as seen in the MgO-Al₂O₃-SiO₂ ternary equilibrium diagram in Fig. 1 [12]. For this reason, natural raw materials such as talc and clay are preferred for the economical production of cordierite. Recently, extensive research has been conducted on the economical production of cordierite with different raw materials. Gören et al. [13] have stated that some of

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Figure 1. MgO-Al₂O₃-SiO₂ ternary equilibrium diagram [12]

the starting raw materials reported in the literature for cordierite production include: a mixture of magnesium compounds and kaolinite; alkali-earth-aluminosilicate glass, kaolin, alumina and magnesite; talc, calcined alumina and fly ash; kaolin, talc, silica and alumina; talc, kaolinitic clay and gibbsite; kaolin, talc and magnesium oxide; talc, kaolin, silica, sepiolite and feldspar; and kaolin and talc.

Apart from the raw materials mentioned above, another natural mineral that can be evaluated in cordierite production is zeolite. As we expressed in previous studies, zeolite is an important SiO_2 source due to its high SiO_2 content (approximately SiO_2 wt.%), low cost, abundance in many countries, easy breaking up and grinding [14,15]. Zeolites are hydrated aluminosilicate minerals with a structure composed of aluminium and silicon tetrahedrons that share oxygen atoms in a threedimensional network [16]. Typically, cordierite ceramics produced from natural raw materials sintered in the temperature range of 1300–1400 °C contain cordierite as the primary phase.

The first purpose of this study is to deliberately produce the secondary phase that can adapt to the structure by reacting with silica and cause dispersion toughening. Zirconia (ZrO_2) additive was preferred for this purpose. ZrO₂ having acid/base character is stable against different oxidizing/reducing environments [17]. Zirconia is thermodynamically unstable at temperatures above 1280 °C in the cordierite matrix due to a reaction resulting in zircon ($ZrSiO_4$) formation [2]. ZrO_2 reacts with silica to form zircon which is a stable and mechanically resistant structure. As it is seen in Fig. 2, cordierite crystals having a hexagonal-shaped order are members of the cyclosilicate group containing rings of linked SiO₄ tetrahedra, ZrSiO₄ includes the nesosilicate group from the silicate structure family. Zirconium atoms are attached to SiO₄ tetrahedrons, and the number of bonds in different planes differs. Although cordierite and zircon crystal structures are different, they have similar hardness values (7-7.5 Mohs scale). However, there are significant differences between them in terms of some mechanical properties. Zircon's elastic anisotropy crystal structure in 3D space is relatively high compared to cordierite. In addition, the shear modulus and bulk modulus of zircon are considerably higher than for cordierite. When the bond patterns of the structures are examined, it is seen that Mg (6 neighbours) atoms make single bonds with 6 O, Al (4 neighbours) atoms make single bonds with 4 O, and Si (4 neighbours) atoms form single bonds with 4 O. In other words, the number of bonds in different directions in the 3D extension is close to each other, and there is almost a homogeneous system. In the zircon system, on the other hand, the Zr (8 neighbours) atom makes a single bond with 8 O, while the Si (4 neighbours) atom makes a single bond with 4 O. This situation causes the number of bonds in different directions to be quite different.

As a simple example to show the difference in homogeneity between the crystal systems of two phases, the calculation of the shear modulus of the phases by Voigt (G_V) and Reuss (G_R) models can be given. Both models assume a homogeneous or constant strain in polycrystalline materials. However, the Voigt model argues that there is compatibility but no equilibrium, while the Reuss model argues that equilibrium is achieved but compatibility is not necessary. At this point, the Voigt model uses stiffness tensor (C_{ij}) for calculations in the shear module, while the Reuss model uses compliance tensor (S_{ij}) [18]. While the G_V and G_R values of the cordierite phase are the same, the fact that these values are different in the zircon phase is an indication of the anisotropy difference between the structures, the calculated modules in the zircon phase are about twice that of the cordierite phase [19].



Figure 2. Illustration of cordierite (orange: Mg, red: O, dark blue: Si, light blue: Al), zircon (green: Zr, blue: Si, red: O) and cordierite-zircon composite structure

One of the important usage areas of ceramics containing cordierite is the refractory industry. Considering the researches on cordierite-containing refractories, it is seen that most of the studies are related to cordieritemullite ceramics [20–23]. Cordierite provides high temperature resistance while mullite provides mechanical resistance. The second aim of this study is to increase the mechanical resistance with zircon silicate phase instead of mullite phase and to produce high-strength cordierite-based ceramic materials with refractory properties. The refractory behaviour of cordierite-based ceramics enhanced with high thermal shock and thermal resistance phase was characterized by high temperature salt corrosion tests

In this study, the wear and high temperature corrosion properties of cordierite-based/ ZrO_2 composites produced from natural zeolite, which is used as an alternative to other raw materials, were investigated. Unlike the classical composite material production process, a type of ceramics was prepared and zirconia phase was formed in a cordierite-based matrix. Thus, the problem in the production of single-phase cordierite was solved by consciously producing the secondary phase other than cordierite by making composite materials.

II. Experimental

2.1. Production of the samples

This study used natural zeolite (clinoptilolite), MgO, Al_2O_3 and ZrO_2 as raw materials. Natural zeolite (90 clinoptilolite, 5 feldspar, and 5 cristobalite wt.%) was supplied from the ZEOMEC Company, Turkey. The chemical composition of zeolite reported by ZEOMEC Company is presented in Table 1. Zeolite was drily ground in a ring mill and sieved with a 75 µm sieve, and sub-sieve powders were used in the experiments. MgO (99% purity, 100 nm) and Al_2O_3 (99% purity, 5 µm) were bought from Alfa Aesar Firm to provide stoichiometry of cordierite. ZrO₂ (99.5% purity, 1 µm), as an additive, was also purchased from Alfa Aesar.

The powder mixture of MgO/Al₂O₃/SiO₂ in the molar ratios of 2 : 2 : 5 according to cordierite stoichiometry was prepared. After ZrO_2 (10 and 20 wt.%) was added to this mixture, the new powder compositions obtained were mechanically activated for 1 h at a planetary high-energy ball mill (Fritsch Mono Mill Pulverisette 6). The milling was performed in dry conditions at 600 rpm, with a ball-to-mass ratio of 20 : 1 using tungsten carbide (WC) balls of 10 mm diameter. Three different compositions were prepared and coded as Z0, Z10 and Z20 corresponding to the samples with 0, 10 and 20 wt.% ZrO₂, respectively. of 25 mm in diameter and 5 mm thick, via uniaxial dry pressing under 110 MPa load after the powder was moistened with 7 wt.% of water. The compacted samples were dried at 110 °C for 24 h in a drying oven and sintered in an electrical furnace at 2 °C/min heating rate at 1250 °C for 1 h in an air atmosphere.

2.2. Characterization of samples

Phase analyses were performed with a Rigaku D/MAX/2200/PC model diffractometer operating with Cu-K α ($\lambda = 1.54056$ Å) radiation. Microstructures of the specimens were examined by SEM (JEOL-JSM 6060 LV) with EDS attachment. Field emission scanning electron microscope (FESEM-FEI Quanta 450) was used to see the crack morphology in wear traces in more detail.

Densification of the samples was evaluated by measuring density and apparent porosity. The density and the apparent porosity values of the sintered specimens were determined by the Archimedes principle.

Vickers microhardness tests (FutureTech FM 700) were performed under a load of 100 g of force for 15 s. The flexural strength was determined by a three-point flexural test (INSTRON branded device) performed on three samples of $5 \times 10 \times 30$ mm from each composition, which were shaped with dry pressing, and sintered at 1250 °C for 1 h.

2.3. Wear tests

The tribological behaviour of the samples sliding against an alumina ball of 9 mm diameter was examined by a Tribometer (CSM Instruments) designed according to DIN 50 324 and ASTM G 99-95a in a ball-on-disk system. The system measures the friction coefficient and time-dependent depth profiles using sensitive transducers. The depth transducer was located vertically on top of the sample. Before the wear test, the sintered disc samples were metallographically prepared and polished. Then, the ball and disc were ultrasonically cleaned in acetone. Dry sliding wear tests were carried out at ambient conditions with relative humidity between 50 and 60% under the 1, 3 and 5 N loads with the 0.3 m/s sliding speed for 200 m sliding distance. The wear tracks were examined using SEM (JEOL-JSM 6060 LV).

2D and 3D profilometer (KLA Tencor P6) images were used to calculate the wear volume (V) by measuring the wear width and depth of the wear tracks formed on the discs. The specific wear rate (*SWR*) was calculated by Eq. 1:

$$SWR = \frac{V}{F \cdot S} \tag{1}$$

where V is the wear volume, S is the sliding distance and F is the applied load [24].

The prepared compositions were shaped into disks

Table 1. Chemical composition of zeolite

Components [wt.%]									
SiO ₂	Al_2O_3	Na ₂ O	K ₂ O	Fe ₂ O ₃	CaO	MgO	TiO ₂	MnO	
76.972	13.123	0.188	4.631	1.669	2.383	0.935	0.099	0.01	

2.4. Hot salt corrosion tests

NaCl and Na₂SO₄ (Merck) were used as alkali, chlorine and sulphur sources for hot salt corrosion of the sintered samples. Each surface of the sample was metallographically prepared and polished with 0.05 µm alumina paste. After polishing, the samples were ultrasonically cleaned with alcohol and distilled water and dried at 110 °C for 24 h in a drying oven. Then, the samples were embedded in NaCl (100 wt.%), Na₂SO₄ (100 wt.%), and NaCl + Na₂SO₄ (50-50 wt.%) salts poured in an alumina crucible and covered with a lid. The cyclic corrosion experiments were carried out in an electrical furnace with a heating rate of 10 °C/min at 850 °C in an open atmosphere for 120 h. After every 24 h of exposure time, the specimens were removed from the crucible. It was seen that the surface of the samples was covered with a water-soluble solid layer. Therefore, after each cycle, the samples were washed with boiling distilled water and dried at 110 °C. The specimens were periodically weighed. After 120 h, the surface morphology of corroded samples was observed using a JEOL JSM 6060 LV scanning electron microscopy (SEM).

III. Results and discussion

3.1. XRD analysis results

XRD patterns of the Z0, Z10 and Z20 compositions sintered at 1250 °C for 60 min are presented in Fig. 3. In the Z0 sample, cordierite was determined as the primary phase. In addition to this phase, $MgAl_2O_4$ spinel phase and a very small amount of glassy phase were determined. ZrO_2 in the Z10 and Z20 compounds reacted with silica to form $ZrSiO_4$ phase. Therefore, the zircon phase is present in these samples besides other phases. In addition, while the intensity of $ZrSiO_4$ peaks increases with the addition of zirconia, the intensity of cordierite peaks decreases due to the silica consumed in zircon formation. The presence of the glassy phase is related to the high SiO_2 content in the zeolite, and the effect of alkaline and alkaline earth oxides from the composition. Due to the presence of this glassy phase, sintering is thought to occur through the liquid phase sintering mechanism.

Other researchers also reported the presence of cordierite and spinel phases detected in undoped samples. Naskar and Chatterjee [25] stated that the $MgAl_2O_4$ spinel phase is an intermediate phase that reacts with SiO₂ to form a cordierite structure. Banjuraizah *et al.* [26] pointed out that the dual reaction tendency between Al_2O_3 and MgO is higher than the ternary reaction between MgO-Al₂O₃-SiO₂ and stated a reaction sequence as follows:

$$MgO + Al_2O_3 \rightarrow MgAl_2O_4$$
 (2)

$$2 \operatorname{MgAl}_2 O_4 + 5 \operatorname{SiO}_2 \to 2 \operatorname{MgO} \cdot 2 \operatorname{Al}_2 O_3 \cdot 5 \operatorname{SiO}_2 \quad (3)$$

Here, spinel phase can be accepted as the precursor of cordierite phase and is a secondary phase frequently seen in cordierite studies. Oliveira and Fernandes [2] also detected $ZrSiO_4$ phase in the samples containing zirconia, similar to our study. It is reported in the article that ZrO_2 reacts with cordierite to form zircon $(ZrSiO_4)$ and spinel $(2 MgAl_2O_4)$, preferably at temperatures above $1280 \,^{\circ}C$. When the ZrO_2 -SiO₂ binary equilibrium diagram is examined, it is seen that zircon and SiO_2 have polymorphic structures in the relevant composition, and the $ZrSiO_4$ structure remains stable up to $1600 \,^{\circ}C$ temperatures. In this study, SiO_2 was not detected as a separate phase and appeared to be included in spinel and cordierite phases. Although the formation



Figure 3. XRD patterns of the Z0, Z10 and Z20 samples sintered at 1250 °C for 60 min

temperature of ZrSiO_4 was reported to be above 1000 °C [27,28], it is stated that it can form even at low temperatures (400–500 °C).

3.2. SEM analysis results

The microstructural examinations were performed to see the changes that occurred in the microstructure due to the ZrO_2 addition, the microstructures in this section were taken before the tests. SEM micrographs and EDS analysis results are shown in Fig. 4. In the Z0 sample, a microstructure with small white grains settling on blocky grey grains is present. Besides, pores and micro-cracks are also observed in the microstructure. Marikkannan and Ayyasamy [29] stated that microcracks occurrence results from a thermal mismatch during the transformation process between low-quartz solid solution and α -cordierite in the sintering treatment. White coloured grains and grey block grains are seen in the SEM images taken from the Z0 sample. EDS analyses from these different structures yielded similar results. The XRD results obtained from the Z0 sample show that the dominant phase is cordierite, and these white grains and grey blocks are thought to be cordierite based. Studies on cordierite in the literature show different morphologies. While Jayaseelan et al. [30] determined a honeycomb-shaped cordierite structure in their study, Shukur et al. [31] mention a block-shaped cordierite structure in their study. In the study of Wu et al. [32], cordierite was presented as light coloured grains and it was reported that the structure of cordierite changes. Thus, it can be concluded that both structures were cordierite. It is known that liquid phase sintering occurs at three stages: particle rearrangement, dissolution and precipitation and solid-state sintering. In the dissolution and re-precipitation process, smaller particles dissolve from areas where they are in contact. The dissolved particles are carried away from the contact areas and re-precipitate on larger particles [33]. There-



Figure 4. SEM micrographs and EDS analysis results of Z0, Z10 and Z20 samples sintered at 1250 °C for 60 min

fore, it is not abnormal for both grey and white grains to be cordierite. In the Z10 and Z20 samples, it is observed that the microstructure has changed significantly with the addition of ZrO_2 . While grey blocky grains appeared more dominant in the ZrO_2 -free sample (white grains accumulated on grey blocks), the grain structure was changed with the addition of ZrO_2 , and the blocky grains turned into smaller grains. In the Z20 sample, the transformation is clearer and a more homogeneous appearance is obtained.

On the other hand, the samples with zirconia exhibited a proportional structural change with increasing ZrO_2 amount. There are white formations distributed homogeneously on the matrix structure, and the amount of these formations increases depending on the rise in the addition of zirconia. This phase is considered zircon because EDS analyses determined these white formations to be a zirconium-rich phase. Also, it has been observed that micro-cracks have decreased in the microstructure. As mentioned in the introduction section, the reduction of micro-cracks can result from the $ZrSiO_4$ grains preventing crack growth by causing crack deflection around them. Thus, it is seen that XRD analysis, EDS analysis and SEM images support each other.

When the SEM images are examined, it is seen that the grain size decreases with the addition of ZrO_2 . While the grain size was between $1-3\,\mu\text{m}$ in the Z0 sample, it decreased to $1\,\mu\text{m}$ in the Z10 sample and below $1\,\mu\text{m}$ in the Z20 sample. The driving force in liquid phase sintering is the capillary pressure at the grain boundaries of the liquid phase and diffusion. It is known that ZrO_2 increases the viscosity in glassy structures or melts and acts as a nucleating agent in glass-ceramics. It was reported [34] that 6 coordinated ZrO_6 octahedra formed by the inclusion of Zr in the structure increase glass network connectivity by replacing SiO₂. In the liquid phase sintering, viscosity is very significant for the movement of the molten phase between the grains.



Figure 5. The fracture surface morphologies of Z0, Z10 and Z20 samples

	Z0	Z10	Z20
Bulk density [g/cm ³]	2.59 ± 0.01	2.73 ± 0.02	2.76 ± 0.02
Apparent porosity [%]	1.05 ± 0.50	$2.71 \pm 0,\!69$	3.63 ± 0.34
Hardness [GPa]	11.29 ± 0.5	12.60 ± 0.3	12.91 ± 0.45
Flexural strength [MPa]	117 ± 16	119 ± 11	122 ± 24

Table 2. Some physical and mechanical properties of the samples

Therefore, it can be expected that the increase in viscosity will affect the sintering negatively and cause a decrease in the average grain size. On the other hand, an alteration in cordierite grain morphology was observed with the addition of ZrO_2 . While the grains are more angular in the Z0 sample, more spherical grains are dominant in the Z10 and Z20 samples. The sintering process that occurred in the Z0 sample is ordinary liquid phase sintering. Viscous liquid moves along grain boundaries, causing condensation at a decreasing rate over time. In that case the dissolution-diffusion-precipitation steps dominate and result in grain growth. At the end of sintering, grain boundary matching (such as flattening) happens to achieve high density and packing, and forms consistent grain boundaries [35]. It is thought that the increase in the viscosity of the liquid phase with the addition of ZrO₂ in the Z10 and Z20 samples complicates the classical liquid phase sintering process, causing a slight increase in porosity and changing the grain morphology.

Fracture surface morphologies of the Z0, Z10 and Z20 compositions sintered at 1250 °C for 60 min are presented in Fig. 5. It is seen from SEM images of the fracture surfaces that all three samples exhibit smooth fracture surfaces. In this case, the brittle fracture occurred without appreciable plastic deformation in all the samples. It is already known that ceramics is a brittle material since plastic deformation by dislocation motion does not happen. It attracts attention that transgranular cleavage fracture occurred in samples. In general, while intergranular fracture occurs in large-grained ceramics, the transgranular fracture effect begins to appear as the grains get smaller. The homogeneity of the stress explains the fact that the fracture is intergranular in materials with coarse grains, and the transgranular cracking in fine-grained materials is defined by the local stress [36]. It is seen from fracture surface images that formed zircon grains are uniformly distributed in the structure. Besides, the decrease in average grain size with the addition of ZrO_2 is supported by the fracture surface images as well as in the SEM images taken from the surface. In addition to the information mentioned in the previous paragraph, it is thought that the growth of hexagonal cordierite in the *c*-axis direction is inhibited by ZrSiO₄ grains, and the blocky grains transform to equiaxed grains.

3.3. Physical and mechanical test results

The samples' densification was evaluated by determining the density and apparent porosity as a function of ZrO₂ addition, and the obtained results were presented in Table 2. There were increases in both density and porosity values with the addition of ZrO_2 . A similar change is also expressed in the study by Oliveria and Fernandes [2]. Density in ceramics can vary depending on the composition or the fundamental events that occur during sintering. In this case, it can be said that the increase in the density value with increasing ZrO₂ addition is due to the composition according to the mixing rule. In fact, the theoretical density of cordierite is expressed as $2.0-2.6 \text{ g/cm}^3$ in various publications [5,11,37], while the density of m-zirconia is 5.85 g/cm^3 [2]. In general, it is expected that the porosity values will decrease with increasing density. However, the fact that the additives added to the composition in ceramics form different phases with high density can affect this relationship differently. As mentioned above, the theoretical density of cordierite is $2.0-2.6 \text{ g/cm}^3$, while the density of the zircon phase is around 4.5 g/cm^3 . Pores are one of the basic structural elements that make up the microstructure in products produced by sintering. Bukhari et al. [38] stated that porosity formation could result from uneven phase distribution, unbalanced diffusion events, reaction with the atmosphere, capillary spreading of a liquid melted and gaseous efflux due to the reactions during sintering. When the results are evaluated, it can be concluded that it is possible to produce dense cordierite-based/ZrO2 composites with very little porosity from natural zeolite at a temperature as low as 1250 °C. As a matter of fact, the sintering temperature used in this study is lower than the temperatures reported in cordierite studies produced using other natural raw materials [39–42].

As seen in Table 2, an increase in both hardness and flexural strength was detected with the addition of zirconia. Other researchers also reported that the hardness of cordierite increased with the addition of ZrO_2 . For example, Senthil Kumar et al. [43] stated that the hardness value of cordierite containing 20 wt.% zirconia was 7.68 GPa. This value increased from 7.06 to 7.68 GPa with the addition of zirconia. Oliveira and Fernandes [2] reported that the mean values of Vickers hardness were between 7.3 and 8.2 GPa. It is seen that the hardness values determined from our study are higher than the hardness values reported by these researchers. Of course, there could be many reasons for this. However, we think that one of the most important reasons is using the mechanical activation process in the powder preparation stage. As a matter of fact, in our previous study [15] we observed and reported that the hardness increased with the increase of the mechanical activation time. Mechanical activation causes certain effects on the material; structural irregularity increases, partial amorphization occurs, the reactivity of powders increases and particle size decreases. Among all these parameters, the decrease in particle size causes an increase in the packing factor and bulk density of the powders. Obradovic *et al.* [44] reported in their study that mechanical activation causes an increase in bulk density, which improves sintering properties.

Hardness measures the material's resistance to local plastic deformation, while brittleness is the fracture of material subjected to stress without significant plastic deformation. Therefore, a relationship can be established between hardness and brittleness; if hardness increases, brittleness also increases. In this case, the addition of zirconia and the increase in both hardness and brittleness support each other. Increasing brittleness in the material facilitates crack propagation. The crack propagation speed in ceramic materials can reach thousands of feet per second. The main reason why the crack propagates so rapidly in the brittle material is the stress discharge. The primary way to prevent deformation in ceramics is to eliminate crack stress. Grain boundaries, grain size, glass phase content, surface cracks, cracklike voids, inclusions and pores affect the strength of ceramics. With the processes applied to reduce the effects of these factors, the microstructure of the ceramics is changed and an improvement in its strength can be achieved.

The resistance to fracture of a material containing cracks to fracture is defined as fracture toughness. Fracture toughness measures the amount of energy required to propagate a pre-existing defect under applied load. Ceramics are materials with low fracture toughness, and one of the methods used to increase toughness is secondary phase dispersion. For example, fine distribution of ZrO₂ in a ceramic matrix induces toughing mechanisms such as stress-induced transformation toughing, micro-cracking, and crack deflection. The effect of zirconia as an additive is explained in detail in the introduction. It is seen that all of the ZrO_2 used in this study transformed into zircon. The formed ZrSiO₄ grains prevent crack growth by causing crack deflection around itself. Thus, micro-cracking is reduced and mechanical properties improve.

The increase in 3-point bending strength of the samples with the addition of ZrO_2 can be explained by the composite effect of the $ZrSiO_4$ secondary phase. It is stated in the literature [2,43,45] that the flexural strength increases as the zirconia content increases, which is also confirmed in our study. The flexural strength values of the Z0, Z10 and Z20 samples are 117, 119 and 122 MPa, respectively. The maximum flexural strength value, found by Kumar *et al.* [43], was 297.62 MPa, while the flexural strength value found by Oliveira and Fernandes [2] was 92.5 MPa. It is evident that the flexural strength values measured in this study are in the

range of values determined by other authors. Bending strength values obtained from different studies may vary according to production conditions and starting raw materials.

3.4. Wear test results

Dry slip wear tests were carried out to determine wear behaviour of the Z0, Z10 and Z20 specimens sintered for 60 min at 1250 °C. Figure 6 shows the variation of the average friction coefficient of the samples depending on the applied load. The friction coefficient decreased with increasing zirconia addition under all applied loads. For example, the average friction coefficient of the Z20 sample was 0.520 under 5 N load, which is lower than the value of both Z0 and Z10 samples under the same load. The average friction coefficient in the Z0 sample varies between 0.633-1.042 depending on the applied load. While the average friction coefficient in the Z10 sample varies between 0.584–0.637, the average friction coefficient in the Z20 sample varies between 0.357–0.545. The friction coefficient is the ratio of the friction force to the load acting perpendicular to the sample. In other words, an increase in friction force causes an increase in friction coefficient. There are four effects that cause frictional force. These are: static, sliding, rolling and fluid frictions. The main effect of solid surface wear is the sliding friction. This friction is the force that two solid surfaces exert on each other as they slide over one another. The main parameters effective here are: mechanical properties of solids, surface roughness, thermal properties of solids and physical/chemical interactions between materials. In this study, it is seen that the ZrO_2 contribution and the formation of $ZrSiO_4$ phase significantly reduce the friction coefficient.

In general, the friction coefficient in ceramic materials is in the range of 0.3-0.7. While the results obtained under 1 and 3 N loads in the experiments were in the 0.3-0.7 range, the friction coefficient increased above 1 when the load increased to 5 N for the Z0 sample. If this value is above 1, it indicates that the shear



Figure 6. Variation graph of the friction coefficient with the applied load to the Z0, Z10, and Z20 samples sintered at 1250 °C for 60 min



Figure 7. 3D profilometry images of the wear tracks obtained under 3 and 5 N loads at the 0.3 m/s sliding speed

force required for friction to occur exceeds the normal force acting on the specimen. The friction coefficients in the tests performed at 5 N in the Z10 and Z20 samples are considerably lower than in the Z0 sample. This indicates that the wear/friction characteristic changes significantly with the addition of ZrO_2 . In the Z0 sample, the friction coefficient increased with increasing the load. This increase is especially high in the transition from 3 to 5 N. This sudden increase in the friction coefficient with increasing load has been interpreted as the scraping effect on the contact surface, and the resulting surface irregularities that increase the friction coefficient. In the Z10 and Z20 samples, an increase in the friction coefficients was observed in the transition from 1 to 3 N, and then a stable trend occured. This can be explained by the fact that the $ZrSiO_4$ phase formed by adding ZrO_2 creates a composite effect and positively affects the wear.

3D surface profilometry scanning the worn surfaces after wear tests was realized, and the wear volume for each sample was calculated from the wear tracks obtained from these images. 3D profilometry images of the wear tracks obtained under 3 and 5 N loads at the 0.3 m/s sliding speed are presented in Fig. 7. It is seen that while the width and depth of wear tracks decreased with zirconia addition, the width and depth of wear tracks increased with the increment in the applied load. While the deep grooves, heavy surface damage, and debris are seen in wear tracks on the pure cordierite, only grooves attract attention in the Z20 sample. The wear trace images support the friction coefficient results and it is seen that the trace width/depths in the Z0 sample are quite high compared to the other samples. In the test of the Z0 sample with 5 N, it is seen that pieces are severely broken from the surface and it is thought that the broken pieces cause the friction coefficient to increase to high values by causing a three-body abrasion effect. In the Z0 sample, the friction coefficient in the test at 5N exceeded the broken pieces cause the friction to increase to higher levels by making the wedge and plow effects.

The wear and specific wear rate were calculated with the wear volume data determined by measuring the wear tracks' width and depth formed on the discs. The change graph in wear rate depending on the applied load and the samples' specific wear rate graph are presented in Fig. 8. As it can be seen, both the wear rate and the specific wear rate decrease with zirconia addition. The specific wear rates of the Z0, Z10 and Z20 samples have been determined from the slope of the wear rate *vs*. applied load graph as 5.0973×10^{-3} , 6.302×10^{-6} and 3.3926×10^{-7} mm³/Nm, respectively. With the addition of ZrO₂, it is seen that the material loss in the samples is clearly reduced.

The wear resistance of ceramic material can be increased by hard particle reinforcement. Here, it is thought that the anisotropic properties of the additive material are essential other than its high hardness. When the crack hits the hard particle, it loses its energy



Figure 8. The wear rate and specific wear rate variation of the samples depending on the applied load



Figure 9. SEM images of the worn surfaces of the Z0, Z10 and Z20 samples under 3 N loads with the 0.3 m/s sliding speed

through mechanisms such as branching and deflection. If the elastic modulus of the particle is greater than that of the matrix, the crack stress reduces.

In ceramics, crack propagation occurs in the form of the bonds breaking. Considering the anisotropic mechanical properties of the particles or secondary phases, the difference in the number of bonds in the x and ydirections causes the crack to encounter different resistances in different directions during crack propagation. This situation may create different results in transmitting crack energy to the material. When the crack reaches these phases, it will move in different directions at different speeds. In this case, it causes dispersion of crack stress. As a result, it is thought that the anisotropic behaviour of the particle or secondary phase regions in the ceramic matrix is effective on crack propagation.

Figure 9 presents SEM micrographs of the worn surfaces of the samples. It can be seen from the images that grooves, debris, cracks, delamination and spalling are present. The existence of grooves along the direction of sliding is a demonstration of predominant abrasive wear. It is also supported by the 3D images given in Fig. 7, where abrasive wear occurs. But it should be remembered that more than one wear mechanism can be active in any one wear process [46]. Wear mechanisms can be divided into four different types according to the fundamental processes that result from the action of the stress on the elements of the tribological system: adhesion, abrasion, tribo-chemical reaction and surface spalling.

Rainforth [47] reported two kinds of wear debris that can be distinguished in zirconia toughened ceramics. These debris types are the smeared ones, existing as bands on the edge of the wear track, and randomly distributed finer "rolls" present as particles within the wear tracks. Both of these debris are present in our samples. If the contact stress is large enough to cause crack propagation in the contact region, blocky or plate-like wear



Figure 10. The FESEM images of the worn surface of the samples

debris are generated mechanically [48]. On the other hand, delamination-type surface damages are caused by cracks formed following deformation hardening or fatigue [24]. In SEM micrographs, the expression surface plasticity used to state smearing is usually associated with the formation of a "tribo-layer", which is the agglomeration of very fine wear particles [47].

It is seen in the SEM images that the width, depth of the wear traces, and material loss decreased with the ZrO_2 additive starting from the Z0 sample. In the Z0 sample, lifts in layers of a few microns were observed. In this sample, adhesive and abrasive wears are seen together, and abrasive wear is thought to be more dominant. Abrasive wear is the removal of a hard part from a relatively soft part. The increase in the surface roughness of the material, which acts softly in abrasive wear, causes two-body abrasion, and the movement of the broken pieces between the surfaces causes three-body wear. These mechanisms accelerate the wear effect and cause a rapid increase in wear loss. It is thought that these effects occurred intensely in the Z0 sample. Increasing hardness and losing the effect of strain hardening can increase the abrasive wear effect in materials. Although the situation regarding hardness is valid for ceramics, the other case is not valid for ceramics as ceramics do not harden by deformation like metals.

In this study, it was seen that the hardness increased with the addition of ZrO_2 and that the wear effect decreases, where the traces become more superficial in the Z10 and Z20 samples with increasing hardness. It is known that harder, tougher particles with high elastic modulus and coarser size than the main phase increase wear resistance. It is thought that the $ZrSiO_4$ phase found in the cordierite matrix has a secondary particle effect.

FESEM images of the samples worn under 3 N loads with the 0.3 m/s sliding speed are presented in Fig. 10 and used to analyse the crack morphology. It is seen that the wear mechanism has changed with the addition of ZrO_2 . Layers occur with adhesive effects on the surface of the Z0 sample and then the cracks take place on these layers. In the Z10 sample, as in the Z0 sample, flake formation, flaking structure, crack formation and separation of the layers are observed. The cracks progress to form flake-shaped pieces, and weight loss occurs in the material by pouring these pieces composed. On the other hand, in the Z20 sample, the abrasive traces were less obvious, the crack shape changed, the cracks branched and the connections between them had been broken. It is understood from the crack morphology that the decrease in grain size with the addition of ZrO_2 affects the localization of the stress. While the cracks in the Z0 sample gain continuity and cause material loss, in the Z20 sample the cracks seem to branch and separate from each other remaining local. It attracts attention that while the severity of abrasive and adhesive wear is higher in the Z0 sample with lower hardness, the adhesive wear occurs less in the Z20 sample with higher hardness.

3.5. Hot salt corrosion test results

Figure 11 shows the weight losses of the samples in the hot salt corrosion tests. The first thing that attracted attention in the results was that the cordierite phase was dominant, and the lowest corrosive resistance was found in the Z0 samples. Takahashi et al. [49] reported that NaAlSiO₄ and SiO₂ were formed as a result of the interaction of cordierite-based structure with NaCl and Na_2SO_4 . In another study by Takahashi *et al.* [50], hot corrosion of cordierite/mullite ceramics against the same salts was studied, and it was explained that the cordierite phase deteriorated as a result of similar interactions. In the current study, it was reported that especially the cordierite phase was weak against Na-based hot salts and that corrosion layers rich and poor in Na atoms were formed. It is thought that these interactions have high corrosion effect in the Z0 sample, in which cordierite is the dominant phase. The results show that the weight loss decreases and the corrosive resistance increases with ZrO₂ addition, which is valid for both Na₂SO₄ and NaCl environments. Corrosion resistance increased with increasing ZrSiO₄ ratio formed in the samples. It is evident that this phase does not interact with NaCl and Na₂SO₄. When the silicate forming abilities of Na and Zr elements are examined, it can be seen from the enthalpies that Na₂SiO₃ is formed much more easily, since Na_2O is a strong base while SiO_2 is a strong acid. In our case, the structure likely to occur in the environment of Na₂O, SiO₂ and ZrO₂ will be Na₂SiO₃. However, the situation changes when switching from the oxide form to the salt form. No silicate is formed when NaCl is used instead of Na₂O, since there is no or



Figure 11. Weight loss change curves versus corrosion time of the Z0, Z10, and Z20 samples in NaCl, Na_2SO_4 and $NaCl + Na_2SO_4$ salt mediums

very limited solubility between NaCl and SiO₂. NaCl is a strongly ionic compound and extremely polar. It wants to react against polar structures, while SiO₂ has strong covalent bonds. Although Si and O bonds appear polar, the bond geometry between Si–O distorts polarity. It also explains why silicate glasses do not interact with most polar covalent structures.

$$\operatorname{ZrO}_2 + \operatorname{SiO}_2 \longrightarrow \operatorname{ZrSiO}_4 \quad \Delta H = -11 \text{ kJ/mol}$$
 (4)
 $\operatorname{Na_2O} + \operatorname{SiO}_2 \longrightarrow \operatorname{Na_2SiO}_3 \quad \Delta H = -201 \text{ kJ/mol}$ (5)

The bond between Na⁺ and SO_4^{2-} ions is similarly ionic and Na2SiO4 is also polar. However, the behaviour of silicate structures in Na2SO4 environment is different from NaCl. Na₂SO₄ is a stable salt under normal conditions, but it can decompose under the effect of pressure and temperature, producing SO_x gases. The structure normally starts to break down above 1000 °C, but pressure changes in the system may cause the breakdown to take place at lower temperatures. Jacobson [51] reported that the decomposition temperature of Na_2SO_4 is a function of pressure, sulphur and sodium contents. Na₂O, which is formed by the disintegration of the sulphate structure, will cause the ZrSiO₄ phase to deteriorate. This is thought to be the reason why the corrosion in the Na_2SO_4 medium is more severe than the corrosion in the NaCl environment. Since the corrosion tests were carried out at 850 °C, this effect remained low. Probably the severity of Na₂SO₄ corrosion would increase with increasing the test temperature. It was observed that the severity of corrosion increased when NaCl and Na₂SO₄

were used together. It is thought that the reason why the simultaneous use of Na salts containing SO_4^{2-} and Cl^{-} increases the severity of corrosion is related to the mutual interaction of the products formed by the corrosion reactions. There is a potential to form Mg-based compounds (MgO, MgCl₂, MgSO₄) as well as NaAlSiO₄ and SiO_2 from the reaction of the cordierite phase with NaCl and Na₂SO₄ salts. In addition, there is a potential for formation of Cl-SO₂ gases depending on ambient conditions. There are many structures that can be formed as a product of corrosion and these are structures that can react with each other. For example, $MgSO_4$ and Cl₂ react to form MgCl₂. Since some of the products react in multiple reactions and the amount of products decreases, the reactions will move towards the creation of products (Le Chatelier principle), and the corrosion potential will increase.

Figure 12 shows SEM images taken from the corroded surfaces of the samples. It is seen that the surfaces of all samples are deteriorated and that corrosion was active. It is noteworthy that while there is nearly a homogeneous image on the entire surface in the Z0 sample, pores and cavities are formed in certain regions in the Z10 and Z20 samples, and these areas are more affected by corrosion. It is thought to be related to the composite effect. The cordierite is the dominant phase in the Z0 sample, while corrosion is observed on the entire surface, while the formation of the $ZrSiO_4$ phase in the cordierite matrix in the Z10 and Z20 samples caused certain areas to be more resistant to corrosion. Another result is the formation of cracks as a result of corro-



Figure 12. SEM micrographs of the Z0, Z10, and Z20 samples in NaCl, Na₂SO₄, and NaCl + Na₂SO₄ salt mediums after corrosion at 850 °C for 120 h



Figure 13. SEM micrographs of Z20 sample at different magnifications after corrosion at 850 °C for 120 h in NaCl salt medium

sion, since significant crack formation was observed in all samples. It is thought that the cracks may be related to the polymorphic transformations in the NaAlSiO₄ phase formed as a corrosion product. It is known that NaAlSiO₄ has polymorphic transformation [52]. It is possible that the accumulation of Na and Mg atoms in

certain regions and the formation of segregation and heterogeneous structures are effective in crack formation. On the other hand, different crystals with flower-like dendrite design were observed in the samples containing zirconia. To see the details, EDS analysis was performed on the Z20 samples that passed the corrosion test (Fig. 13). In the analysis taken from the region where the cracks are intense, strong Na, Al and Si peaks seen in these areas correspond to NaAlSiO₄ structures, which are probably corrosion products. In the EDS analysis of flower-like crystals, in addition to these elements, a strong Zr peak was observed. It is thought that these structures were formed by Na-based corrosion products on ZrSiO₄ crystals.

IV. Conclusions

In this study, cordierite-based materials were produced from natural zeolite and 10 and 20 wt.% ZrO_2 were added to improve mechanical and wear properties. In the ZrO_2 -free samples, cordierite as the main phase was identified and in addition to this phase, the MgAl₂O₄ spinel phase and a very small amount of glassy phase were determined. In the composite samples, ZrO_2 formed $ZrSiO_4$ phase by reacting with the silica. The intensity of $ZrSiO_4$ peaks increases

with increment zirconia addition, while the intensity of cordierite peaks decreases. Zirconia content increase has been seen to cause decline in the micro-cracks, whereas density and porosity values slightly increased. It was found that transgranular cleavage fracture occurred in all samples. Also, the grain size decreases with the increase of zirconia additive. The sample's hardness/flexural strength increased with increasing zirconia addition, i.e. 11.29 GPa/117 MPa, 12.60 GPa/119 MPa and 12.91 GPa/122 MPa for the Z0, Z10 and Z20, respectively. Specific wear rates of the Z0, Z10 and Z20 samples were determined from the slope of the wear rate *vs.* applied load graph as 5.0973×10^{-3} , 6.302×10^{-6} and 3.3926×10^{-7} mm³/Nm, respectively. Abrasive wear was the predominant wear mechanism; however, it has been accompanied by other mechanisms such as adhesion, tribo-chemical reaction and surface spalling. It was determined that flexural strength had been the least affected by the addition of zirconia, whereas wear had been seen to be the most affected. In addition, it was observed that the addition of ZrO₂ caused a significant increase in hot salt corrosion resistance, and the weight losses as a result of corrosion decreased approximately 2-20 times depending on the additive and the corrosive media.

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References

- E. Ozel, S. Kurama, "Effect of the processing on the production of cordierite-mullite composite", *Ceram. Int.*, 36 [3] (2010) 1033–1039.
- F.A. Costa Oliveira, J. Cruz Fernandes, "Mechanical and thermal behaviour of cordierite–zirconia composites", *Ceram. Int.*, 28 [1] (2002) 79–91.
- P. Rohan, K. Neufuss, J. Matejícek, J. Dubský, L. Prchlik, C. Holzgartner, "Thermal and mechanical properties of cordierite, mullite and steatite produced by plasma spraying", *Ceram. Int.*, **30** [4] (2004) 597–603.
- 4. M. Senthil Kumara, A. Elayaperumal, G. Senguttuvan, "Zirconia's characteristic influence on cordierite mechanical properties", *J. Ovonic Res.*, **7** [5] (2011) 99–106.
- H. Gökçe, D. Ağaoğulları, M.L. Öveçoğlu, İ. Duman, T. Boyraz, "Characterization of microstructural and thermal properties of steatite/cordierite ceramics prepared by using natural raw materials", *J. Eur. Ceram. Soc.*, **31** [14] (2011) 2741–2747.
- A. Benhammou, Y. El Hafiane, L. Nibou, A. Yaacoubi, J. Soro, A. Smith, J.P. Bonnet, B. Tanouti, "Mechanical behavior and ultrasonic non-destructive characterization of elastic properties of cordierite-based ceramics", *Ceram. Int.*, **39** [1]) (2013) 21–27.
- S. Sembiring, W. Simanjuntak, R. Situmeang, A. Riyanto, P. Karo-Karo, "Effect of alumina addition on the phase transformation and crystallisation properties of refractory cordierite prepared from amorphous rice husk silica", *J. Asia. Ceram. Soc.*, 5 [2] (2017) 186–192.

- 8. D. Kuscer, I. Bantan, M. Hrovat, B. Malic, "The microstructure, coefficient of thermal expansion and flexural strength of cordierite ceramics prepared from alumina with different particle sizes", *J. Eur. Ceram. Soc.*, **37** [2]) (2017) 739–746.
- K.H. Zum Gahr, P. Neumann, "Oscillating sliding wear of cordierite glass and ceramic in liquid media", *Wear*, 203-204 (1997) 107–118.
- R. Bejjaoui, A. Benhammou, L. Nibou, B. Tanouti, J.P. Bonnet, A. Yaacoubi, A. Ammar, "Synthesis and characterization of cordierite ceramic from Moroccan stevensite and andalusite", *Appl. Clay Sci.*, 49 [3] (2010) 336–340.
- M.A. Camerucci, G. Urretavizcaya, A.L. Cavalieri, "Sintering of cordierite based materials", *Ceram. Int.*, **29** [2] (2003) 159–168.
- M. Lesniak, J. Partyka, K. Pasiut, M. Sitarz, "Microstructure study of opaque glazes from SiO₂-Al₂O₃-MgO-K₂O-Na₂O system by variable molar ratio of SiO₂/Al₂O₃ by FTIR and Raman spectroscopy", *J. Mol. Structure.*, **1126** (2016) 240–250.
- R. Gören, H. Göçmez, C. Özgür, "Synthesis of cordierite powder from talc, diatomite and alumina", *Ceram. Int.*, **32** [4] (2006) 407–409.
- 14. T. Tunç Parlak, A.Ş. Demirkıran, "Zeolite usage as source of silica to produce cordierite in MgO-Al₂O₃-SiO₂ system", *J. Adv. Ceram.*, **7** [4] (2018) 370–379.
- 15. T. Tunç, A.Ş. Demirkıran, "The effects of mechanical activation on the sintering and microstructural properties of cordierite produced from natural zeolite", *Powder Technol.*, **260** (2014) 7–14.
- T. Wajima, Y. Ikegami, "Synthesis of zeolitic materials from waste porcelain at low temperature via a two-step alkali conversion", *Ceram. Int.*, 33 [7] (2007) 1269–1274.
- F. Maleki, G. Pacchioni, "Characterization of acid and basic sites on zirconia surfaces and nanoparticles by adsorbed probe molecules: A theoretical study", *Top. Catal.*, 63 (2020) 1717–1730.
- R. Dewit, "Elastic constants and thermal expansion averages of a nontextured polycrystal", *J. Mech. Mater. Structure.*, 3 [2] (2008) 195–212.
- M. De Jong, W. Chen, T. Angsten, A. Jain, R. Notestine, A. Gamst, M. Sluiter, C.K. Ande, S. Van der Zwaag, J.J. Plata, C. Toher, S. Curtarolo, G. Ceder, K.A. Persson, M. Asta, "Charting the complete elastic properties of inorganic crystalline compounds", *Sci. Data*, 2 (2015) 150009.
- D.M. Ibrahim, S.M. Naga, Z. Abdel Kader, E. Abdel Salam, "Cordierite-mullite refractories", *Ceram. Int.*, 21 (1995) 265–269.
- N. Ariyajinno, S. Thiansem, "Effect of firing temperature on sintering of cordierite-mullite refractories from raw materials and Narathiwat clay in Thailand", *Mater. Today: Proceedings*, 5 (2018) 14036–14040.
- N.E. Hipedinger, A.N. Scian, E.F. Aglietti, "Phase development during thermal treatment of a fast-setting cordierite-mullite refractory", *Proc. Mater. Sci.*, 9 (2015) 305–312.
- D.N. Boccaccini, C. Leonelli, M.R. Rivasi, M. Romagnoli, A.R. Boccaccini, "Microstructural investigations in cordierite-mullite refractories", *Ceram. Int.*, **31** (2005) 417–432.
- H. Akbulut, G. Hatipoğlu, H. Algül, M. Tokur, M. Kartal, M. Uysal, T. Çetinkaya, "Co-deposition of Cu/WC/graphene hybrid nanocomposites produced by

electrophoretic deposition", Surf. Coat. Technol., 284 (2015) 344–352.

- M.K. Naskar, M.A. Chatterjee, "A novel process for the synthesis of cordierite (Mg₂Al₄Si₅O₁₈) powders from rice husk ash and other sources of silica and their comparative study", *J. Eur. Ceram. Soc.*, **24** [13] (2004) 3499–3508.
- J. Banjuraizah, H. Mohamad, Z.A. Ahmad, "Effect of excess MgO mole ratio in a stoichiometric cordierite (2 MgO · 2 Al₂O₃ · 5 SiO₂) composition on the phase transformation and crystallization behavior of magnesium aluminum silicate phases", *Int. J. App. Ceram. Technol.*, 8 (2011) 637–645.
- T. Mori, H. Yamamura, H. Kobayashi, T. Mitamura, "Formation mechanism of ZrSi0₄ powders", *J. Mater. Sci.*, 28 (1993) 4970–4973.
- Musyarofah, R. Nurlaila, N.F. Muwwaqor, M. Saukani, A. Kuswoyo, Triwikantoro, S. Pratapa, "Phase study of SiO₂-ZrO₂ composites prepared from polymorphic combination of starting powders via a ball-milling followed by calcination", *IOP Conf. Series: J. Physics*, **817** (2017) 012033.
- S.K. Marikkannan, E.P. Ayyasamy, "Synthesis, characterisation and sintering behavior influencing the mechanical, thermal and physical properties of cordierite-doped TiO₂", *J. Mater. Res. Technol.*, 2 [3] (2013) 269–275.
- D.D. Jayaseelan, W.E. Lee, "In situ formation of silicon carbide nanofibers on cordierite substrates", *J. Am. Ceram. Soc.*, **90** [5] (2007) 1603–1606.
- M.M. Shukur, M.A. Aswad, Z.J. Kadhim, "Preparation of cordierite ceramic from Iraqi raw materials", *Int. J. Eng. Technol.*, 5 (2015) 172–175.
- J. Wu, C. Ding, X. Xu, X. Xu, "Preparation and characterization of cordierite glass-ceramics for bonding solar thermal transmission pipelines", *Int. J. Appl. Ceram. Technol.*, 18 (2021) 1764–1772.
- E.M. Hamzawy, A.A. El-Kheshen, M.F. Zawrah, "Densification and properties of glass/cordierite composites", *Ceram. Int.*, **31** [3] (2005) 383–389.
- X. Lu, L. Deng, S. Kerisit, J. Du, "Structural role of ZrO₂ and its impact on properties of boroaluminosilicate nuclear waste glasses", *NPJ Mater Degrad.*, 2 (2018) 19.
- 35. F. Lemoisson, L. Froyen, "Understanding and improving powder metallurgical processes", pp. 471–502 Ch. 12 in *Fundamentals of Metallurgy*, Woodhead Publishing Series in Metals and Surface Engineering, 2005.
- F.L. Liang, C. Laird, "Control of intergranular fatigue cracking by slip homogeneity in copper. I: Effect of grain size", *Mater. Sci. Eng. A*, 17 (1989) 95–102.
- B. Fotoohi, S. Blackburn, "Effects of mechanochemical processing and doping of functional oxides on phase development in synthesis of cordierite", J. Eur. Ceram. Soc.,

32 [10] (2012) 2267–2272.

- M.Z. Bukhari, M.S.J. Hashmi, D. Brabazon, "The effects of sintering parameter to the microstructure and thermal properties of CuSiC composite for electronic packaging application", *Aust. J. Bas. App. Sci.*, 7 [5] (2013) 350–365.
- A. Yamuna, R. Johnson, Y.R. Mahajan, M. Lalithambika, "Kaolin-based cordierite for pollution control", *J. Eur. Ceram. Soc.*, 24 [1] (2004) 65–73.
- T. Ogiwara, Y. Noda, K. Shoji, O. Kimura, "Solid state synthesis and its characterization of high density cordierite ceramics using fine oxide powders", *J. Ceram. Soc. Jpn.*, **118** [1375] (2010) 246–249.
- R. Gören, C. Özgür, H. Göçmez, "The preparation of cordierite from talc, fly ash, fused silica and alumina mixtures", *Ceram. Int.*, **32** [1] (2006) 53–56.
- S. Yürüyen, N. Toplan, K. Yıldız, H.Ö. Toplan, "The nonisothermal kinetics of cordierite formation in mechanically activated talc-kaolinite-alumina ceramics system", *J. Therm. Anal. Calor.*, **125** (2016) 803–808.
- M.S. Kumar, A.E. Perumal, T.R. Vıjayaram, G. Senguttuvan, "Processing and characterization of pure cordierite and zirconia-doped cordierite ceramic composite by precipitation technique", *Bull. Mater. Sci.*, **38** [3] (2015) 679– 688.
- 44. N. Obradovic, W.G. Fahrenholtz, "The effect of mechanical activation on synthesis and properties of MgAl₂O₄ ceramics", *Ceram. Int.*, **45** (2019) 12015–12021.
- Y.J. Oh, T.S. Oh, H.J. Jung, "Microstructure and mechanical properties of cordierite ceramics toughened by monoclinic ZrO₂", *J. Mater. Sci.*, **26** (1991) 6491–6495.
- 46. *Breviary Technical Ceramics*, Edited by Informationszentrum Technische Keramik (IZTK). ISBN 3-924158-57-6, Fahner Verlag, Lauf, Germany, December 2004.
- 47. W.M. Rainforth, "The wear behaviour of oxide ceramics-A review", J. Mater. Sci., **39** (2004) 6705–6721.
- 48. K. Kato, K. Adachi, "Wear of advanced ceramics", *Wear*, **253** [11-12] (2002) 1097–1104.
- J. Takahashi, Y. Kawai, S. Shimada, "Hot corrosion of cordierite ceramics by Na- and K-salts", *J. Eur. Ceram. Soc.*, 18 (1998) 1121–1129.
- J. Takahashi, Y. Kawai, S. Shimada, "Hot corrosion of cordierite/mullite composites by Na-salts", *J. Eur. Ceram. Soc.*, 22 (2002) 1959–1969.
- 51. N.S. Jacobson, "Sodium sulfate: Deposition and dissolution of silica", *Oxid. Met.*, **31** (1989) 91–103.
- A. Deshkar, J. Marcial, S.A. Southern, L. Kobera, D.L. Bryce, J.S. McCloy, A. Goel, "Understanding the structural origin of crystalline phase transformations in nepheline (NaAlSiO₄)-based glass-ceramics", *J. Am. Ceram. Soc.*, **100** (2017) 2859–2878.