

Fabrication, structure, mechanical and thermal properties of zirconia-based ceramic nanocomposites

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Received 7 July 2004; received in revised form 23 February 2005; accepted 5 March 2005

Available online 31 May 2005

Abstract

The paper addresses the new nanocomposite prepared by pressureless sintering method (PSM). The properties of the yttrium stabilized zirconia (Y-TZP)/zircon (ZrSiO₄) composite obtained by PSM are discussed in terms of its structure and fabrication conditions that include the content of cordierite in the initial mixture of cordierite and Y-TZP nanopowders and sintering temperature. The structural information has been obtained by X-ray diffraction (XRD), high-resolution scanning and transmission microscopy, density measurements, as well as differential thermal analysis (DTA) and thermogravimetry (TG), while mechanical examinations included both measurements of fracture toughness and flexural strength. The obtained results point towards possibility of control the amount of tetragonal zirconia with nano-size grains in a final composite, by a selection of the proper sintering temperature. The interesting finding of this study concerns the coefficient of thermal conductivity of Y-TZP-based composites with zircon, fabricated from the powder with more than 15 vol.% content of cordierite, which appears to be lower than that of pure zirconia, despite the mixed materials exhibit high thermal conductivity. The DTA–TG examination confirmed excellent stability of the composite at the elevated temperatures and proved the lack of the nanocomposite oxidation.

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Keywords: Y-TZP; Composite; Thermal conductivity; Strength

1. Introduction

The improvement of diverse physical properties has already been demonstrated for variety of nanophase and nanocomposite ceramics obtained in the past decade.¹ Consequently, the development of advanced ceramics encountered nowadays is frequently limited to the search for a proper combination of a specific matrix and dispersed phase that should provide a required string of characteristics of final material. Indeed, fabrication of composites is nowadays a common strategy to design a new substance with properties that cannot be achieved for a monolithic material.²

The present research started with the above-mentioned concept, and aimed originally to obtain the new nanocom-

posites that fuse widely appreciated advantages offered by already “traditional advanced ceramics”, namely, yttrium stabilized zirconia (Y-TZP) and cordierite. Consequently, the influence of the content of these particular ceramics in the initial nano-powder mixture and applied sintering temperature on the structure and properties of final nanocomposites is investigated.³

The uniqueness of cordierite (2MgO·2Al₂O₃·5SiO₂) – the component material of our initial powder mixture – is associated with its very low coefficient of thermal expansion caused by the negative lattice expansion coefficient in the *c*-direction, which provides high resistance to thermal shock as well as its low thermal conductivity.^{4,5} The cordierite compound was extensively investigated during past decades. The study of the effect of composition on its microstructural development,⁶ mechanism of thermal expansion,^{4,7,8} formation of cordierite,⁹ indentation deformation,¹⁰ doping and phase transformation,¹¹ crystallization kinetics¹²

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and sintering processes,¹³ as well as ion-beam induced amorphization¹⁴ contributed to our common knowledge, to name only a few.

In a consequence, cordierites are often used as refractory materials for industrial furnaces, heat exchangers, gas turbine engines and honeycomb shaped catalyst carriers in automobile exhaust systems.^{7,8} Furthermore, they began to replace Al_2O_3 as a substrate material for semiconductor packaging, due to their low dielectric constant in high-frequency region and high electrical resistivity ($\rho > 10^{14} \Omega \text{ cm}$).^{15,16}

Despite numerous advantages listed here, cordierite's narrow range of sintering temperatures¹³ and moderate mechanical properties are among the main drawbacks for its application as a thermal barrier material. Consequently, there were recently multiple attempts to improve the performance of cordierite by dispersing zirconia in its volume, something that provides interesting characteristics of the obtained new nanocomposites.^{2,17–20}

In contrast to cordierite, yttrium stabilized tetragonal zirconia ceramics are frequently considered as a candidate for thermal barriers, e.g.,²¹ In order to develop Y-TZP material with required properties, the information on microstructural optimization, properties control, and understanding of the role of their nanostructure are strongly required—something already pointed out by Sekino et al.²²

Y-TZP poses a high tensile strength (approximately of 1 GPa) combined with moderate fracture toughness (approximately value of $5 \text{ MPa} \sqrt{m}$).²³ Its fracture behaviour is susceptible to a stress-induced tetragonal-to-monoclinic ($t \rightarrow m$) phase transformation that does not occur, however, at elevated temperatures. Usually, the grains of tetragonal zirconia spontaneously transform to monoclinic structure in absence of a stabilizer, which results in a substantial degradation of the mechanical properties of this material.^{23–25} This phenomenon is more pronounced for a larger grain size (when the amount of stabilizer remains constant) and in a presence of external stress.^{26–28}

Furthermore, the properties of Y-TZP ceramics depend on microstructure of the sintered bodies,^{20,29} and therefore their fracture toughness is expected to decrease with increasing temperature.²³ The discussed $t \rightarrow m$ transformation is also dependent on environmental conditions,^{30–32} while the effect of the proper amount of so called stabilizers (e.g., Y_2O_3 , MgO or TiO_2) prevents degradation of mechanical properties that apparently becomes negligible when the content of Y_2O_3 stabilizer exceeds 6 mol%.^{33,34}

The present study does not follow previous efforts that aimed modification of the cordierite matrix by introduction of the dispersed zirconia particles.^{2,17–20} In contrast, we made attempt to combine Y-TZP and cordierite initial nanopowders in order to obtain the composite that combines superior mechanical and thermal properties of each component, respectively. This is expected to help the selection of the best material for spray or plasma deposited thermal insulators.

Hence, the present research examines the effect of addition of cordierite powder (up to 20 wt.%) on the both thermal conductivity and mechanical properties of fabricated nanocomposites with Y-TZP matrix as well as their structure. The presented results follow the original findings by Niihara, Sekino and coworkers^{17–20} that targeted cordierite-based composites with Y-TZP. However, the present authors faced the reaction that occurs between ZrO_2 and cordierite powders during sintering, which results in fabrication Y-TZP/zircon (ZrSiO_4) composite, instead the anticipated Y-TZP-cordierite combination. The newly obtained nanocomposite exhibits interesting properties that run contrary common expectation, namely, lower than anticipated coefficient of thermal conductivity.

2. Experimental procedure

2.1. Initial powders and fabricated composites

The materials investigated within the present work were prepared by solid-state reaction sintering of the appropriate proportion of three individual oxide powders, namely, ZrO_2 powder (TZ-0, TOSOH Co., Japan) with a mean particle size of 30 nm, the 2.5 μm grade powder of near-stoichiometric cordierite (SS-600, Maruso Yuyaku Joint Vent. Setoshi, Japan), and Y_2O_3 -powder with a mean grain-size of 33 nm (RU-P, Shin-Etsu Earth's Co., Japan) used as a stabilizer for monoclinic ZrO_2 . The investigated contents of cordierite within the initial powder mixture varied from 5 to 20 wt.%, while the prepared powder-mixture contained always 3 wt.% of the used stabilizer.

The powders were grounded after mixing together by means of wet-ball-milling in ethanol for 24 h using zirconia balls diameter of 5 mm. Subsequently, the slurries were dried and dry-milled for the additional consecutive 12 h. The resulting granulates were uniaxially pressed at 29.4 MPa into pellets with the diameter of 15 mm, or alternatively, into rectangular specimens (55 mm \times 25 mm \times 5 mm). The obtained samples were cold isostatically pressed (CIP) under a pressure of 196 MPa, which enabled us to achieve maximum green density as well as to compensate the density gradients that usually arise during uniaxial pressing. The prepared green compacts were sintered in air at three selected temperatures, namely, 1400, 1500 and 1600 °C. The process performed with the heating rate of 10 °C/min longed for four consecutive hours.

2.2. Characterization of the obtained composites

The sintered compacts were analyzed by X-ray diffraction technique (XRD, $\text{Cu K}\alpha$ $V = -50 \text{ kV} - 150 \text{ mA}$, RU-200B, Rigaku Co. Ltd., Tokyo, Japan) to identify the phase structure caused by the applied processing, and their bulk density was determined using the Archimedes' method.

The thermal analysis was carried out in air atmosphere up to 1500 °C with the applied heating rate equalled 10 °C/min, while annealing was for 1 h. In particular, the oxidation of composite containing 10 vol.% of cordierite was analysed in detail using differential thermal analysis (DTA) and thermogravimetry (TG) method (equipment: Bruker AXS, TG-DTA 2000SA).

The microstructure of the obtained materials was observed by means of scanning and transmission electron microscopy (SEM and TEM). Sintered specimens were polished with diamond pastes (grade of 1 µm) and subsequently thinned by thermal etching—the procedure applied exclusively to the samples with a perfect, mirror surface. Then the specimens were additionally annealed for 30 min at the temperatures that were 50 °C lower than the level of sintering temperature used to obtain the specific material (1350, 1450, 1550 °C), while the applied heating and cooling rates equalled 10 °C/min. The final samples aimed for TEM observation were thinned to approximately 100 µm by dimpling and subsequent ion milling.

Based on the results of structural investigations, the materials sintered at 1400 and 1500 °C were selected for further inspection that was accomplished by means of conventional, standard mechanical tests and evaluation of the coefficient of thermal conductivity. The latter was measured at room temperature by the laser flash thermal analyzer (ULVAC-RICO, TC 7000) for the samples of sintered materials ground and polished with diamond slurry (the dimensions of pellets were 12 and 1 mm in diameter and thickness, respectively).

It is worth emphasize that the rectangular specimens (3 mm × 4 mm × 40 mm) were grounded and polished prior to mechanical testing, with fine diamond paste (grade of 2 and 0.5 µm), to avoid the surface effect on the strength measurement, and through this to obtain reliable results. Strength of the newly fabricated composites was measured using the three-point bending method with a span of 30 mm and a crosshead speed of 0.5 mm/min.

The fracture toughness of sintered specimens was determined by the indentation-fracture method performed under the nominal applied load of 20 N, while the critical stress intensity factor (K_{Ic}) was estimated according to the formula proposed for ceramics by Niihara et al.³⁵:

$$K_{Ic} = \beta \left(\frac{PH}{4C} \right)^{1/2} \quad \text{and} \quad \beta = 0.025 \left(\frac{E}{H} \right)^{0.4}, \quad (1)$$

where E , H , P and C stand for Young's modulus, hardness, the applied indentation load and Palmquist crack length, respectively.

3. Results and discussion

3.1. Material and its structure

The fabrication process applied by us was aimed at fabrication of the desired material, i.e., a novel composite in

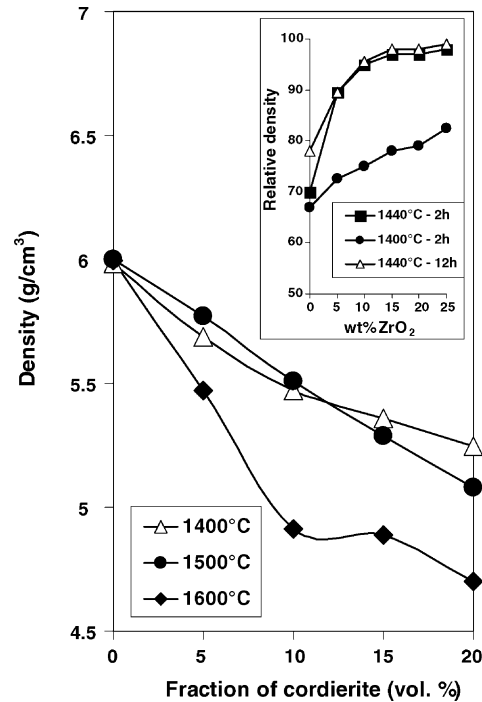


Fig. 1. The variations of the density of the Y-TZP-based composite versus the amount of cordierite powder used for preparation of the material. The relationship is presented for three different sintering conditions, while the inset illustrates the changes in relative density³⁶ of the cordierite/ZrO₂ nanocomposite reported by Sun et al.²⁰

which at least one of constituents has a grain size in nanometer range. Simultaneously, the present authors tried to avoid major problems in the processing of nanopowders associated with the formation of large agglomerates during pressing, and extensive grain growth that occurs during conventional sintering of nanophase green bodies, as already indicated by Vaßen and Stöver.¹ In a consequence, the pressureless sintering process applied after Niihara, Sekino, and coworkers^{17–20,22} was chosen by the present authors to secure production of the desirable structure. The performed structural observations confirmed that the required configuration was accomplished.

The present study provides evaluation of the effect of the cordierite-fraction in the initial nano-powders mixture on the structure of the fabricated Y-TZP-based composites and their properties. We found that the variations of the density of the obtained materials depend on the amount of cordierite in the green body as well as the selected level of sintering temperature, something apparently illustrated in Fig. 1.

It is worth noting that the present data (Fig. 1) are consistent with these demonstrated by Sun et al.²⁰ for cordierite/ZrO₂ composite (refer to the inset in Fig. 1), which indicates that composite density systematically increases with the content of zirconia in the sintered body. The discussed relationship appears evident; despite the previous results (see Ref. 17, Table 1 and Ref. 20) refer to the relative density parameter³⁶ that cannot be quantitatively compared with the explicit values obtained by us (see Fig. 1). Hence, we contend that the density of final composite de-

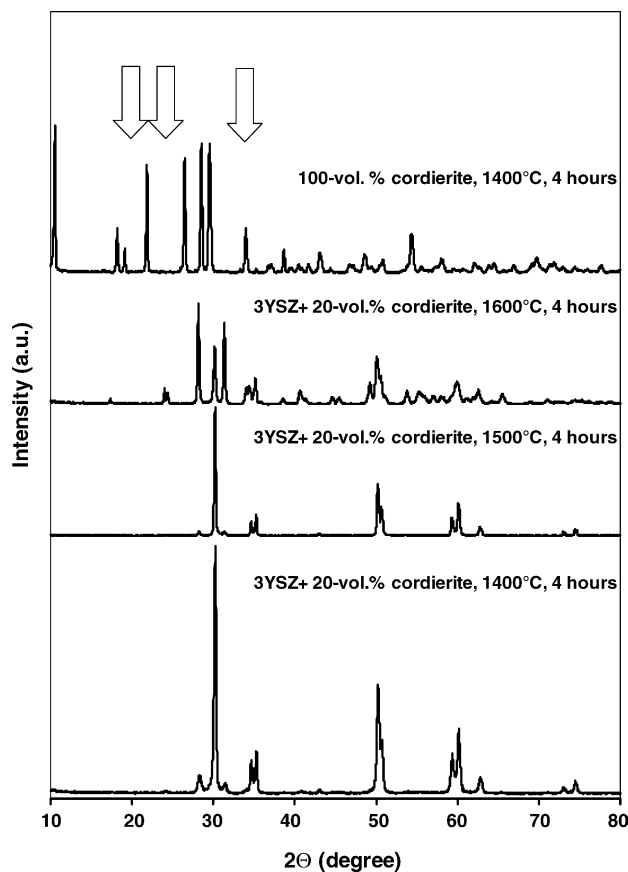


Fig. 2. Examples of X-ray diffraction patterns registered for the obtained 3Y-TZP-based composites sintered at various temperatures. The data for pure cordierite are demonstrated for sake of comparison, while the positioning of zircon peaks is indicated by arrows.

creases in general with the rise of the applied sintering temperature for the green compacts that contain equal amounts of cordierite.

The examination of the fabricated material by XRD powder technique enabled us to identify the component-phases formed after sintering. It is worth emphasize that the present authors did not register, the cordierite peaks in the spectra recorded for the obtained composites, although the cordierite content in the initial mixtures was relatively high (Fig. 2).

The above-reported result does not come as a surprise, since the formation of zircon was expected for sintering temperatures close to 1600 °C. This result agrees with that of Nieszery et al.,³⁷ who used rate-controlled sintering with soaking at 1400 °C for 1 h to produce dense cordierite/ZrO₂ composites, and who found zircon in the obtained material. The lack of cordierite reflex is due to the reaction that occurs between silica (component of MgO·2Al₂O₃·5SiO₂) and ZrO₂, which results in formation of zircon (the detailed account of the reactions during Y-TZP-cordierite sintering process is given elsewhere¹⁹). Interestingly, our X-ray analysis detected the stabilized tetragonal ZrO₂ in all the samples, even though non-stabilized monoclinic ZrO₂ powder was used as a starting material.

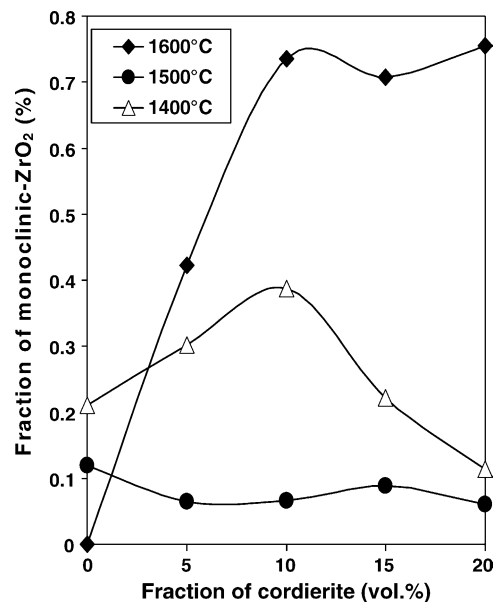


Fig. 3. The amount of ZrO₂ that appears in monoclinic form in the nanocomposite estimated from XRD data. Please note the dependence of the *m*-zirconia on fraction of cordierite in the initial mixture and on sintering temperature.

The results of XRD analysis (Fig. 2) led the present authors to the conclusion that it is possible to control the amount of tetragonal zirconia which would undergo (*t* → *m*) transformation, by a selection of the proper sintering temperature (compare the relative peak intensities for tetragonal and monoclinic phases highlighted in Fig. 2). Indeed, the straightforward account for the amount of monoclinic phase (*m*-ZrO₂) in the composite was obtained from XRD results by exploring the relationships by Garvie and Nicholson³⁸:

$$V_m = \frac{pX_m}{[1 + (p - 1)X_m]} \quad \text{and}$$

$$X_m = \frac{[m_{(11\bar{1})} + m_{(111)}]}{[m_{(11\bar{1})} + M_{(111)} + t_{(111)}]}, \quad (2)$$

where *p* parameter equals 1.311 according to Toraya et al.,³⁹ while *X_m*, *m* and *t* stand for the integral intensity ratio, integral intensity of the monoclinic zirconia and tetragonal phases, respectively.

One can conclude the presence of tetragonal zirconia in the case of absence of the characteristic peak located close to 2θ = 30°, while display of this reflex proves appearance of monoclinic ZrO₂ phase (Fig. 2). Consequently, the analysis of XRD data proved that the fraction of monoclinic zirconia considerably increases for higher contents of cordierite in the initial powder mixture, when the sintering temperature is as high as 1600 °C (see Fig. 3).

The structure of the obtained nanocomposites observed using scanning electron microscopy of the fractured surfaces revealed predominant sub-micron size grains of Y-TZP accompanied by continuous zircon glassy grain boundary phase (Fig. 4). The morphology of the investigated material did not

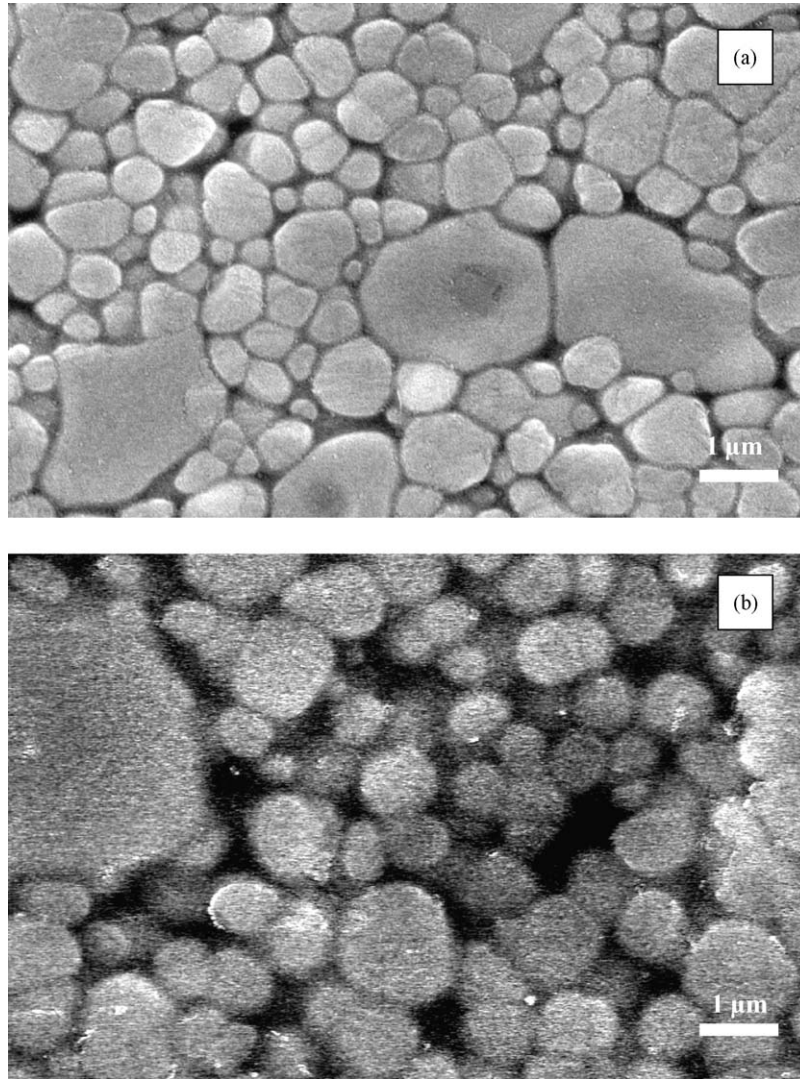


Fig. 4. SEM-micrographs of the polished and thermally etched surfaces of nanocomposites obtained by sintering at 1500 °C the nanopowder mixture containing 5 vol.% (a) and 20 vol.% (b) of cordierite. Please note the sub-micron size of the grains in final material.

differed significantly with the applied sintering temperature (compare Fig. 4a and b), and the TEM observations (Fig. 5) revealed again the existence of $ZrSiO_4$ – detected already by XRD (Fig. 2) and located by means of SEM (Fig. 4) – which appears at the interface among Y-TZP matrix grains. $ZrSiO_4$ was also identified using the energy dispersive X-ray microanalysis (EDAX), while the TEM-micrograph (Fig. 5) proves as well that zirconia-component of our composite remains in the form of nanophase (or at least sub-micron size crystallites).

In contrast to the recent findings by Niihara, Sekino and coworkers,^{17,18,20,22} which concern direct observation of ZrO_2 nanoparticles (size of 10–30 nm) dispersed in cordierite matrix and their fine structure, the present authors obtained nanocomposites with the matrix composed predominantly of nanosized grains with $ZrSiO_4$ glassy phase largely located in the vicinity of grain boundaries. The obtained mixture

of two high-strength materials displays, however, interesting combination of mechanical properties coupled with required lower thermal conductivity, which is discussed in what follows.

3.2. Mechanical properties of the obtained nanocomposites and their thermal conductivity

The aim of the present research was to obtain a new composite that combines low thermal conductivity with excellent mechanical properties (refer to the introductory part). Consequently, the combination of Y-TZP zirconia that exhibits outstanding mechanical behaviour with cordierite that possesses very low coefficient of thermal conductivity (1.5 and 1.9 W/mK at 800 °C and RT,⁴⁰ respectively) seemed originally a correct approach to the problem. However, our structural analysis suggests that the obtained composite contains

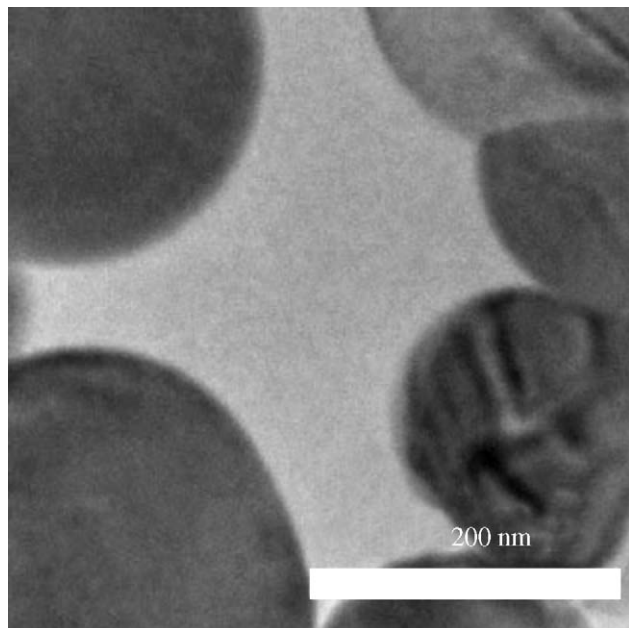


Fig. 5. TEM-image of the nanocomposites fabricated from 3Y-TZP and 20 vol.% of cordierite powders using sintering at 1500 °C for 4 h.

exclusively Y-TZP and $ZrSiO_4$ glassy phase, the two materials that exhibit high thermal conductivity.^{4,41}

To our contentment, the coefficient of thermal conductivity (CTC) measured for the obtained Y-TZP-based composites with zircon and fabricated from the powder with high content of cordierite (more than 15 vol.%), is lower than the one evaluated for pure zirconia (refer to Fig. 6). This result comes as a surprise, since it is well known that $ZrSiO_4$ is considerably better thermal conductor than ZrO_2 , which proved Jin and Chou.⁴¹ The registered effect clearly points towards higher contents of cordierite powders as the recommended initial materials for fabrication of thermally insulating material (Fig. 6). Furthermore, the data displayed in Fig. 6 point towards higher sintering temperatures (1500 °C) that secure low CTC-value of the composite, for a wider range of cordierite contents in the initial powder mixture.

The present authors admit that the obtained CTC data run contrary to common expectations, and they require further thorough study to clarify their cause (preferably an analysis of phonon dynamics in the obtained complex nano-structure). It is worth emphasise that the presented results are consistent, i.e., confirmed through numerous repeating of the CTC-measurement and appear to be interesting enough to justify disclosure at the present stage of research. Moreover, the output of the research agrees with the recent findings by Sekino et al.⁴² who lately elaborated on the influence of the stress on thermal conductivity of apparently two-dimensional layered nano-structured ceramic coatings.

The present study concerns Y-TZP/zircon nanocomposite instead the originally targeted cordierite nanoparticles dispersed within zirconia matrix, which does not come as an ultimate surprise, since the reaction between cordierite and

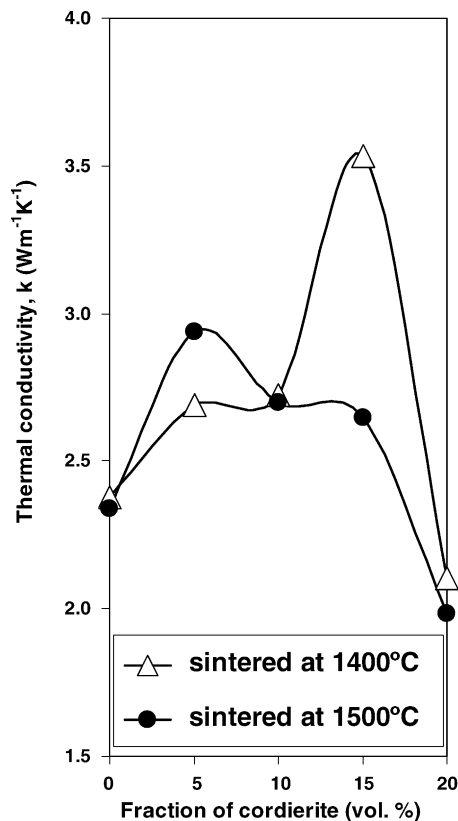


Fig. 6. The coefficient of thermal conductivity measured for the Y-TZP-based nanocomposites sintered from the powders with different initial content of the cordierite and sintered at two selected temperatures: 1400 and 1500 °C.

ZrO_2 was expected based on previous reports (see e.g., Ref. 19). The obtained material appears to be an interesting candidate for thermal insulation, and its production involves the phenomena that need further clarification to be applied in a controlled manner. Indeed, the combination of cordierite with zircon attracted recently much attention¹⁹ and resulted in thorough account for the reactions that occur in the cordierite- ZrO_2 —something being essential for our research, although it targets the novel zirconia/zircon composite.

As far as the mechanical properties are concerned, the idea of reinforcement of cordierite by zirconia come into light already in early 1990s (see e.g., Wadsworth et al.⁴³), while the concept of introduction of $ZrSiO_4$ into Y-TZP matrix (given his notably small bulk expansion coefficient of $4 \times 10^{-6}/^\circ$ reported by Subbarao and Gokhale⁴⁴) was put forward by the present authors and also by earlier study of porous zirconia–zircon structure offered by Jin and Chou⁴¹.

It is a common knowledge that ZrO_2 undergoes phase transformation from tetragonal to monoclinic structure (at the temperature around 950–1150 °C during cooling at atmospheric pressure) and the instability of tetragonal grains largely depends on the matrix-structure one is dealing with. The latter dependence explains that one is able to provide limited prediction of the phase content produced at given sintering conditions (refer to the precedent chapter). Despite the

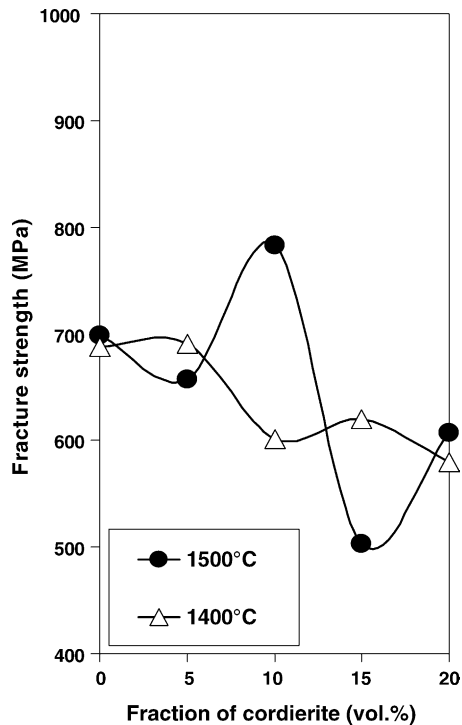


Fig. 7. Fracture strength as a function of cordierite content measured by three-point bending technique for the 3Y-ZrO₂/zircon composites sintered at two selected temperatures.

indicated drawback, the result that stem from the diffraction data, which point towards zircon instead of cordierite as the dispersed material, is not disappointing to the present authors, since ZrSiO₄ is frequently indicated as a proper candidate for high temperature ceramics, and as a such, it matches the requirements concerning components of our “new composite”. Indeed its low thermal expansion, conductivity and thermal shock resistance combined with good chemical stability below dissociation temperature of 1700 °C^{44,45} provides proper account of usefulness of this material, in spite of rather moderate flexural strength (200–300 MPa) and fracture toughness (2–3 MPa \sqrt{m})⁴⁶ that are lower than the values recorded for other ceramic oxides such as Y-TZP or Al₂O₃.

The present study revealed that the toughness determined by indentation technique as well as the fracture strength of the obtained zirconia/zircon nanocomposites depend on the weight percent of cordierite present in the initial powder mixture (refer to Figs. 7 and 8). Unfortunately, from the technological point of view, the observed gradual deterioration of fracture strength (Fig. 7) and fracture toughness with increasing cordierite content fails short from required characteristics. In spite of glass phase formation, decrease of mechanical properties room temperature was minimized. It is therefore the seed of our further study to combine the improved thermal properties manifested for high cordierite contents (see Fig. 6) with improved mechanical behaviour (refer to Figs. 7 and 8) of the composites in the centre of interest, since there are several toughening mechanisms available in zirconia/zircon system that may be explored to achieve the goal.⁴⁷ Enhance-

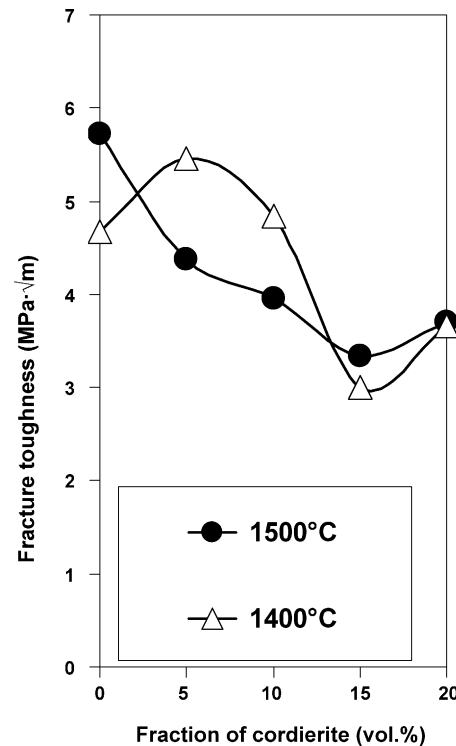


Fig. 8. Fracture toughness as a function of cordierite content measured by indentation technique for the 3Y-ZrO₂/zircon composites sintered at two selected temperatures.

ment of the fracture toughness in composites related strongly to the aspect ratio of zircon particles⁴⁸ what is same kind of phenomena, which has been shown up by Okada et al.

Moreover, the TG and DTA examination of the obtained nanocomposites that contained 10 vol.% of cordierite, point toward excellent stability of the produced material. Indeed, the material did not start to oxidize even annealed at 1500 °C for 1 h in air, and any weight loss was detected during the tests (refer to Fig. 9).

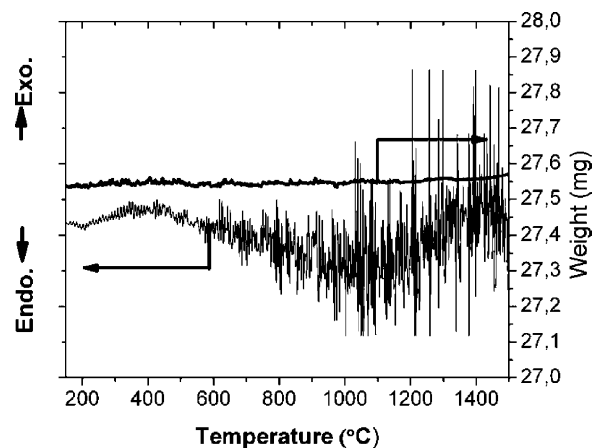


Fig. 9. TG and DTA data registered during 1 h annealing (1500 °C) of the 3Y-TZP based composite that contained 10 vol.% of cordierite. The obtained curves indicate high stability of the material at elevated temperatures.

4. Conclusions

The present paper reports fabrication and characterization of 3YSZ/zircon composites prepared by pressureless sintering of nanopowders of zirconia and cordierite, while the initial content of the latter component varied from 5 to 20 wt.%.

The study revealed the effect of the cordierite-fraction in the initial nano-powders mixture on the structure of the fabricated Y-TZP-based composites. They proved that the density of final composite increases with the content of zirconia in the sintered body, while it decreases with the rise of the sintering temperature for the green compacts with the equal amount of cordierite.

The XRD examination of the fabricated new materials detected exclusively stabilized, tetragonal zirconia and zircon phases, which proves that all the volume of cordierite (silica) reacted with ZrO_2 during fabrication by pressureless sintering, despite the high content of cordierite in the initial powder mixture. The fraction of monoclinic zirconia considerably increases for higher contents of cordierite in the initial powder mixture, when the sintering temperature is as high as 1600 °C. This led one to a conclusion that it is possible to control the amount of tetragonal zirconia in a final composite, by the selection of the proper sintering temperature.

The microscopic observations of the obtained nanocomposites confirmed nano-size of Y-TZP grains accompanied by continuous zircon glassy grain boundary phase, the two materials that exhibit rather high thermal conductivity. Surprisingly, the coefficient of thermal conductivity of Y-TZP-based composites with zircon and fabricated from the powder with high content of cordierite (more than 15 vol.%), was found lower than that of pure zirconia. The registered effect together with results of DTA analysis points towards higher contents of cordierite powders as the suggested initial substance for possible stable, thermal insulator.

It was observed that toughness and fracture strength of the obtained zirconia/zircon nanocomposites depend on the weight percent of cordierite present in the initial powder mixture. Unfortunately, the observed small deterioration of fracture strength and fracture toughness with increasing cordierite content fails short of required characteristics. The present authors claim that this drawback can be improved by proper selection of the fabrication conditions, since there are several toughening mechanisms available in zirconia/zircon system.

Moreover the study form basis for further extension of the research towards preparation of the zirconia composite with nano-dispersed cordierite phase. It seems that this process might be available when one uses re-precipitation technique.

Acknowledgements

One of the authors (A.H.) thanks the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) for the research scholarship as well the Scandinavia-Japan Sasakawa Foundation for financial support.

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