

Structural and mechanical characterization of mullite and aluminium titanate reinforced yttria stabilized zirconia ceramic composites

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3 mole % yttria stabilized zirconia (YSZ) ceramic and 20 wt. % mullite (M), and 20 wt. % aluminium titanate (AT) reinforced YSZ ceramic composites were produced using a conventional ceramic production process. After a combined method of wet ball milling and dry pressing, these samples were sintered at 1500 °C and 1600 °C for 1hr and 5hrs, respectively. Physical properties, microstructural and phase characterizations of the sintered samples were analyzed using Archimedes method, a scanning electron microscope with energy dispersive spectroscopy and X-ray diffraction technique, respectively. Thereafter, micro Vickers and three-point bending tests were performed. The density, relative density and firing shrinkage of the sintered samples increased with addition of M and AT and the increased sintering temperature at each time. However, both porosity and loss of water properties determined were inversely proportional to M and AT addition and sintering temperature and time increase. An increase in M and AT content influenced the grain morphology as is presented in the microstructures of the composites produced thus bringing about a rise in grain size, as well as homogeneity and density in YSZ samples. Promising results were observed with the Vickers and bending strength in the mullite reinforced YSZ samples sintered at 1600 °C for 5hrs due to mullite addition, which provides excellent mechanical features to the YSZ ceramic composites.

Key words: YSZ, Mullite, Aluminium Titanate, Ceramic composites, Mechanical properties, Characterization.

Introduction

Due to several interesting features such as, excellent resistance to heat, corrosion and abrasion, the application of ceramic materials as a high temperature structural material is on the rise, in numerous areas like, cutting tools, extrusion dies, adiabatic diesel engine compartments [1-3]. However, ceramic materials do come with many disadvantages, low reliability and fracture toughness, and poor processibility being few. The structural and mechanical properties of ceramics can be improved through the formation of composite compounds using conventional ceramic production techniques such as direct sintering, slip casting, sol-gel and powder metallurgy routes [1, 4]. Among ceramic materials, zirconia (ZrO_2) has recently become the focus of growing scientific and technological interest because of its better mechanical strength, high temperature stability, low thermal conductivity and high chemical stability [4, 5]. At room temperature, zirconia usually exists in monoclinic phase [6]. The high temperature tetragonal phase can be stabilized by introduction of some stabilizing oxides such as MgO, CaO, CeO_2 , and Y_2O_3 (yttria) in appropriate molar concentrations at room temperature [7]. Among these

oxides- ZrO_2 ceramic composite systems, Y_2O_3 - ZrO_2 composites can form ceramic at room temperature with a tetragonal phase only, called yttria stabilized zirconia (YSZ) [6]. YSZ materials, containing 3 mole % Y_2O_3 are completely constituted by tetragonal grains which are of the micrometre size [8]. Moreover, this ceramic composite can be produced as a ceramic material with high hardness and high strength. Therefore, zirconia stabilized with 3 mole % Y_2O_3 is widely regarded as one of the most interesting ceramic candidates due to its excellent mechanical properties such as: high compressive strength, high hardness, good thermal and chemical stability and high elastic modulus. However, one of the main drawbacks of YSZ is its low fracture toughness that may limit its use in high mechanical applications.

Several studies have focused on the possibility of enhancing the performance of YSZ ceramics, in particular corrosion resistance, thermal shock behaviour and mechanical properties, by varying amount of raw materials [6-9]. For example, by increasing the mullite amount, the crack healing ability of the ceramic composites improved through a significant induction of density and reduction of porosity [10]. In the literature, mullite ($3Al_2O_3 \cdot 2SiO_2$) is defined as the unique stable intermediate crystalline phase of the Al_2O_3 - SiO_2 binary system, it is cost-friendly and exhibits good refractory ability [10]. This makes mullite a desirable material for a diverse range of applications which span from the

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refractory field to technical applications. Moreover, due to its favourable thermos-mechanical properties such as excellent high temperature strength and creep resistance, good chemical and thermal stability, mullite is also widely used as structural material [3]. Furthermore, its low thermal expansion coefficient brings about good thermal shock resistance ability [11-17]. At high temperature, mullite reinforced Yttria stabilized zirconia ceramic composites have been developed with a tetragonal phase transformation under optimized parameters in order to obtain a proper ratio between crystalline and glassy phases.

Several studies have been conducted to explore an inevitable low thermal-shock resistance of Y_2O_3 stabilized zirconia ceramic composites [10, 18]. This poor feature in YSZ ceramic composites has been widely seen because of their high thermal expansion and low thermal conductivity [6]. However, there are many applications demanding good or even excellent thermal-shock resistance, is required [19]. Generally, achieving this requires optimizing the level of stabilization or varying amounts of raw materials for each application. Among the thermal shock resistant materials, aluminium titanate (Al_2TiO_5) has been widely used in several applications such as glass industry, automotive and thermal processing industries due to their favourable features like low thermal conductivity and thermal expansion coefficient, good chemical resistance in molten metals and excellent thermal shock resistance [20-22]. Thus, these properties, particularly thermal shock resistance ability make Al_2TiO_5 a high demanding reinforce material for ceramic composite systems, despite its anisotropic thermal expansion coefficient, which leads to a large mismatch with matrix phase, alumina [19, 22-25].

In recent years, although many researchers have investigated the mullite additives in yttria stabilized zirconia ceramic composites and most of them deal with its enhancement of mechanical properties [9, 19]. However, there is no study as of yet on the improvement of both mechanical and thermal-shock resistance of yttria stabilized zirconia ceramic composites. In this study, M and AT reinforced ceramic composites containing different M and AT ratios were produced at 1500 °C and 1600 °C for 1hr, 5hrs by a combined method of wet-ball milling, dry pressing and sintering. The precursory materials used were commercially available Y_2O_3 , ZrO_2 , SiO_2 , Al_2O_3 and TiO_2 powders. All the mixtures used were prepared in-house. The effects of M, AT contents and sintering temperature and time on the physical properties, microstructure, phase formation, hardness and bending properties of the sintered materials were discussed.

Experimental

All precursory powder materials (Y_2O_3 , ZrO_2 , Al_2O_3 , SiO_2 , and TiO_2) used in the present work were

purchased from Eczacibasi Company (Eczacibasi Esan, Turkey) and Cisco Chemical, USA). A conventional ceramic production processing route was performed to produce mullite and aluminium titanate reinforced YSZ porcelain ceramic composites in this study. Initially, mechanical alloying process is used to prepare mixtures by inserting alumina balls (\varnothing 10 mm) into the closed box to homogenize the blend with acetone as medium. Then, a drying of the powders prepared in an oven at 110 °C for 24 hrs was performed before mixing. To achieve homogenous composite compacts, %3 mole Y_2O_3 -stabilized zirconia (YSZ), aluminium titanate (Al_2TiO_5) and mullite ($3Al_2O_3 \cdot 2SiO_2$) ceramics were synthesized by reaction sintering from Y_2O_3 , ZrO_2 , Al_2O_3 , SiO_2 and TiO_2 powders which process consisted of using wet ball milling followed by sintering of YSZ, Al_2TiO_5 (AT) and $3Al_2O_3 \cdot 2SiO_2$ (M) in air at 1300 °C, for 2 hrs, 1550 °C for 2 hrs and 1400 °C for 2 hrs, respectively. Different amounts of AT and M (for example: 0 and 20 wt. %) were blended with yttria stabilized zirconia (YSZ). YSZ was denoted as "Y" when AT and M reinforced YSZ ceramic composites produced (see Table 1). Then, different experimental formulations (named as; YSZ, YAT, YM, YMAT) were weighed and prepared, respectively (see Table 1). AT and M reinforced YSZ ceramic composites were produced by using a powder metallurgy method. Acetone and zirconia balls (\varnothing 10 mm) were added to the samples, which were then completely blended by using wet ball milling process for 3 h to achieve homogenous composites and the obtained samples were sieved. To extract acetone and make dry powder samples, green samples were placed in desiccators. Then, the dried samples were pressed by uniaxial pressing at 200 MPa

Table 1. Compositions of yttria stabilized ZrO_2 - Al_2TiO_5 - $3Al_2O_3 \cdot 2SiO_2$ powders used in this experimental work.

Specimen ID	Chemical composition (% mole)		
	Yttria stabilized ZrO_2	Al_2TiO_5	$3Al_2O_3 \cdot 2SiO_2$
YSZ	100	-	-
YAT	80	20	-
YM	80	-	20
YMAT	60	20	20

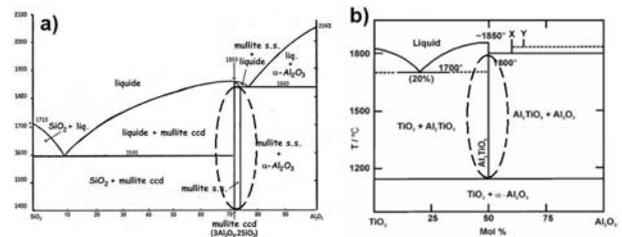


Fig. 1. (a) Binary phase diagram of Al_2O_3 - SiO_2 system proposed and (b) Binary phase diagram of Al_2O_3 - TiO_2 system proposed by Goldberg et al. in 1968 [26, 27].

into $56 \times 12 \times 10 \text{ mm}^3$ specimens, respectively. The resulting green compacts were then sintered at 1500°C and 1600°C for 1 and 5 h under air using a heating rate of 5°C min^{-1} in a high temperature furnace (Protherm™ Furnace, Turkey). The Binary phase diagrams of $\text{Al}_2\text{O}_3\text{-SiO}_2$ and $\text{Al}_2\text{O}_3\text{-TiO}_2$ system proposed provided information to form ceramic composite systems in this study depicted in Fig. 1.

The bulk and relative densities, porosity and water absorption of the sintered samples were measured using the Archimedes method. The % firing shrinkage values were determined by reduction in length. To study morphological features of the various phases of the sintered samples obtained, scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) results of the resultant samples sintered at 1600°C for 5 hrs were taken using a JEOL-JSM-6060LV after sample's surface polishing and Au coating process. To determine the phases obtained at 1600°C for 5 hrs sintering process, X-ray powder diffractometer (XRD) with $\text{Cu K}\alpha$ radiation (Rigaku, Dmax, IIC) was used. Micro hardness (Hv) was determined on the polished surface of the resultant samples using the Shimadzu Vickers indenter under a peak load of 1000 gr and a loading time of 20 s. A three-point bending test at room temperature with a span of 36 mm and a crosshead speed of 0.5 mm / min was performed to assess the bending strength of the resultant samples sintered at different temperatures and periods. To obtain high reliability, at least three measurements for all samples were performed.

Results and Discussion

Fig. 2 shows a change in physical properties of the YSZ, YAT, YM, YMAT ceramic composite structures

produced when an addition of mullite and aluminium titanate content at different sintering temperature for several periods. An increase in the sintering temperature and period applied for each specimen used leads to a decrease in density (g cm^{-3}), relative density (%) and firing shrinkage (%) properties of the all resultant specimens obtained was indicated in Fig. 2. However, it was observed that an increased sintering time and period applied brings about a decrease in both porosity (%) and loss of water (low, %) values (Fig. 2). With regards to addition of the other ceramic compounds, like mullite and aluminium titanate to the YSZ specimen, Fig. 2(a) shows that increasing both AT and M contents considerably increased density of the YSZ specimen. A smaller increase in density was observed in the YMAT when compared to that of the YM and YAT specimens is associated with an addition of AT and M together (Fig. 2(a)). In Fig. 2(b), it was seen that the increased addition of AT, M and MAT led to an increase in relative density values compared to that of the YSZ specimen. Fig. 2(c) presents the firing shrinkage properties of the resultant samples, and it can be observed that the AT, M and MAT content increase caused an increase on firing shrinkage of the YSZ specimen. In Figs. 2(d) and 2(e), both the porosities and loss of water values of the ceramic composites decreased with increasing AT, M and MAT contents compared to that of the YSZ specimen.

Fig. 3 shows surface view SEM images of the YSZ, YAT, YM, YMAT specimens sintered at 1600°C for 5hrs with different mullite and aluminium titanate contents. The average grain size in the ceramic samples tends increase with increased amounts of mullite and aluminium titanate added to the system. It can be seen that the YSZ specimen has a homogenous and dense structure and the average grain size is determined as

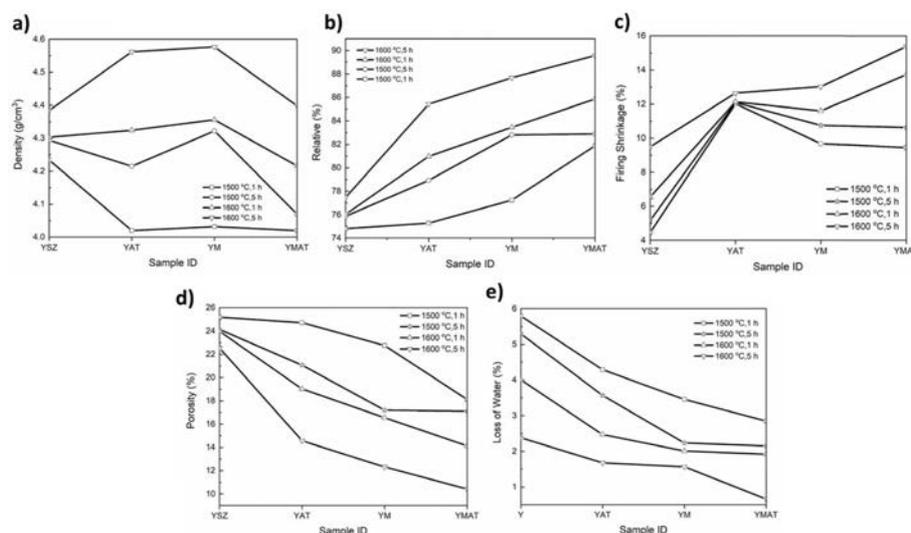


Fig. 2. Physical properties: (a) Density, (b) Relative density, (c) Firing shrinkage, (d) Porosity, and (e) Loss of water of the sintered samples at different temperatures and periods.

approximately 2 μm (Fig. 3(a)). When the added amounts of aluminium titanate are 20 wt. %, the sintered body samples have high density and few pores. In comparison between Fig. 3(a), the sintered body sample in Fig. 3(b) has slightly larger grain size, 3 μm , thereby imparting various excellent mechanical properties to the ceramic sample, YAT. Also, an increase in an added amounts of mullite brings about a rise in density and decrease in porosity which is depicted in Fig. 3(c). Moreover, the average grain size of the YM ceramic specimen was determined as 12 μm and a remarkable arise in grains was indicated when the mullite content increases, thereby contributing better physical features to the ceramic specimen, YM. Fig. 3(c) also clearly represents partially melted mullite grains with a flake shape. When comparing Fig. 3(c), the microstructure of the YMAT ceramic specimen in Fig. 3(d) has smaller average grain size, 10 μm and less mullite flakes due to an influence of aluminium titanate on grain growth mechanism. To evaluate phases formed in the YSZ, YAT, YM, YMAT specimens sintered at 1600 $^{\circ}\text{C}$ for 5hrs with different mullite and aluminium titanate contents, EDS analysis results as in Fig. 3(e),

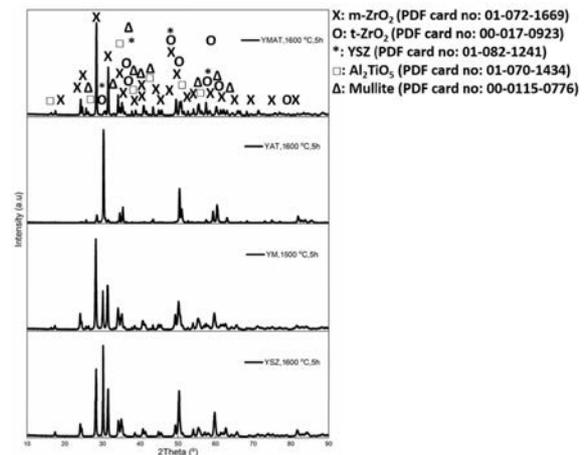
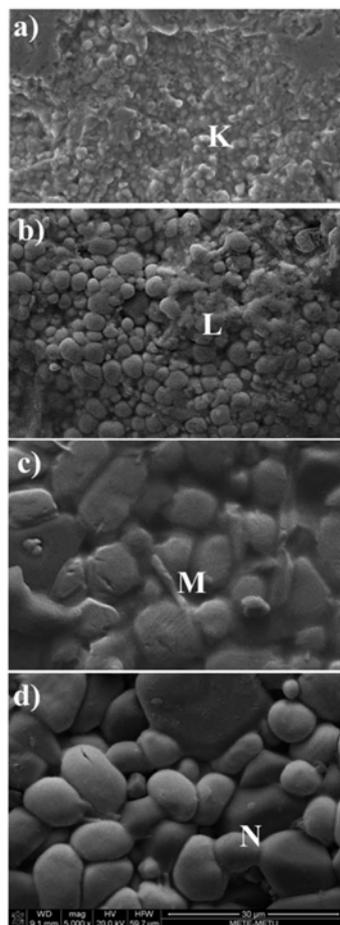


Fig. 4. XRD patterns obtained from YSZ, YAT, YM and YMAT samples sintered at 1600 $^{\circ}\text{C}$ for 5 hrs.

presented that there is a homogenous composition throughout each microstructure. Region K consists of two main phases (yttria and ZrO_2) because it contained Y, Zr and O. Region L is composed of Zr, Al, Ti and O



e)

Sample ID	K	L	M	N
Oxygen, wt. %	18.146	21.756	10.350	31.989
Yttria, wt. %	9.715	-	4.249	-
Zirconia, wt. %	72.138	72.306	73.029	36.149
Aluminium, wt. %	-	0.686	-	10.098
Titanium, wt. %	-	5.211	-	17.351
Silicon, wt. %	-	-	12.372	4.414

Fig. 3. SEM images obtained from (a) YSZ, (b) YAT, (c) YM and (d) YMAT samples sintered at 1600 $^{\circ}\text{C}$ for 5 hrs, and (e) EDS results measured.

the YSZ specimen. Region M consists of Zr, Y, Si and O, which depicts an addition of mullite to the YSZ specimen. Zr, Al, Ti, Si and O EDS peaks were depicted in Region N, which corresponds to YMAT ceramic composite prepared with an addition of mullite and aluminium titanate in YSZ specimen.

Fig. 4 shows the XRD analysis results of YSZ, YAT, YM, YMAT ceramic composite samples obtained at 1600 °C for 5hrs. The characteristic diffraction peaks of the starting materials all correlate with the standard cards of ZrO_2 , YSZ, mullite, aluminium titanate (Al_2TiO_5), respectively. Comparing XRD patterns presented in Fig. 4 reveals that an increase in mullite and aluminium titanate content in the mixed ceramic composite materials (for example; YM, YAT and YMAT), the diffraction peaks of mullite and aluminium titanate in the XRD pattern gradually increase. These finding is consistent with the previously measured bulk density results.

In order to determine the effect of mullite and aluminium titanate contents on the mechanical properties of the YSZ, Vickers hardness, and bending strength of YSZ, YAT, YM, YMAT ceramic composite samples obtained were observed. Fig. 5 shows the Vickers hardness of the as-received YSZ specimen and

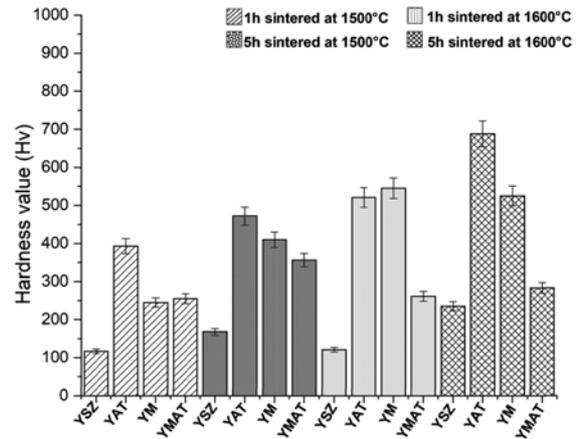


Fig. 5. Vickers microhardness values obtained from YSZ, YAT, YM and YMAT samples sintered at different temperatures and periods.

the ceramic mix (YAT, YM and YMAT) specimens. The trend shows an increase up to highest hardness at a sintering temperature of 1600 °C for 5hrs, which is approximately 700 HV. The increase in hardness can be attributed to a higher sintering temperature and for a longer time. Also, the increase in the mullite content

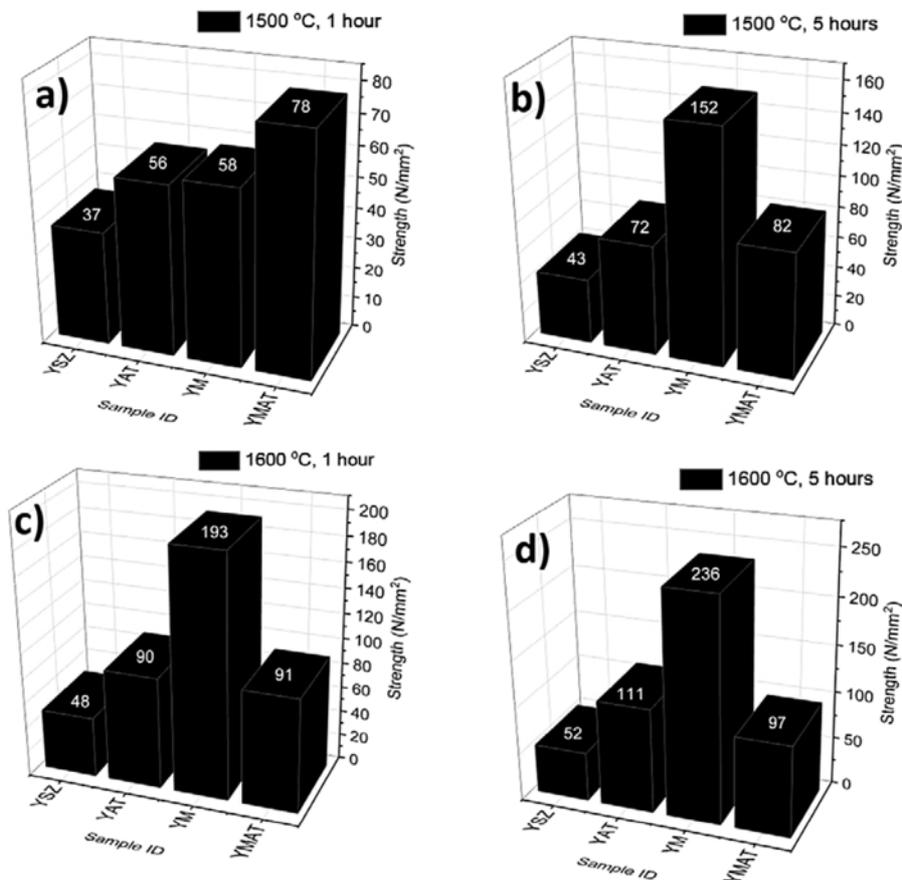


Fig. 6. Three point bending results obtained from YSZ, YAT, YM and YMAT samples sintered at different temperatures and periods: (a) 1500 °C for 1 hr, (b) 1500 °C for 5 hr, (c) 1600 °C for 1 hr, (d) 1600 °C for 5 hrs.

resulted in a rise in hardness, particularly at 1600 °C for 5 hrs which was 700 HV.

Fig. 6 shows three point bending strengths for the YSZ, YAT, YM, YMAT specimens sintered at 1500 °C and 1600 °C for 1hr and 5hrs per each. The bending strengths of the YSZ, YAT, YM, YMAT specimens sintered at 1600 °C for 5hrs were approximately 53, 111, 235 and 97 MPa, respectively (see Fig. 6(d)). These are remarkably larger than the above-mentioned samples sintered in this study (see Fig. 6(a-c)). The YSZ denoted specimen with addition of mullite showed crack-healing, and the strength was increased by the addition of mullite. The strength of the all compacts was also increased due to an influence based on the duration of the sintering process performed (Fig. 6(a-d)). Although AT addition into the as-received YSZ specimen did not show a remarkable influence on the strength of the YSZ sample, an increase on the strength of the YSZ sample was indicated (Fig. 6).

Conclusions

This study evaluated the structural features and mechanical properties of mullite and aluminium titanate reinforced YSZ composite ceramics at 1500 °C and 1600 °C for 1hr and 5hrs. Results obtained showed, the physical properties of YSZ and mullite (M) and aluminium titanate (AT) reinforced YSZ ceramic composites, including the density, relative density, firing shrinkage, increased with increasing sintering temperature and time. Other physical features of the specimens produced, including porosity and loss of water decreased with the increase in sintering temperature and time. While a considerable increase in density, relative density and firing shrinkage of YSZ ceramic composites was noted with an increasing addition of mullite and aluminium titanate compounds, a noticeable decrease in porosity and loss of water of the YSZ ceramic composites was determined when increasing the content of the compounds used.

The average grain size, homogeneity of the phases, and density of the YSZ and AT-M reinforced YSZ ceramic composites increased with increased amounts of mullite and aluminium titanate added to the system. A noticeable small decrease in average grain size of the YMAT specimen was observed due to an influence of the aluminium titanate on grain growth mechanism. In addition, through the various analysis using EDS and XRD, it is confirmed that ZrO₂, Ytria, mullite and aluminium titanate and different forms of these phases formed. The Vickers hardness of the specimens obtained in this study increased with increasing sintering temperature and time. The highest Vickers hardness value measured at 1600 °C for 5 hrs for mullite reinforced YM specimen due to the effect of mullite addition. The bending strengths of the YSZ, YAT, YM, YMAT specimens increased with increasing sintering

temperature and time. The highest bending strengths of the above-mentioned samples were achieved under a sintering temperature of 1600 °C for 5h. The noticeable bending strength increase was depicted in the mullite reinforced yttria stabilized specimens in each sintering temperature and time, which imparted a crack-healing ability to YSZ samples. Hence, the produced YM and YMAT ceramic composites can be utilized for a wide range of future applications, which desire excellent resistance to heat, strength, corrosion and abrasion.

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