

Fabrication of Mullite Reinforced Y₂O₃ Added ZrO₂ Ceramics and Characterization of These Composites

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Abstract - Mullite (3Al₂O₃.2SiO₂) and 3 mol% yttria added zirconia (3 mol% Y₂O₃ - 97 mol% ZrO₂) powders by conventional ceramic production method. We prepared the mixtures in acetone environment by mechanical alloying method. To synthesize mullite, we prepared Al₂O₃ and SiO₂ powders mixture with stoichiometric proportions and fired in air at 1600 °C for 3 h. And we fired yttria added zirconia composites at 1300 °C for 2 h. Thus, yttria - zirconia and mullite composite phases were obtained and grinding and sieving processes were carried out. Then, we prepared with powder metallurgy method the mullite-free and 10% by weight mullite reinforced yttrium oxide added zirconia mixtures. The powders were pressed by uniaxial pressing after drying. The formed samples were sintered in a high temperature furnace in air conditions for 1 and 5 h at 1500 and 1600 °C sintering temperatures. Finally, microstructure investigations, phase analysis, 3-point bending, hardness, wear tests, absorption of water, porosity, shrinkage and density results were examined on the composites. For the result, we understand that the amounts of m-ZrO₂, t-ZrO₂ and c-ZrO₂ in the structure varies depending on the sintering temperature and time. So, along with all physical and mechanical properties, especially bending strengths varied. In addition, while the addition of mullite increased the flexural strength, water absorption and porosity values of the composites; It was concluded that hardness, wear, shrinkage and density values decreased.

Keywords: Zirconia, Mullite, Yttria, Characterization, Wear.

Mullit Takviyeli Y₂O₃ Katkılı ZrO₂ Seramiklerinin İmalatı ve Bu Kompozitlerin Karakterizasyonu

Öz - Bu çalışmada, mullit (3Al₂O₃.2SiO₂) ve %3 mol itriya katkılı zirkonya (%3 mol Y₂O₃ - %97 mol ZrO₂) tozları geleneksel seramik üretim yöntemi ile sentezlenmiştir. Karışımları aseton ortamda, mekanik alaşımlama yöntemiyle hazırladık. Mullit sentezi için stokiometrik oranlarda hazırladığımız Al₂O₃ ve SiO₂ tozları karışımını hava ortamında 1600 °C'de 3 saat fırınladık. İttriya katkılı zirkonya kompozitlerini ise, 1300 °C'de 2 saat fırınladık. Böylece, itriya - zirkonya ve mullit kompozit fazları elde edildi ve öğütme ve eleme işlemleri yapıldı. Daha sonra mullit katkısız ve %10 mullit takviyeli itriyum oksit katkılı zirkonya karışımları toz metalurjisi yöntemiyle hazırlanmıştır. Kurutulduktan sonra, tozlar tek eksenli presleme ile sıkıştırılmıştır. Şekillendirilen numuneler, yüksek sıcaklıklı bir fırında hava koşullarında 1500 ve 1600 °C sıcaklıklarda, 1 ve 5 saat sürelerle sinterlenmiştir. Son olarak kompozitler üzerinde mikroyapı incelemeleri, faz analizi, 3 nokta eğilme, sertlik, aşınma testleri, su emme, gözeneklilik, büzülme ve yoğunluk sonuçları incelenmiştir. Sonuç olarak yapıdaki m-ZrO₂, t-ZrO₂ ve c-ZrO₂ miktarlarının sinterleme sıcaklığına ve süresine bağlı olarak değiştiğini anlıyoruz. Bu nedenle, tüm fiziksel ve mekanik özelliklerle birlikte, özellikle eğilme mukavemetleri değişmiştir. Ayrıca mullit ilavesi kompozitlerin eğilme mukavemeti, su emme ve gözeneklilik değerlerini artırırken; sertlik, aşınma, çekme ve yoğunluk değerlerini azalttığı sonucuna varılmıştır.

Anahtar kelimeler: Zirkonya, Mullit, İttriya, Karakterizasyon, Aşınma

1. Introduction

Among ceramics, zirconia (ZrO_2) and its composites have become very popular for technological and many scientific studies because of their good mechanical properties, corrosion resistance, low thermal conductivities, higher temperature stabilities and higher chemical stabilities [1-3]. They are preferred as important main materials for refractory materials, high temperature furnaces, components that are resistant to wear, various cutting tools, dental studies and other a lot of fields [1-4]. High-purity zirconia (ZrO_2) exhibits three polymorphs depending on temperature: monoclinic ($m-ZrO_2$) phase is stable at temperatures up to 1170 °C. After this temperature, the conversion from the monoclinic phase to the tetragonal phase begins and the tetragonal zirconia ($t-ZrO_2$) phase is stable up to 2370 °C temperatures. From this temperature to the melting temperature of 2680 °C, it is in the cubic zirconia phase ($c-ZrO_2$) [1,4]. Depend on the cooling processes, transformation from the $t-ZrO_2$ to $m-ZrO_2$ occurs. Transformation is very important because of resulting in a volumetric change of around 3% to 5% and so, leads to cracks. To prevent this transformation and stabilize the zirconia, it is common to use stabilizers. Addition of stabilizers to zirconia, lowers temperature of the transformations, reduces volumetric growth or shrinking and blocks the polymorphic transformations. With using stabilizers, it is possible to make stable the high-temperature phases at low temperatures too [4]. Different stabilizers, such as, Al_2O_3 , CaO , CeO_2 , MgO , SiO_2 , TiO_2 , Y_2O_3 and even a combination of them, stabilize and keep stable the zirconia in the $t-ZrO_2$ and/or $c-ZrO_2$ forms at low temperatures [5-7]. It is possible to produce materials consisting of only $t-ZrO_2$ or $c-ZrO_2$ or a mixture of these with $m-ZrO_2$ phases by adding different quantities of stabilizer. If less than sufficient stabilizing oxide is added, partially stabilized zirconia (PSZ) is obtained instead of fully stabilized zirconia. PSZ usually consists of two or more closely mixed phases. As a result of using stabilizers and obtaining fully or partially stabilized zirconia, could be achieved superb mechanical properties for example bending strength, hardness, fracture toughness [8].

Although, zirconia exhibits better mechanical properties than other ceramics, but like all other ceramics, it is fragile and cannot be formed at room temperature. So, we want to increase the toughness of these materials. For this, some energy absorbing mechanisms such as transformation toughening and fiber reinforcement are used in ceramic matrices [1].

In the method of increasing fracture toughness with transformation toughening, it works on the principle of a phase transformation caused by tension, by reducing the driving force that propagates existing cracks in the material structure [1]. The best example of this is zirconia. Zirconia which is added to the ceramic main phase, keeps important role in increasing fracture toughness and thus the bending strength with its tetragonal - monoclinic transformation toughening feature. With the discovery of the transformation toughening that occurs in zirconia, this material has found wide use. Because the main factor limiting the use of ZrO_2 in advanced engineering applications was the low toughness of this material. Increasing the toughness property with transformation toughening has also increased the interest in zirconia. The volume increase of 3 - 5%, which occurs with the tetragonal - monoclinic phase transformation in zirconia, prevents crack propagation, so increases the toughness of the material and its resistance to fracture [9]. The t-m transformation in zirconia can occur in different ways. For example: $t-ZrO_2$ can be free as a single particle or crystal; It can also be found in a compacted form in a matrix as a precipitate phase. Tetragonal zirconia particle size and the matrix in which the particles are compacted are the most important factors. A critical $t-ZrO_2$ grain size determine in ZrO_2 . If the grain size is below this critical size, there will be no transformation; above, the t-m transformation occurs either continuously or as a result of applying a stress [10].

In the ceramic - ceramic mixed structure formation process, which is the other method of increasing the fracture toughness, the strength and toughness are increased by adding ceramic whiskers, fibers or particles to the main phase. This method is based on creating a physical barrier to the progressive crack. Having higher tensile strength than polycrystalline material, whiskers are a good barrier to propagation cracking. So, the fracture toughness of zirconium dioxide can be

increased more by adding some secondary phases for example nano particles, nano sized fibers or nano sheets into zirconia matrix [11]. For the last decades, improvement of nanomaterials offers new alternatives to reinforce ceramic composites. Carbon nanotubes have attracted important caution as reinforcement materials because of their magnificent properties. However, at high temperatures, they are prone to react with oxide matrixes leading to reduction in some mechanical properties of carbon nanotubes and limited the reinforcing effect on the composites [12,13]. So, it is stated that incorporation of mullite which is another type of ceramic toughening method with its high temperature oxidation and corrosion resistance and the other superior properties, might be preferred [11]. In the literature, mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is described as the matchless stable middle crystalline phase for Al_2O_3 - SiO_2 binary system, cost-friendly and exhibiting good refractory ability [14,15]. Mullite has received significant attention for technological applications because of its well properties like low coefficient of thermal expansion, high melting temperature, good resistance to creep, good chemical stability and satisfactory hardness [16,17]. In short, fracture toughness of zirconia can be advanced with mullite reinforcement as the secondary phase into the ZrO_2 matrix and so, the other mechanical properties can be improved too [11]. In addition, the temperature of sintering is also important, because of affecting some properties of ceramics through changing of the crystalline phases and microstructure [18].

In this study, we synthesized mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and 3 mol % yttrium oxide doped zirconium dioxide powders by conventional ceramic production method. We examined whether there are phase differences in the Y_2O_3 - ZrO_2 mixture depend on sintering temperatures and times and the effect of mullite on the physical, mechanical and microstructural properties of these mixtures.

2. Materials and Methods

Mullite and yttria doped zirconia powders were produced by conventional ceramic production method in this study. All precursory powder materials (Al_2O_3 , SiO_2 , Y_2O_3 and ZrO_2) were obtained from Company Eczacıbaşı, Alfa Aesar and Chemicals of Handan Yaxiang Trading Co., Ltd (Eczacıbaşı Esan, Turkey; Alfa Aesar, United States of America and Handan Yaxiang Chemicals Trading Co., Ltd, China). The powders were mixed in acetone environment by mechanical alloying method. The powders were heated for 24 hours in oven at $110\text{ }^\circ\text{C}$ before and after mixing. Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and 3 mol% yttria doped zirconia (Y_2O_3 - ZrO_2) powders were synthesized by sintering from the prepared powders with stoichiometric ratios of Al_2O_3 , SiO_2 , Y_2O_3 and ZrO_2 powders after homogenized in ball mill. Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) was synthesized for 3h at $1600\text{ }^\circ\text{C}$ and 3 mol% yttria doped zirconia (Y_2O_3 - ZrO_2) composite powders were synthesized for 2 h at $1300\text{ }^\circ\text{C}$. Thus, yttria - zirconia and mullite composite phases were obtained and grinding and sieving processes were carried out. Then, we prepared mullite-free and 10% by weight mullite reinforced cerium oxide added zirconium oxide composites with powder metallurgy technique (these mixtures were coded as YZ0M and YZ10M). The sample was coded as YZ10M16005 (YZ: Yttria doped zirconia; 10M: 10% Mullite addition and 16005: $1600\text{ }^\circ\text{C}$ sintering temperature and 5 hours sintering time). After the composite powders were milled for 24 h in acetone environment with zirconia ball mill, sieved and dried. Then, the composite mixtures were pressed to 56×12 mm sizes mold gap by uniaxial pressing machine at 200 MPa load. The pressed samples were sintered in a high temperature oven (Protherm) and in air conditions for 1-5 h sintering times and 1500 - $1600\text{ }^\circ\text{C}$ temperatures. The heating rate was $5\text{ }^\circ\text{C}/\text{min}$. Then, with SEM, microstructure investigations, phase analysis with XRD, 3-point bending, hardness and wear tests, absorption of water, porosity, shrinkage and density results were examined on the composites.

The three-point flexural strength tests were executed with $0.5\text{ mm}/\text{min}$ (crosshead speed) in a Shimadzu brand tensile-compression device. For each sample, measurements were taken five times and their average were taken as the bending strength results of the samples. The strength calculations were made with the formula (1):

$$\sigma = 3/2 * P * L / (b * h^2) \quad (1)$$

(In (1) the letters mean that, P: maximum force, L: the distance of between supports, b: width of samples, h: height of samples).

After 180, 320, 600, 1200 and 2500 grit sanding process, polishing is done for each sample. With Vickers hardness tester that was Mitutoyo brand, the measurements of hardness were executed by 1 kg load for 10 seconds. For each sample, measurements were taken five times and their average were taken as the hardness results of the samples [19-24]. The wear tests of samples were executed with Plint brand wear tester. For wear tests, steel discs were used. For each sample, wear tests were executed at 400 rpm rate, 5, 10 and 15 min wear durations and 100 N force. The samples were weighted with a precision scale of 10^{-4} g. After the assigned wear times, the samples were scaled again and the wear amounts were calculated [22,23]. To determine the phases, XRD with Cu K α radiation (Bruker AXS D8 Advance; 20kV-60kV, 6mA-80mA and $\theta = 10^{\circ}$ - 90° , 0.002°) was used. The phases of the samples seen in XRD patterns were defined with the Panalytical X'Pert program. The microstructural characterization of the samples was made with the Mira3XMU FE-SEM (Tescan, Czech Republic) brand SEM (scanning electron microscope) machine with EDS (energy dispersion spectrum). The results were presented in various graphics and tables and some comments on these results were made.

3. Results and Discussions

Physical (shrinkage, water absorption, density and porosity tests) and mechanical (wear, 3-point bending and hardness) tests, SEM, EDS and XRD analysis results were included in this section. Calculations and measurements were repeated 5 times and arithmetic averages were taken.

The shrinkage, porosity, water absorption, relative density and bulk density results are shown in Table 1, and also Fig. 1. In Fig. 1, the relative density values were taken at the rate of 1/3 of the actual values for the graph to be more understandable.

Table 1. Physical test results of YZ0M and YZ10M samples.

Samples	Bulk density g/cm ³	Relative density (%)	Water Absorption (%)	Porosity (%)	Shrinkage (%)
YZ00M15001	5,06	89,47	2,09	10,53	12,64
YZ00M15005	5,48	96,80	0,22	3,20	14,71
YZ00M16001	5,56	98,31	0,19	1,69	15,28
YZ00M16005	5,57	98,44	0,18	1,56	15,50
YZ10M15001	4,66	87,59	2,02	12,41	11,38
YZ10M15005	4,90	92,13	0,41	7,87	12,75
YZ10M16001	5,12	96,15	0,14	3,85	13,64
YZ10M16005	5,03	94,60	0,18	5,40	13,50

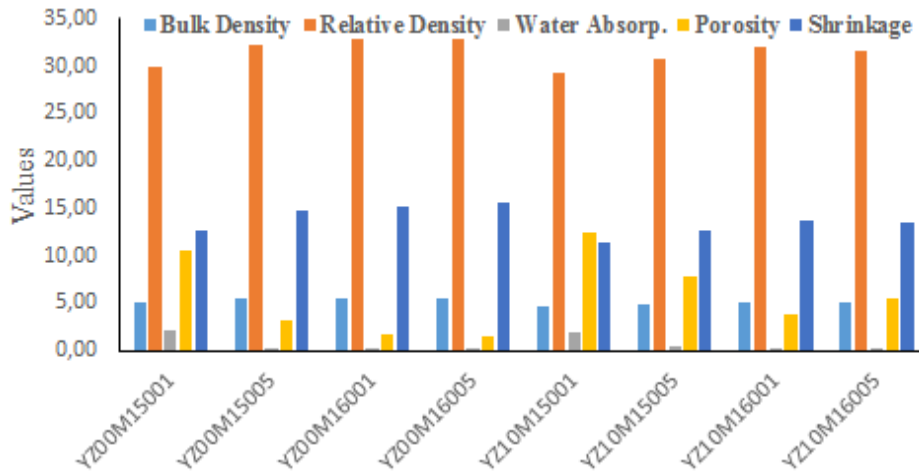


Figure 1. Physical test results graph of YZ0M and YZ10M samples.

When the results were examined, it was found that with increasing sintering temperature and time, the shrinkage values increased in general. We know that when the shrinkage values are higher, the water absorption and porosity values decrease and our results confirm this. And so, it is seen that experimental density and relative density values increase.

Due to the lower density of mullite compared to the ZrO_2 - Y_2O_3 composite, the mullite-added samples have lower density and shrinkage values and contrary to this, higher porosity and water absorption. We think that the decrease in the density value of the mullite-added 16005 sample is caused by defects such as excessive grain growth and formation of large pores in the microstructure depending on the sintering time.

Table 2, Figure 2 and Figure 3 indicated hardness and three-point flexural strength results of YZ0M and YZ10M samples.

Table 2. Hardness and three-point flexural strength results of YZ0M and YZ10M samples.

Samples	Hardness (HV)	3 Point Bending Strength (MPa)
YZ00M15001	526,35	82,71
YZ00M15005	767,33	110,99
YZ00M16001	928,85	189,88
YZ00M16005	920,13	111,15
YZ10M15001	512,00	77,31
YZ10M15005	673,83	142,23
YZ10M16001	840,87	176,19
YZ10M16005	792,95	251,63

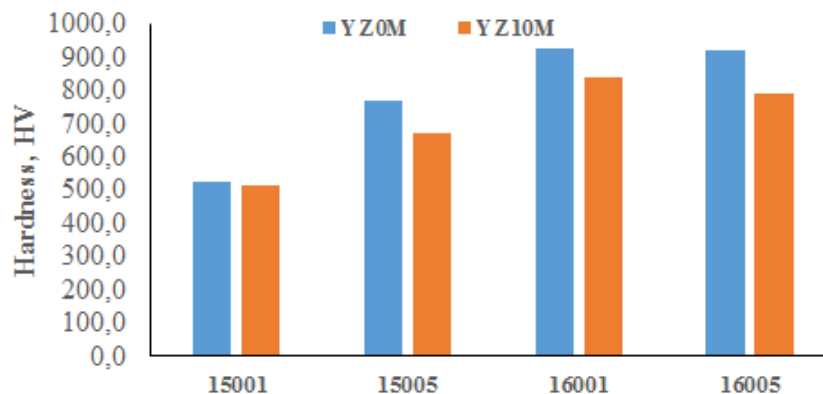


Figure 2. Hardness graph of samples.

When the hardness test results are examined, with increasing sintering temperature and time, we see the hardness values generally rise related to the shrinkage, porosity and density values. Because of higher porosity, hardness values of mullite-added samples are lower than mullite-free samples similar to density results. It is seen that hardness values of 16005 specimens with and without mullite additives decreased. The decrease in hardness values of 16005 samples is a result of large pores formed in the microstructure and possible phase changes.

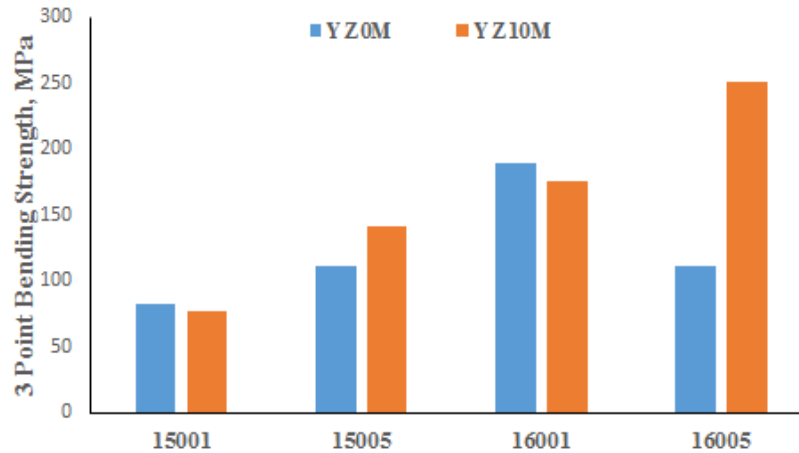


Figure 3. 3-Point bending strength graph of samples.

According to the results, it is seen that the three-point bending strength values generally increase with higher sintering temperature and time, and the highest value is obtained in the mullite-added 16005 sample. We think that the decrease in the three-point bending strength of the mullite-free sample 16005 is due to possible phase changes in the structure.

Considering that the flexural strength results change significantly with the amount of tetragonal phase in the structure, this situation is thought to be a result of the effect of the sintering temperature and time on the phases in the structure, as stated in the XRD analysis section. However, this is not exactly the case in mullite-added samples. Although lower amount of tetragonal ZrO_2 phase, bending strength values of the mullite-added samples for 15005 and 16005 specimens are higher. This shows that the mullite additive acts as toughening and increases the flexural strength of these samples.

The wear tests of samples were executed with Plint brand wear tester. For wear tests, steel discs were used. For each sample, wear tests were executed at 400 rpm rate, 5, 10 and 15 min wear durations and 100 N force. The samples were weighed with a precision scale of 10^{-4} g. After the assigned wear times, the samples were scaled again and the wear amounts were calculated. Wear results are seen in Table 3 and Fig. 4.

Table 3. Wear results of YZ0M and YZ10M samples.

Samples	Wear Volume (mm ³), 100 N		
	5 min.	10 min.	15 min.
YZ00M15001	0,161	0,288	0,511
YZ00M15005	0,110	0,183	0,329
YZ00M16001	0,072	0,114	0,203
YZ00M16005	0,090	0,126	0,216
YZ10M15001	0,214	0,377	0,715
YZ10M15005	0,162	0,273	0,596
YZ10M16001	0,124	0,215	0,352
YZ10M16005	0,098	0,178	0,295

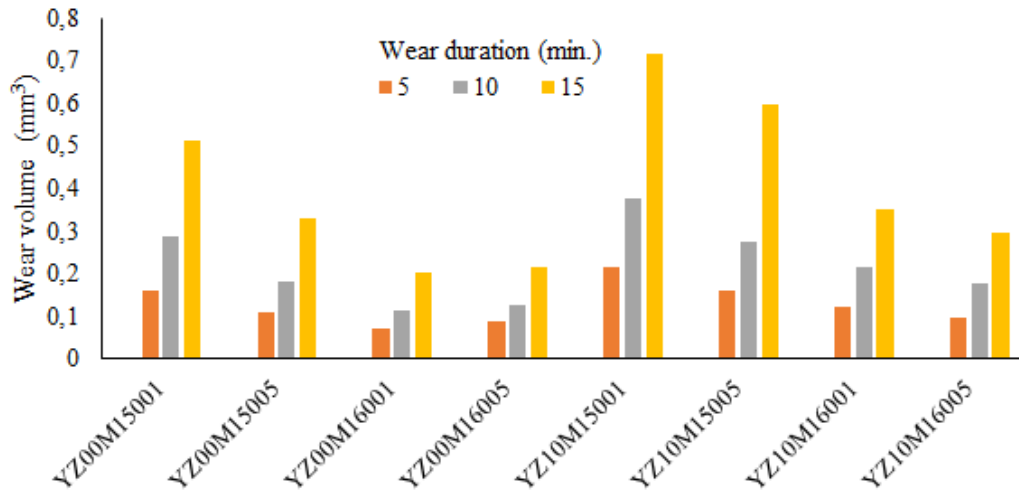


Figure 4. Wear test results graph of samples.

When the data obtained are examined, it is seen that the wear results vary depending on the hardness, bending strength and wear time of the samples. In general, as the wear time increased, the amount of wear of the samples also increased. It is understood that the wear resistance of the samples with high hardness and bending strength is better. Because of the lower hardness and higher porosity, mullite additive affected these samples negatively and decreased the wear resistance a little bit. Although the hardness value of the mullite-added 16005 sample decreased, the wear resistance was good, indicating that besides the hardness values, the flexural strengths of these samples have a significant impact on the wear properties too. Adhesive type wear was observed in these samples.

The phase changes in the sample structure related with the temperature and time of YZ0M and YZ10M samples were analyzed and the basic phases that emerged in the structure were shown in Figure 5 and Figure 6.

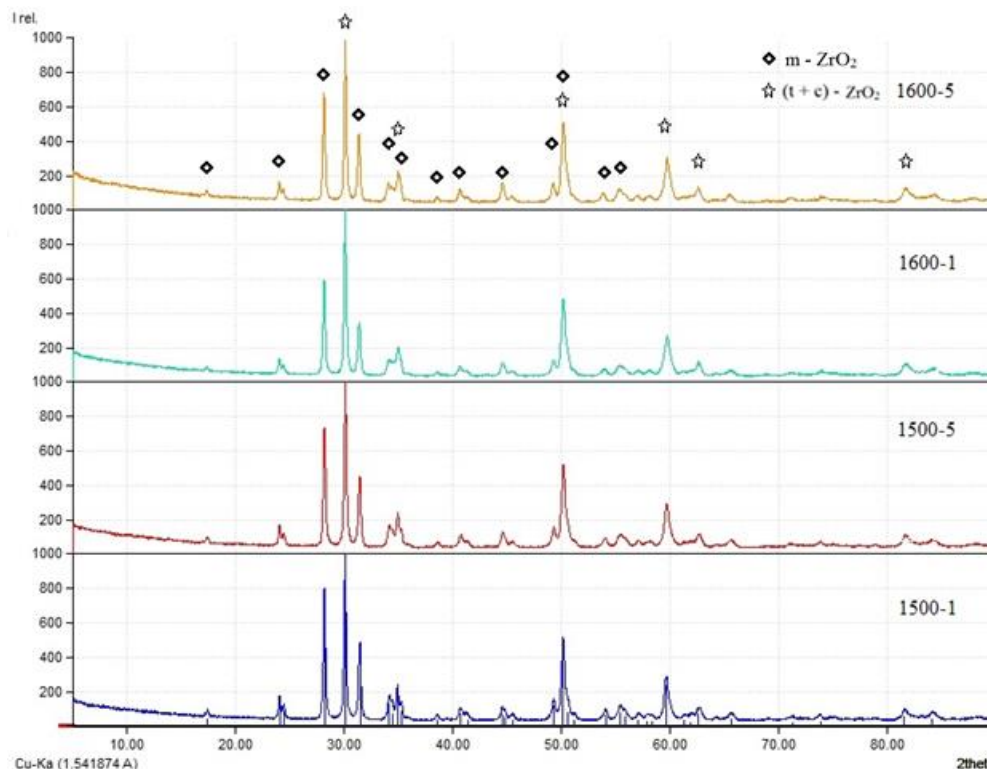


Figure 5. XRD patterns of YZ0M samples.

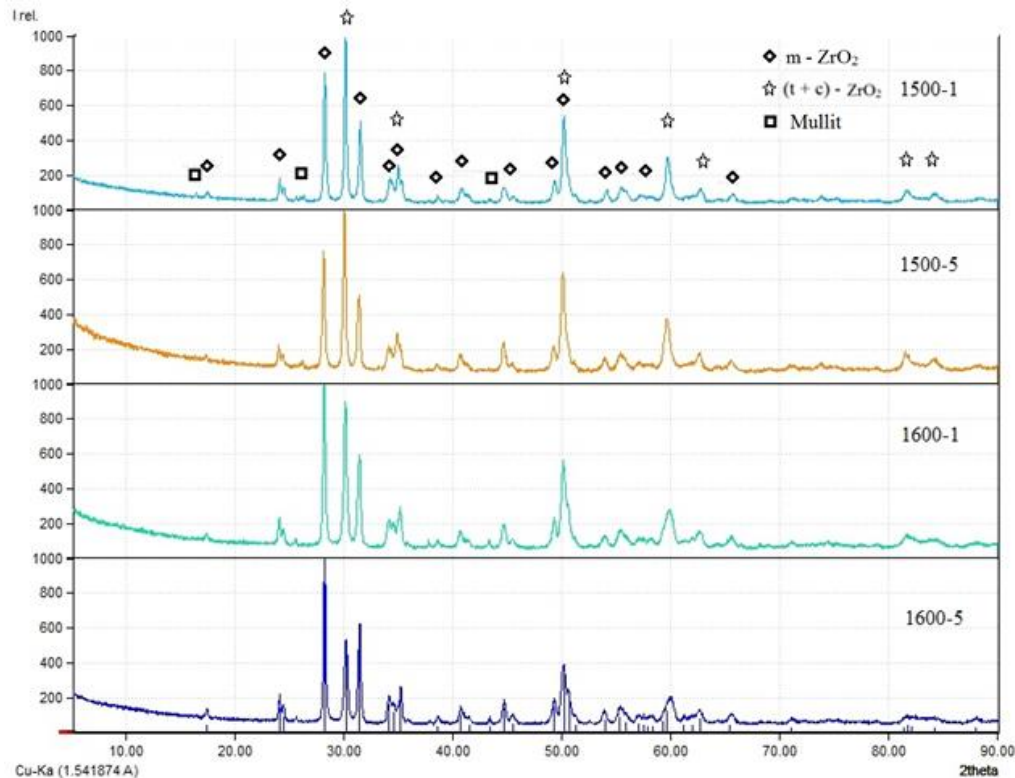


Figure 6. XRD patterns of YZ10M samples.

Stawarczyk et al [25] produced $Y_2O_3 - ZrO_2$ composite ceramics by sintering for 2 hours at temperatures between 1350 °C and 1700 °C. They stated that above 1600 °C, grain growth and voids occurred and the highest bending strength was obtained between 1400 °C and 1550 °C temperatures.

Çevlik [26], in his thesis study, gives the information that the superior mechanical properties are largely dependent on the critical grain size. This is stated that above the critical grain size, the tetragonal ZrO_2 phase spontaneously transforms into the monoclinic ZrO_2 phase, reducing the fracture toughness and bending strength.

The highest m- ZrO_2 phase ratio is seen in the 15001 sample in the XRD patterns of the mullite-free samples given in figure 5. Therefore, the bending strength value was also the lowest in this sample. The highest flexural strength value belongs to the 16001 sample with the lowest monoclinic phase. As the monoclinic ZrO_2 phase ratio increased again in the 16005 sample, the bending strength decreased.

In the XRD figures of the mullite added samples given in Figure 6, it is seen that the tetragonal and cubic ZrO_2 phases decrease, while the m- ZrO_2 phase increases with rising sintering temperature and time. Although the m- ZrO_2 phase increasing, the increase in the bending strength of the specimens is explained with the study of Huang et al [27]. In this study, it was stated that as a result of the homogeneous distribution of the ZrO_2 particles in the mullite, some mechanical properties of the mullite improve and thus the composite structure is strengthened. In addition, the alumina particles that do not react and remain in the structure are evenly distributed in the structure and advance the mechanical properties of the sample. They stated that the mullite formed as a result of the reaction was distributed in the ZrO_2 matrix and the mullite amount and size raised with the increasing the sintering temperature.

In this direction, although the most prominent feature for flexural strength in mullite-free samples is the high amount of tetragonal ZrO_2 in the structure, and therefore due to t-m transformation

toughening; It is understood that this situation is not valid alone in mullite added samples. The flexural strength of these samples varies mostly depending on the state of the mullite in the structure. In addition, in the mentioned study, it was stated that residual alumina and SiO₂ appeared in the structure of the mullite-doped specimens, and the secondary phase toughening mechanism increased the bending strength with the effect of these particles. It was also stated that Si and Al elements occur outside the mullite region and do not completely react while forming mullite. However, it was noted that a small quantity of residual Si element can be found in the zirconia matrix. Additionally, we think that the decrease in the density value in mullite added 16005 samples may be due to the swelling effect as a result of the growth of mullite grains and the increase in the amount of m-ZrO₂ phase in the structure.

Liu et al [28] stated in their study that by adding mullite to 3Y-TZP, the bending strength values increased with the addition of mullite, although the hardness values decreased. This toughening effect of mullite is explained by Liu et al as follows: Even if the crack emerging in the structure passes by breaking apart a mullite grain, its energy will decrease, and when it coincides with the next mullite grains, the energy will decrease and the crack will change direction. Again, by being blocked by secondary phase particles such as residual alumina in the structure, the crack will change direction again, lose its energy and stop its progress by damping [28].

The SEM images and EDS analyzes of YZ00M16005 and YZM10M16005 samples are given in Figure 7 and Figure 8.

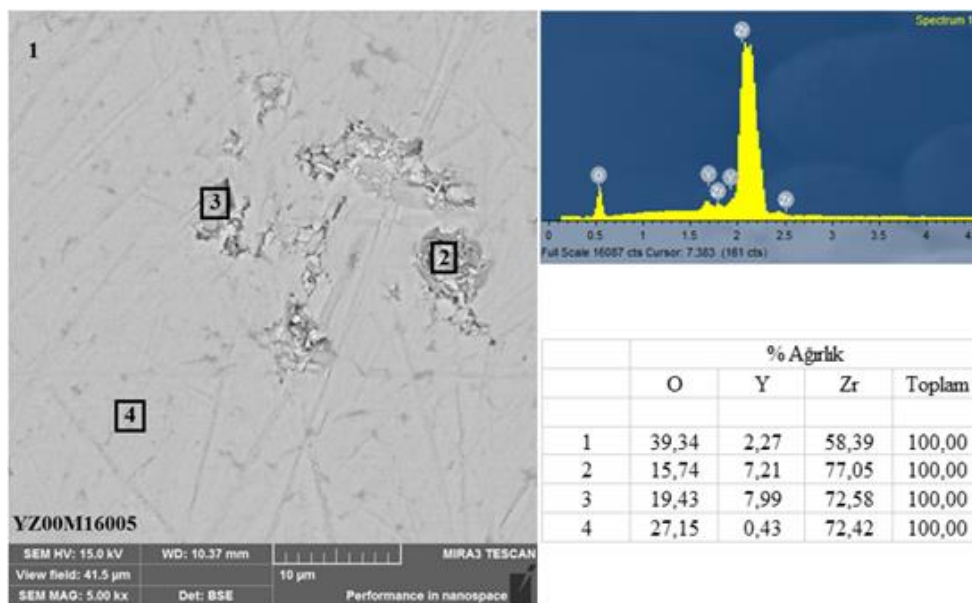


Figure 7. SEM image and EDS analyses of YZ00M16005 sample.

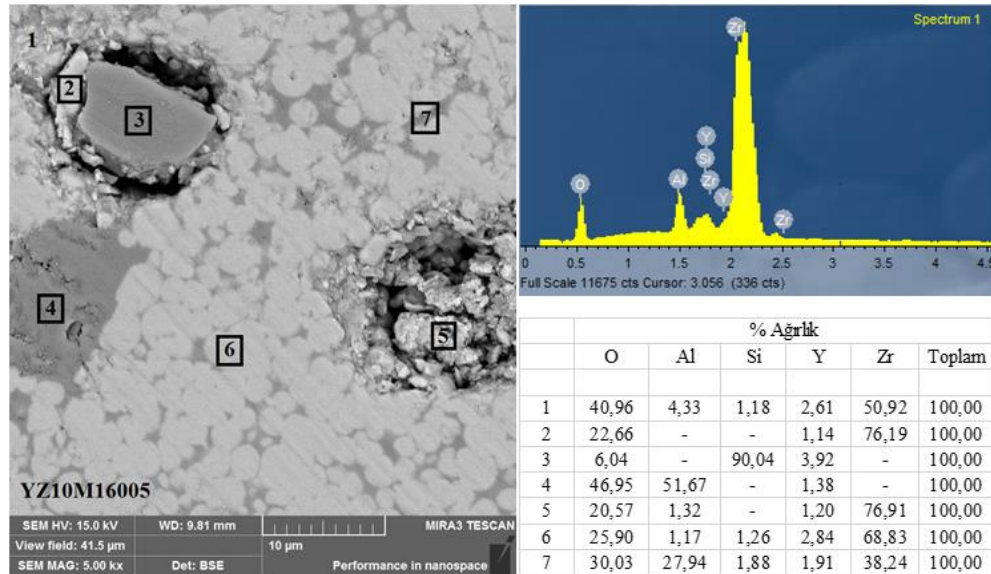


Figure 8. SEM image and EDS analyses of YZ10M16005 sample.

From the SEM images of the specimens given in Figure 7 and Figure 8, it is understood that the grain size and distribution are generally homogeneous in the mullite added sample, but some different particles on the surface form pores and disrupt the homogeneous structure. It can be predicted that this situation will have a negative effect on the hardness values of the specimens and decrease the hardness value of the mullite added sample. As a matter of fact, in the experimental results, the hardness value of the YZ10M16005 sample was found to be lower than the hardness value of the YZ00M16005 sample.

According to the EDS analyzes given in Figure 7 and Figure 8, the evaluation of the EDS results for the YZ00M16005 and YZ10M16005 samples was made from general (1) and parts 2, 3, 4, 5, 6, 7. It has been observed that the results of the EDS elemental analysis made from the general field survey (1) and other parts are compatible with the contribution rates and XRD results made to the samples.

4. Conclusions

In YZ0M coded samples, with increasing sintering temperature and time, generally shrinkage, experimental density, relative density, hardness and three-point bending strength values and wear resistance increased; It was observed that the water absorption and porosity values decreased. Among these samples, the three-point flexural strength and hardness values of the 16005 sample and the wear resistance decreased. The highest m-ZrO₂ phase ratio was found in sample 15001 in mullite-free samples. Therefore, the bending strength value is also the lowest in this sample. The highest flexural strength value belongs to the 16001 sample with the lowest m-ZrO₂ phase. As the m-ZrO₂ phase ratio increased in the 16005 sample, the flexural strength and hardness decreased.

In YZ10M coded mullite added samples, with increasing sintering temperature and time, generally shrinkage, experimental density, relative density, hardness and three-point bending strength values and wear resistance increased; It was observed that the water absorption and porosity values decreased. A decrease was observed in the density and hardness values of the mullite added 16005 sample. It was determined that t-ZrO₂ and c-ZrO₂ phases decreased, m-ZrO₂ phase increased and 16005 sample had the highest m-ZrO₂ phase with increasing the sintering temperature and time in mullite added YZ10M samples. So, we think that the decrease in the density value in mullite-doped 16005 samples may be related with the increase in the amount of m-ZrO₂ phase in the structure and the swelling effect as a result of the growth of mullite grains. The mullite additive reduced the

shrinkage, experimental density, relative density, hardness values and wear resistance of the samples. But It was observed that the water absorption, porosity and three-point flexural strength values increased in general and the highest flexural strength value was obtained in the 16005 specimen with mullite additive. This shows that the mullite additive acts as toughening and increases the flexural strength of these samples. Despite the decrease in hardness value of the mullite-added 16005 sample, the good wear resistance shows that the bending or flexural strength of these specimens has an effect on the wear properties.

While m-ZrO₂, t-ZrO₂ and c-ZrO₂ phases were detected in mullite-free samples; It was determined that in addition to these phases, mullite phase was also present in the mullite added samples.

This study proves that, mullite additive can be used to increase the bending strength of the ZrO₂-Y₂O₃ ceramic composites. Although lower hardness results with adding mullite reinforcement, good wear properties can be obtained from higher bending strength with mullite additive. In addition, it is understood that lighter and stronger composites can be obtained with mullite additive.

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References

- [1] Boyraz, T., 2008. "An investigation on physical and electrical properties of CaO/MgO-stabilized zirconia ceramics formed with different methods," Ph.D. dissertation, Metallurg. Eng., Istanbul Technical Univ., Istanbul.
- [2] Pekdemir, A. D., 2018. "Preparation and characterization of boron carbide at low-temperature from boric acid and polyols," Ph.D. dissertation, Dept. Chem., Ankara Univ., Ankara.
- [3] Ceylan, A., 2006. "The production of functionally graded SiAlON ceramics by tape casting method," Ph.D. dissertation, Dept. Cer. Eng., Anadolu Univ., Eskişehir.
- [4] Abi, C. B., 2009. "An investigation on fracture toughness of traditional and technical ceramics," Ph.D. dissertation, Dept. Metallurg. Eng., Afyon Kocatepe Univ., Afyon.
- [5] Hafizoğlu, M. A., Boyraz, T. and Akkuş, A., 2021. "Fabrication, characterization and wear properties of mullite reinforced silica-doped zirconia ceramic composites," in Proc. IMSMATEC'21, p. 175 – 180.
- [6] Hafizoğlu, M. A., Akkuş, A. and Boyraz, T., 2021. "Fabrication, characterization and wear properties of mullite reinforced Al₂O₃-doped ZrO₂ ceramic composites," in Proc. GLOBECER'21, p. 673 – 686.
- [7] Hafizoğlu, M. A., Boyraz, T. and Akkuş, A., 2021. "Fabrication and characterization of mullite reinforced TiO₂ added ZrO₂ ceramics," International Joint Science Congress of Materials and Polymers (ISCMP'21).
- [8] Cutler, R. A., Reynolds, J. R. and Jones, A., 1992. "Sintering and characterization of polycrystalline monoclinic, tetragonal, and cubic zirconia," Journal of the American Ceramic Society, 75(8), pp. 2173-2183.
- [9] Boyacıoğlu, T., 2007. "Improvement of room temperature mechanical properties of various amount of metal oxide doping cubic zirconia (c-ZrO₂) used as electrolyte material for solid oxide fuel cells," Master thesis, Dept. Metallurg. Eng., Gazi Univ., Ankara.
- [10] Boyraz, T., 1998. "Dental porcelain powders," Master thesis, Dept. Metallurg. Eng., Sakarya Univ., Sakarya.

- [11] Liu, P. F., Li, Z., Xiao, P., Luo, H. and Jiang, T. H., 2018. "Microstructure and mechanical properties of in-situ grown mullite toughened 3Y-TZP zirconia ceramics fabricated by gelcasting," *Ceramics International*, 44(2), pp. 1394-1403.
- [12] Eichler, J., Rödel, J., Eisele, U. and Hoffman, M., 2007. "Effect of grain size on mechanical properties of submicrometer 3Y-TZP: fracture strength and hydrothermal degradation," *Journal of the American Ceramic Society*, 90(9), pp. 2830-2836.
- [13] Sun, J., Gao, L., Iwasa, M., Nakayama, T. and Niihara, K., 2005. "Failure investigation of carbon nanotube/3Y-TZP nanocomposites," *Ceramics International*, 31(8), pp. 1131-1134.
- [14] El Ouatib, R., Guillemet, S., Durand, B., Samdi, A., Rakho, L. E. and Moussa, R., 2005. "Reactivity of aluminum sulfate and silica in molten alkali-metal sulfates in order to prepare mullite," *Journal of the European Ceramic Society*, 25(1), pp. 73-80.
- [15] Kucuk, I. and Boyraz, T., 2019. "Structural and mechanical characterization of mullite and aluminium titanate reinforced yttria stabilized zirconia ceramic composites," *Journal of Ceramic Processing Research*, 20(1), pp. 73-79.
- [16] Kumar, P., Nath, M., Ghosh, A. and Tripathi, H. S., 2015. "Enhancement of thermal shock resistance of reaction sintered mullite-zirconia composites in the presence of lanthanum oxide," *Materials Characterization*, 101, pp. 34-39.
- [17] Roy, J., Das, S. and Maitra, S., 2015. "Solgel-processed mullite coating—a review. *International Journal of Applied Ceramic Technology*, 12, pp. E71-E77.
- [18] Denry, I. and Kelly, J. R., 2008. "State of the art of zirconia for dental applications," *Dental materials*, 24(3), pp. 299-307.
- [19] Çitak, E. and Boyraz, T., 2014. "Microstructural characterization and thermal properties of aluminium titanate/YSZ Ceramics," *Acta Physica Polonica A*, 125(2), pp. 465-468.
- [20] Önen, U. and Boyraz, T., 2014. "Microstructural characterization and thermal properties of aluminium titanate/spinel ceramic matrix composites," *Acta Phys. Pol. A*, 125(2), pp. 488-490.
- [21] Sacli, M., Onen, U. and Boyraz, T., 2015. "Microstructural characterization and thermal properties of aluminium titanate/porcelain ceramic matrix composites," *Acta Physica Polonica A*, 127(4), pp. 1133-1135.
- [22] Boyraz, T. and Akkuş, A., 2021. "Investigation of wear properties of mullite and aluminium titanate added porcelain ceramics," *Journal of Ceramic Processing Research*. Vol. 22, No. 2, pp. 226-231.
- [23] Akkus, A. and Boyraz, T., 2018. "Investigation of wear properties of CaO, MgO added stabilized zirconia ceramics produced by different pressing methods," *J. Ceram. Proc. Res.*, Vol. 19, pp. 249-252.
- [24] Kucuk, I., Boyraz, T., Gökçe, H. and Öveçoğlu, M. L., 2018. "Thermomechanical properties of aluminium titanate (Al₂TiO₅)-reinforced forsterite (Mg₂SiO₄) ceramic composites," *Ceramics International*, 44(7), pp. 8277-8282.
- [25] Stawarczyk, B., Özcan, M., Hallmann, L., Ender, A., Mehl, A. and Hämmerlet, C. H., 2013. "The effect of zirconia sintering temperature on flexural strength, grain size, and contrast ratio," *Clinical oral investigations*, 17(1), 269-274.
- [26] Talay Çevlik, E., 2015. "Low thermal degradation of three yttria-stabilized tetragonal zirconia polycrystalline and effect of low thermal degradation on flexural strength," Ph.D. dissertation, Dept. Dent., Selçuk Univ., Konya.
- [27] Huang, Y. Q., Liu, P. F., Li, Z. and Xiao, P., 2018. "Effects of the content of insitu grown

mullite on the microstructure and mechanical properties of 3Y-TZP ceramics fabricated by gel-casting,” *Ceramics International*, 44(17), pp. 21882- 21892.

[28] Liu, P. F., Li, Z., Xiao, P., Luo, H. and Jiang, T. H., 2018. “Microstructure and mechanical properties of in-situ grown mullite toughened 3Y-TZP zirconia ceramics fabricated by gelcasting,” *Ceramics International*, 44(2), pp. 1394-1403.