Fabrication and Characterization of Mullite Reinforced CaO Added ZrO₂ Ceramics

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Abstract

In this study, mullite (3Al₂O₃.2SiO₂) and 11 mol % calcia added zirconia (11 mol % CaO - 89 mol % ZrO₂) ceramic powders were synthesized by conventional ceramic production processing route. The mixtures were prepared by mechanical alloying method in acetone environment with zirconia ball mill. The powders were dried in oven at 110 ºC for 24 hours before mixing. Mullite (3Al₂O₃.2SiO₂) and 11 mol% calcia added zirconia (CaO-ZrO₂) ceramic powders were synthesized by reaction sintering from the powders made up of stoichiometric proportions of Al₂O₃, SiO₂, CaO and ZrO₂ powders after being homogenized in acetone environment in ball mills. Mullite (3Al₂O₃.2SiO₂) and 11 mol% calcia added zirconia (CaO-ZrO₂) ceramic powders were synthesized in air at 1600 ºC for 3 h and 1300 ºC for 2 h, respectively. Then, the ceramic phases formed were made ready to form ceramic - ceramic composites by crushing, grinding and sieving processes. Then 0 and 10% by weight mullite (M) added calcia doped zirconia (CaZ) mixtures were prepared by powder metallurgy method. The prepared mixtures were wet milled with zirconia ball mill for 24 h and sieved. After drying, the powders were compacted to preforms of 56x12x10 mm by uniaxial pressing at 200 MPa. The green compacts were sintered at 1500-1600 ºC for 1-5 h in air conditions using a heating rate of 5 ºC min-1 in a high temperature furnace. Then, microstructure (SEM), phase analysis (XRD), mechanical (hardness, 3-point bending and wear) and physical properties (% shrinkage, water absorption, porosity and density) tests were performed on the mullite added calcia doped zirconia ceramic composites. In this study, whether there is a phase change in the ZrO₂ - CaO mixture at high sintering temperatures and the effect of mullite additive on the properties of this mixture was investigated. The data obtained were presented in graphs and tables and their comments were made.

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

Mullit Takviyeli CaO Katkılı ZrO₂ Seramiklerinin İmalatı ve Karakterizasyonu

Öz

Bu çalışmada, mullit (3Al₂O₃.2SiO₂) ve %11 mol kalsiyum oksit katkılı zirkonya (%11 mol CaO - %89 mol ZrO₂) seramik tozları geleneksel seramik üretim yöntemi ile sentezlenmiştir. Karışımlar, zirkonya bilyalı değirmende aseton ortamında mekanik alaşımlama yöntemiyle hazırlanmıştır. Tozlar karıştırılmadan önce 110 ºC'de 24 saat etüvde kurutulmuştur. Al₂O₃, SiO₂, CaO ve ZrO₂ tozlarının stokiyometrik oranlarından oluşan tozların aseton ortamında bilyeli değirmende homojenize edildikten sonra geleneksel sinterleme yöntemiyle Mullit (3Al₂O₃.2SiO₂) ve %11 mol kalsiyum oksit katkılı zirkonya (CaO-ZrO₂) seramik tozları sentezlenmiştir. Mullit ve %11 mol kalsiyum oksit katkılı zirkonya seramik tozları sırasıyla 1600 ºC'de 3 saat ve 1300 ºC'de 2 saat sentezlenmiştir. Daha sonra oluşan seramik fazlar kırma, öğütme ve eleme işlemleri ile seramik - seramik kompozitleri oluşturmaya hazır hale getirilmiştir. Daha sonra ağırlıkça %0 ve %10 mullit (M) takviyeli kalsiyum oksit katkılı zirkonya (CaZ) karışımları toz metalurjisi yöntemiyle hazırlanmıştır. Hazırlanan karışımlar zirkonya bilyalı değirmende 24 saat yaş öğütülmüş ve elenmiştir. Kurutulduktan sonra, tozlar 200 MPa'da tek eksenli presleme ile 56x12x10 mm'lik preformlara sıkıştırılmıştır. Devamında, yüksek sıcaklıklı bir fırında 5 ºC/dak ısıtma hızı kullanılarak hava koşullarında 1500-1600 oC'de 1-5 saat sinterlenmiştir. Daha sonra mullit takviyeli kalsiyum oksit katkılı zirkonya seramik kompozitler üzerinde mikroyapı (SEM), faz analizi (XRD), mekanik (sertlik, 3 nokta eğme ve aşınma) ve fiziksel özellikler (% küçülme, su emme, gözeneklilik ve yoğunluk) testleri yapılmıştır. Bu çalışmada, yüksek sinterleme sıcaklıklarında ZrO₂ - CaO karışımında faz değişimi olup olmadığı ve mullit katkı maddesinin bu karışımın özelliklerine etkisi araştırılmıştır. Elde edilen veriler grafik ve tablolar halinde sunulmuş ve yorumları yapılmıştır.

Anahtar Kelimeler: Zirkonya, Mullit, Kalsiyum oksit, Karakterizasyon, Aşınma.

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1. Introduction

Ceramic materials as a high temperature structural material due to their several interesting features such as, excellent resistance to heat, corrosion and abrasion, are preferred, in numerous areas like, cutting tools, extrusion dies, adiabatic diesel engine compartments [1-3]. However, ceramic materials have many disadvantages, such as low impact strength and fracture toughness, fragility and limited processability. So, a lot of studies focus on these issues to improve the structural and mechanical properties of ceramics. Among ceramic materials, zirconia (ZrO_2) and its composites have recently become the focus of scientific and technological studies because of their better mechanical properties, corrosion resistance, high temperature stability, low thermal conductivity and high chemical stability. [1]. They are used as structural materials in the manufacture of refractory crucibles for melting pure metals, components of furnaces, engines, heat barriers, wear resistant components, blade cutting tools and wire mesh drawing machines, dental studies and other a lot of fields [1-4]. High-purity zirconia (ZrO_2) exhibits three polymorphs depending on temperature: monoclinic phase is stable up to about 1170 °C. After this temperature, the conversion from the monoclinic phase to the tetragonal phase begins and the tetragonal phase is stable up to 2370 °C. From this temperature to the melting temperature of 2680 °C, it is in the cubic phase. [1,4]. During the cooling process, transition from the tetragonal to monoclinic phase occurs. This 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. The addition of stabilizers to ZrO_2, lowers the temperature of polymorphic transformations, reduces the volume changes and blocks the transformation. With using stabilizers, it is possible to ensure the existence of high-temperature phases at room temperature 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 ZrO_2 in the tetragonal and/or cubic forms at room temperature [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, achieve excellent mechanical properties such as bending strength, fracture toughness, hardness [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 toughness, 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, plays an important role in increasing the 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 toughness 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 and 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 the submicrometric or nanocrystalline zirconia can be further increased by adding secondary phases into zirconia matrix, such as nanotubes, nanofibres or nanoplatelets [11]. During the last decades, the development of nanomaterials has offered a new alternative for reinforcing ceramics. Carbon nanotubes (CNTs) have attracted increasing attention as reinforcement because of their excellent properties. However, the CNTs are prone to reacting with an oxide matrix at high temperature, leading to the degradation in mechanical properties of CNTs and a limited reinforcing effect on the ceramics [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 Al_2O_3.2SiO_2) is defined as the unique stable intermediate crystalline phase of the Al_2O_3-SiO_2 binary system, cost-friendly and exhibiting good refractory ability [14,15]. Mullite has received significant attention for technological applications due to its good properties such as high melting point, low coefficient of thermal expansion, high chemical stability, high creep resistance and sufficient hardness [16,17]. In summary, the fracture toughness of the submicron or nanocrystalline zirconia can be further improved by adding mullite being the secondary phase into the zirconia matrix and so, the other mechanical properties can be improved too [11]. In addition, the sintering temperature is also particularly important, because it affected the properties of ceramics through alteration of the microstructure and crystalline phases [18]. Studies continue on the effect of different sintering temperatures on the microstructure and mechanical properties of mullite-zirconia ceramics.

In this study, mullite (3Al_2O_3.2SiO_2) and 11 mol % calcia doped zirconia (CaO-ZrO_2) ceramic powders were synthesized by conventional ceramic production processing route. Then, the effect of mullite additive on the properties of this mixture was investigated. The data obtained were presented in graphs and tables and their results were commented.

2. Material and Method

Mullite and calcia doped zirconia ceramic powders were produced by conventional ceramic production processing route in this study. All precursory powder materials (Al_2O_3, SiO_2, CaO and ZrO_2) used in the present work were purchased from Eczacıbaşı Company, Alfa Aesar and Handan Yaxiang Chemicals Trading Co., Ltd (Eczacıbaşı Esan, Turkey; Alfa Aesar, United States of America and Handan Yaxiang Chemicals Trading Co., Ltd, China). The mixtures were prepared by mechanical alloying method in acetone environment with zirconia ball mill. The powders were dried in oven at 110 ºC for 24 hours before mixing. Mullite ($3Al_2O_3.2SiO_2$) and 11 mol% calcia doped zirconia (CaO-ZrO_2) ceramic powders were synthesized by reaction sintering from the powders made up of stoichiometric proportions of Al_2O_3, SiO_2, CaO and ZrO_2 powders after being homogenized in acetone environment in ball mills. Mullite ($3Al_2O_3.2SiO_2$) and 11 mol% calcia doped zirconia (CaO-ZrO_2) ceramic powders were synthesized in air at 1600 ºC and 1300 ºC for 3h and 2 h, respectively. Then, the ceramic phases formed were made ready to form ceramic - ceramic composites by crushing, grinding and sieving processes. Then 0 and 10% by weight mullite added calcia doped zirconia mixtures were prepared by powder metallurgy method (hereinafter these mixtures will be named CaZ0M and CaZ10M respectively). The sample was coded as CaZ10M16005 (CaZ: Calcia doped zirconia; 10M: 10% Mullite addition and 16005: 1600 °C sintering temperature and 5 hours sintering time). The prepared mixtures were wet milled with zirconia ball mill for 24 h and sieved. After drying, the powders were compacted to preforms of 56x12x10 mm by uniaxial pressing at 200 MPa. The green compacts were sintered at 1500-1600 ºC for 1-5 h in air conditions using a heating rate of 5 ºC min^{-1} in a high temperature furnace (Protherm™ Furnace). Then, microstructure (SEM), phase analysis (XRD), mechanical (hardness, 3-point bending and wear) and physical properties (% shrinkage, water absorption, porosity and density) tests were performed on the mullite added calcia doped zirconia ceramic composites.

The 3-point bending strength tests of the samples were performed on with a crosshead speed of 0.5 mm/min in a Shimadzu brand tensile-compression device. Five measurements were made for each sample and average results were accepted as the strength values of the samples. The strength calculations were made with the formula:

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

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

The samples were polished on a velvet broadcloth using a 1 μm diamond solution after the 180, 320, 600, 1200 and 2500 grit sanding process, respectively. The diagonal field traces on the polished specimens were created using a square pyramid diamond tip with a 136° apex angle and 1 kg load for 10 seconds on the Mitutoyo brand vickers hardness tester. When calculating the hardness values, five measurements were taken and the results were given as average [19-24]. Plint brand wear tester was used for the wear tests of ceramics. Steel discs were used as wear disc. Wear tests were performed on each sample at 400 rpm rate, 5, 10 and 15 min wear durations and 100 N force. First, the specimen was measured with a precision scale of 0.0001 g, and the amount of wear was determined by measuring again after the specified wear time [22,23]. To determine the phases, X-ray powder diffractometer with Cu Kα radiation (Bruker AXS D8 Advance;

20kV-60kV, 6mA-80mA and θ = 10º-90º, 0.002º) was used. The phase analysis of the XRD patterns was determined using the Pananalitical X'Pert High Score program. The microstructural characterization of the samples was made with the Mira3XMU FE-SEM (Tescan, Czech Republic) brand scanning electron microscope (SEM) with an energy dispersion spectrum (EDS). The data obtained were presented in graphs and tables and their comments were made.

3. Results and Discussion

Specified to sintered samples: Physical tests (total shrinkage, water absorption, porosity and density tests), mechanical tests (hardness, 3-point bending and wear), scanning electron microscopy (SEM) for EDS analysis and XRD for phase analysis. Measurements and calculations were made 5 times replicates, and their arithmetic averages were obtained.

Table 1. Physical test results of CaZ0M and CaZ10M samples

Samples	Bulk dens. g/cm³	Rel. dens. (%)	Water Absorp. (%)	Por. (%)	Shir. (%)
CaZ00M15001	4,77	86,77	3,41	13,23	9,79
CaZ00M15005	5,16	93,89	1,75	6,11	12,20
CaZ00M16001	5,17	94,04	1,20	5,96	12,43
CaZ00M16005	5,26	95,67	0,36	4,33	12,76
CaZ10M15001	4,72	90,89	1,33	9,11	9,52
CaZ10M15005	4,74	91,28	1,02	8,72	9,76
CaZ10M16001	4,71	90,70	1,41	9,30	9,47
CaZ10M16005	4,58	88,19	1,79	11,81	8,65

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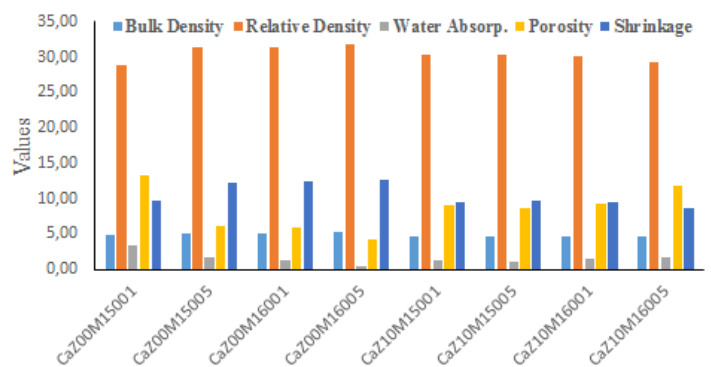

Figure 1. Physical test results graph of CaZ0M and CaZ10M samples

From the physical test results, it is found that the shrinkage values increased with increasing sintering temperature and time in mullite-free samples, and accordingly, the water absorption and porosity values decreased; it is seen that the experimental density and relative density values increase. In the mullite added samples, while the experimental density, relative density and shrinkage values increased in 1500 samples; these values decrease in 1600 samples. We think that this is a result of the defects and phase

changes occurring in the microstructure at 1600 ºC temperature. In addition, it is seen that the shrinkage, experimental density and relative density values are lower in mullite added samples, and the water absorption and porosity values are higher.

Table 2, Figure 2 and Figure 3 indicated hardness and 3-point bending strength values of CaZ0M and CaZ10M samples.

From the Table 2 and Figure 2, when the hardness test results are examined, it is seen that the hardness values increase with increasing sintering temperature and time in mullite-free samples. It is seen that the hardness values of 1600 samples decreased in mullite added samples. We think that this is related to the large pores formed in the microstructure and in addition possible phase changes. In addition, it is seen that the hardness values of the mullite added samples are lower.

Table 2. Hardness and 3-point bending strength values of CaZ0M and CaZ10M samples

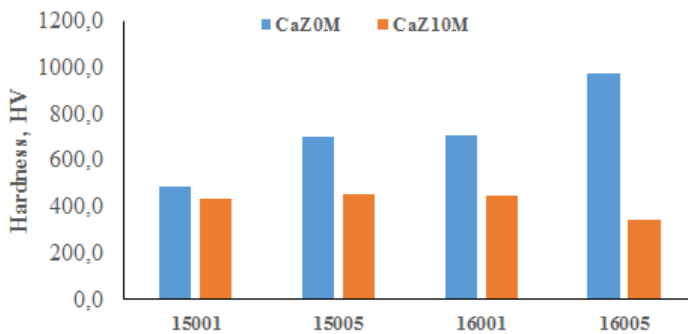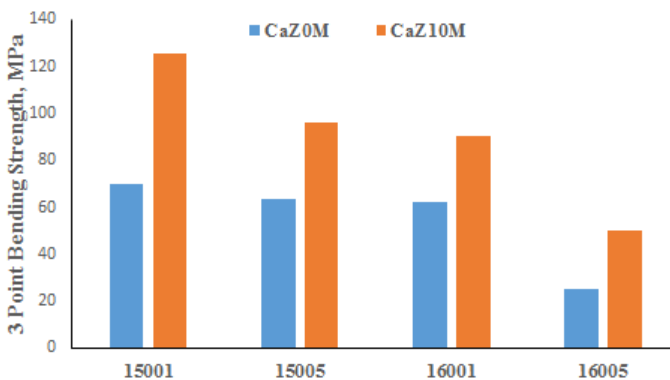| Samples	Hardness (HV)	3 - Point Bending Strength (MPa)
CaZ00M15001	489,98	69,89
CaZ00M15005	702,25	63,52
CaZ00M16001	705,40	62,01
CaZ00M16005	977,84	25,29
CaZ10M15001	435,97	125,62
CaZ10M15005	453,78	95,98
CaZ10M16001	445,23	90,41
CaZ10M16005	341,9	49,80

Figure 2. Hardness graph of samples

Figure 3. 3-Point bending strength graph of samples

The bending test results show that that three - point bending strength values decrease with increasing sintering temperature and time in all samples. In addition, it is seen that the three-point

bending strength values of the mullite added samples are higher. We think that this is a result of the differences in the microstructure and possible phase changes depending on the sintering temperature, sintering time and mullite additive.

Plint brand wear tester was used for the wear tests of ceramics. Steel disc is used as wear disc. Wear tests were performed on each sample at 5,10 and 15 min wear durations and 100 N force (400 rpm constant speed). First, the specimen was measured with a precision scale of 0.0001 g, and the amount of wear was determined by measuring again after the specified wear time. The wear results are shown in Table 3 and Figure 4.

Table 3. Wear Results of CaZ0M and CaZ10M Samples

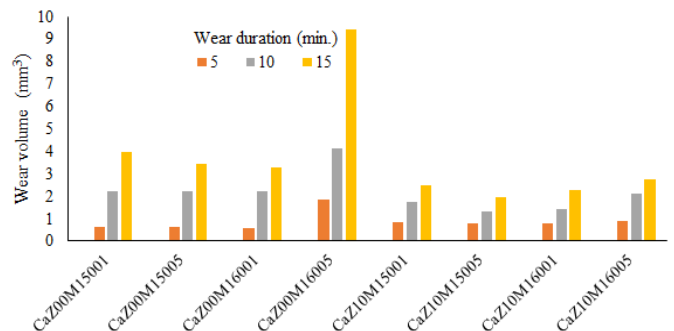| Samples	Wear Volume (mm³), 100 N		
	5 min.	10 min.	15 min.
CaZ00M15001	0,658	2,224	3,978
CaZ00M15005	0,616	2,232	3,421
CaZ00M16001	0,605	2,199	3,298
CaZ00M16005	1,855	4,114	9,443
CaZ10M15001	0,868	1,745	2,501
CaZ10M15005	0,802	1,296	1,977
CaZ10M16001	0,774	1,416	2,258
CaZ10M16005	0,881	2,109	2,766

Figure 4. Wear test results graph of samples

When we look at the wear test results, we can say that the 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. The wear resistance of the samples with high hardness and bending strength is higher and the mullite additive improves the wear resistance of these samples. Although adhesive type wear was observed in the samples in general, it was observed that with the increase in the wear time in some samples, cracks occur on the worn surface and very small pieces break off and cause abrasive wear too. Although it has especially high hardness, the high amount of wear seen in the CaZ00M16005 sample is due to the brittle and easily breakable structure of the sample, and its three-point bending strength is very low compared to the other samples.

The phase changes in the sample structure depending on the sintering temperature and time of CaZ0M and CaZ10M samples were analyzed and the basic phases that emerged in the structure were shown in Figure 5 and Figure 6.
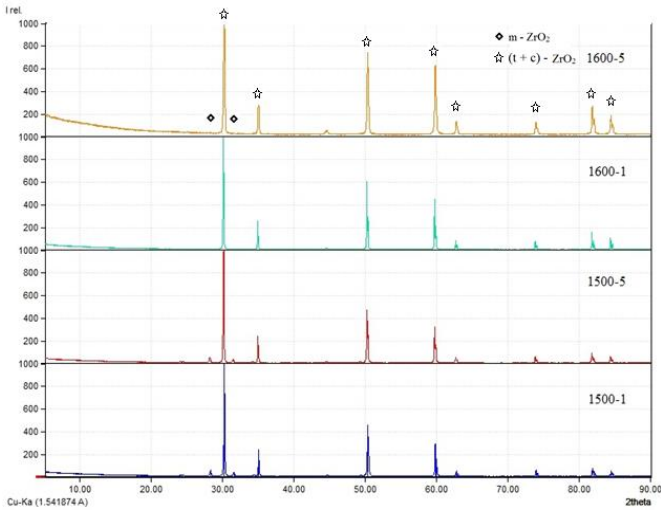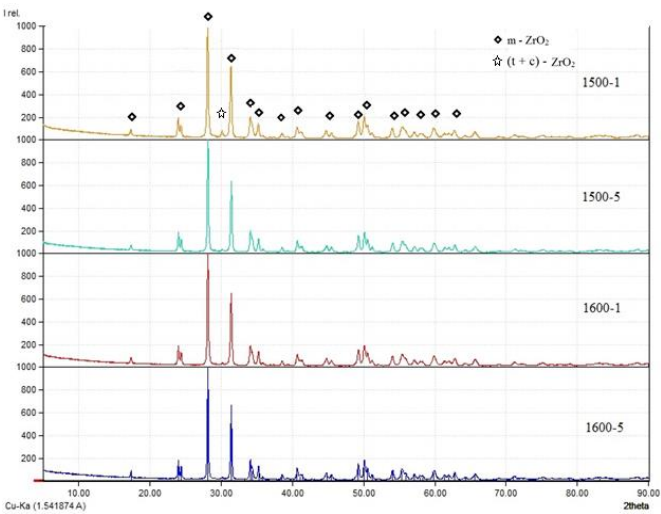
Figure 5. XRD patterns of CaZ0M samples

Figure 6. XRD patterns of CaZ10M samples

The microstructure image of CaZ00M16005 and CaZ10M16005 samples is given in Figure 7.
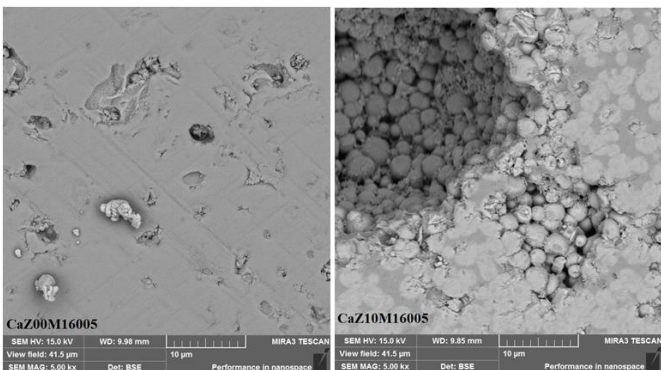

Figure 7. SEM images of CaZ00M16005 and CaZ10M16005 samples

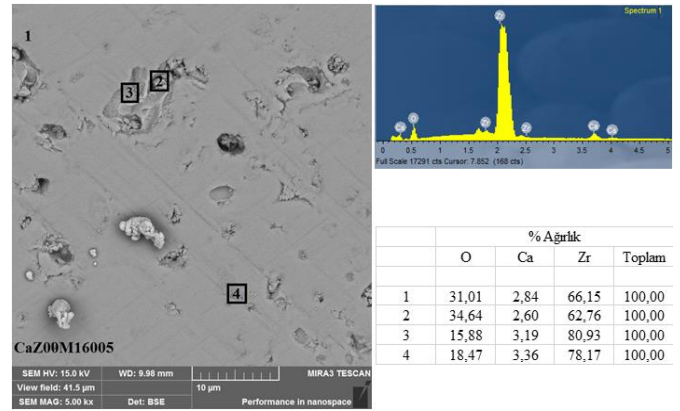Elemental analyzes of CaZ00M16005 and CaZ10M16005 samples with EDS are given in Figure 8 and Figure 9.

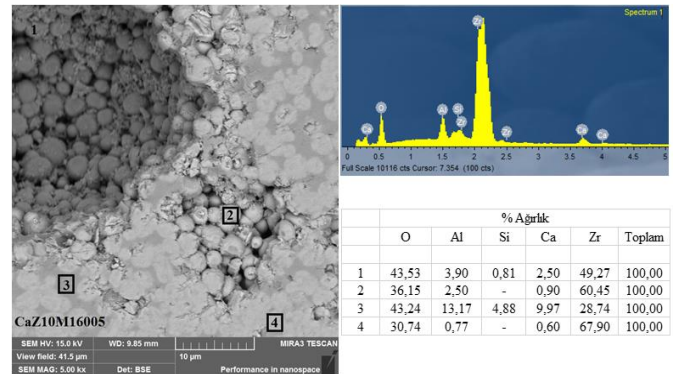*Figure 8. EDS analyses of CaZ00M16005 samples*

	% Ağırlık			
	O	Ca	Zr	Toplam
1	31,01	2,84	66,15	100,00
2	34,64	2,60	62,76	100,00
3	15,88	3,19	80,93	100,00
4	18,47	3,36	78,17	100,00

Figure 9. EDS analyses of CaZ10M16005 samples

	% Ağırlık				
	O	Al	Si	Ca	Zr	Toplam
1	43,53	3,90	0,81	2,50	49,27	100,00
2	36,15	2,50	-	0,90	60,45	100,00
3	43,24	13,17	4,88	9,97	28,74	100,00
4	30,74	0,77	-	0,60	67,90	100,00

Nath et al [25] obtained partially stabilized zirconia with 8 mol% CaO and fully stabilized zirconia with 16 mol% CaO in their study. For PSZ, the c-ZrO_2 phase increased at temperatures of 1550 and 1585 °C; They stated that the t-ZrO_2 phase decreased to a negligible extent. Although the density values of PSZ materials are higher than FSZ materials, the hardness values of single-phase c-ZrO_2 FSZ materials are higher because the m-ZrO_2 phase is softer than the t-ZrO_2 and c-ZrO_2 phases.

Accordingly, as can be seen from the XRD graphs given in Figure 5, while there is a small amount of m-ZrO_2 phase in the mullite-free 1500 samples; In 1600 samples, the structure completely transformed into the c-ZrO_2 phase. As the c-ZrO_2 phase increases, the amount of t-ZrO_2 phase in the structure decreases, and as a result, the fracture toughness and bending strength decrease as the t-m transformation toughness decreases [26].

Therefore, since the c-ZrO_2 phase increases significantly in the 1600-5 samples, the hardness will increase, but the bending strength will take the lowest value, confirming the values we obtained.

Kumar et al [27] produced mullite-zirconia ceramics using 0 – 12 mol% CaO with 2 hours sintering at temperatures of 1450 – 1600 °C. It has been stated that CaO increases the mechanical properties by forming the t-ZrO_2 phase. They stated that the density values decreased from 1500 to 1600 with 12 mol% CaO and the highest density value was obtained at 1500 °C.

Chandra et al [28] produced mullite-zirconia ceramics using 2.5 - 10% by weight of CaO by sintering for 3, 4, 5 hours at temperatures of 1450 – 1550 °C. It has been stated that the mullite phase is not present in the structure due to the formation of a small

amount of different phases in the samples with 10% CaO by weight. It is stated that the wear resistance is worse due to the absence of mullite formation. It was also stated that the effect of CaO on the m-ZrO$_2$ phase crystallite size is not regular.

In this direction, as can be seen from the XRD graphs given in Figure 6, it is seen that there is no mullite phase in the structure of the mullite added samples, and this result confirms the work of Chandra et al.

In our study, while t-ZrO$_2$ phase was observed in XRD 1500-1 in mullite-doped samples, this phase decreased in 1500-5, and it almost completely turned into m-ZrO$_2$ phase in 1600 samples. For this reason, the highest value of bending strength is in the 1500-1 sample. The lowest flexural strength in the 1600-5 samples is due to the decrease in t-m transformation toughness as a result of the decrease in the t-ZrO$_2$ phase and also due to grain coarsening. Our density values also yielded results in line with the work of Kumar et al.

Also in the SEM image given in Figure 7, the presence of large pores in the mullite added sample confirms that the density has decreased. As can be seen from the SEM image given in Figure 7, the amount and size of the pores on the surface increased significantly with the addition of mullite. It can be predicted that this situation will have a negative effect on the hardness values of the samples and decrease the hardness value of the mullite added sample. As a matter of fact, in the experimental results, the hardness value of the CaZ10M16005 sample was found to be lower than the hardness value of the CaZ00M16005 sample.

According to the EDS analyzes given in Figure 8 and Figure 9, the evaluation of the EDS analysis results on the CaZ00M16005 and CaZ10M16005 samples was made from general (1) and parts 2, 3, 4. 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 and Recommendations

In this study, utilization of mullite in the manufacturing of calcia doped zirconia was investigated and it has been evaluated the effect of CaO and mullite contribution to ZrO$_2$ main matrix.

In all samples, it was observed that 3 - point bending strength values decreased with increasing sintering temperature and time. With increasing sintering temperature and time, shrinkage, experimental and relative density, hardness values and wear resistance of the CaZ0M coded mullite-free samples except for the 1600-5 sample increased; the water absorption and porosity values decreased. Although it has especially high hardness, the high amount of wear seen in the CaZ00M16005 sample is due to the brittle and easily breakable structure of the sample, and its three-point bending strength is very low compared to the other samples. The low flexural strength value of this sample despite its high hardness was explained by XRD phase analysis and the work of Nath et al. [25]. Accordingly, as the sintering temperature and time increase, the c-ZrO$_2$ phase increases significantly, especially in 1600-5 samples, and the hardness will also increase; However, it was stated that while the c-ZrO$_2$ phase increased, the amount of t-ZrO$_2$ phase in the structure was decreasing, and as a result, the t-m transformation toughening was reduced, so the bending strength got the lowest value.

In CaZ10M coded mullite added samples, while shrinkage, experimental and relative density, hardness values and wear resistance increased in 1500 samples; in the 1600 samples these values fall in line with the results obtained by Kumar et al [27]. We think this is a result of the differences in the microstructure and phase changes at 1600 ºC temperature. While t-ZrO$_2$ phase was observed in XRD 1500-1 in mullite-doped samples, this phase decreased in 1500-5, and it almost completely transformed into m-ZrO$_2$ phase in 1600 samples. For this reason, the highest value of bending strength is in the 1500-1 sample. The lowest flexural strength in the 1600-5 samples is due to the decrease in t-m transformation toughness as a result of the decrease in the t-ZrO$_2$ phase and also due to grain coarsening.

While the shrinkage, experimental density, relative density, and hardness values of the samples with mullite additives decreased in general compared to the samples without additives; It was observed that water absorption, porosity and three-point flexural strength values and wear resistance increased. While m-ZrO$_2$, t-ZrO$_2$ and c-ZrO$_2$ phases were detected in the samples, mullite phase could not be detected in the phase analysis of the samples with mullite additives, and this result compatible with the work of Chandra et al [28].

5. Acknowledge

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