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Effect of Ceria on the properties of Ceria Stabilized Zirconia/Alumina /Ceria (ZTA/Ce) composites

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ABSTRACT

Ceria stabilized zirconia toughened alumina (ZTA) /ceria composites for industrial ceramic applications have been studied. Five samples were prepared, ceria was added to ceria stabilized zirconia/alumina composites by various amounts of (0-20 wt. %). The fabricated samples were sintered at 1600 - 1700°C. The sintered samples were characterized for their physical properties such as bulk density and apparent porosity. The samples were characterized by XRD, SEM and TEM and mechanical tests. It was observed that the formation of cerium hexaaluminate and cerium zirconate in the studied bodies deteriorates the Vicker hardness and fracture toughness of the ceria stabilized ZTA bodies.

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I. Introduction

Al₂O₃ can be considered as an all-rounded for engineering ceramic. The properties of this ceramic are particularly attractive for structural applications such as in motor, aerospace and biomedical fields [1]. Brittleness and poor damage tolerance have limited the scope of use as advanced engineering materials [2]. The fracture toughness of alumina is low because the dislocation motion in the materials extremely limited due to the nature of the chemical bonds which are ionic and / or covalent. The use of ZrO₂-based ceramics is one of the possible alternatives to circumvent the limitation of low fracture toughness [3, 4]. The problem of low fracture toughness in the ceramic can be overcome by designing and preparing the composite materials. Zirconia toughened alumina (ZTA) is a promising structural material due to its excellent mechanical properties such as bending strength, fracture toughness and hardness [5, 6]. In the ZTA system, the stress induced transformation toughening mechanism occurs when the crystal structure of zirconia particles in the region near the tip of the crack changes from metastable tetragonal phase to the stable monoclinic phase. The change enlarges the volume of the particles and produce compressive stresses in the alumina matrix. These stresses effectively close the crack and block further crack growth, which can improve the strength, fracture toughness and hardness of the ZTA [7-9].

The utilization of sintering additives such as Cr_2O_3 , TiO_2 , NiO and MgO were selected by researchers because these additives enable the achievement of fine grain size and high density at low sintering temperature [10]. Tsukuma *et al.* [11] found that, with the addition of CeO_2 in to tetragonal zirconia polycrystals (TZP), the fracture toughness were very dependent on the CeO_2 content and grain size of the sintered body. Cerium oxide (CeO₂) is used to stabilize zirconia completely in its tetragonal phase (t-phase) [12]. Previous work done by Mangalaraja *et al.*, and Akin *et al.*, [13, 14] indicated that the presence of CeO_2 in the Al_2O_3 matrix reduces the mechanical properties of ZTA due to the higher apparent porosity and the formation of elongated $CeAl_{11}O_{18}$ grains, which possibly resulted from the addition of CeO_2 .

However, there are only scarce reports about the effects of CeO₂ addition on the phase composition, microstructure and mechanical properties of ZTA. Therefore, in this study, we examined the effects of CeO₂ addition (0-20 wt. %) on the phase composition, microstructure and mechanical properties of ZTA system. The phase composition and microstructure of the samples were investigated by using XRD and SEM respectively. The mechanical properties, such as fracture toughness, bending strength and Vickers hardness, were measured to determine the potential of the ZTA-CeO₂ compositions.

II.1. Materials

Aluminium oxide having a purity of 99.98% (provided by Almatis GmbH, Ludwig shaven/RH, Germany), cerium (IV) oxide (99.5%min (RED) from Alfa Aesar, UK), zirconium (IV) -n-butoxide (Strem Chemicals USA) and cerium nitrate were used as starting materials in this study.

II.2. Methods of preparation

Ce-PSZ (17.5 mol %) composite was prepared by hydrolysis of zirconium (IV)-*n*-butoxide with the addition of cerium nitrate (CeO₂ in HNO₃). While, ZTA composites doped with CeO₂ were prepared by the addition of CeO₂ to the prepared 17.5 mol % of Ce-PSZ sol in step prior to gelation. The batch compositions of the prepared batches are represented in the Table. (1). The prepared gel was dried and calcined at 900°C to get rid of all organic and nitrate materials. The calcined powders were grounded in an automatic agate mortar to remove all particles agglomerations and then further milling for 3h. All powders were mechanically mixed for 2h using a ball mill with 5 mm zirconia balls as grinding media in a polypropylene container at constant speed of 300 rpm. The obtained powders were formed by uniaxial pressing at 220 MPa into discs of 13 mm diameter and 4 mm height (for physical and microstructural characterization) and rectangular bars of dimensions of 6 X 6 X 60 mm (for mechanical evaluation). The pressed samples were dried in the air overnight and then at 110°C for 24h. Samples were pressure less sintered in an electric furnace at 1600°C up to 1700°C with 25°C intervals and one hour soaking time at the maximum firing temperature. Heating and cooling rates were conducted with 5°C/min.

Specimen	Al ₂ O ₃ (wt, %)	ZrO ₂ (wt, %)	CeO ₂ (wt, %)
C1	90	10	-
C2	85	10	5
C3	80	10	10
C4	75	10	15
C5	70	10	20

Table 1. LTA uopeu with CeO ₂ batch compositi	tions	compositi	batch	CeO ₂	with	doped	ZTA	1.	Fable]
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II.3. Characterization

The densification parameters of the fired samples in terms of bulk density and apparent porosity were evaluated with the liquid displacement method (ASTM C-20). The different phases in the powdered samples developed during firing were identified by means of X-ray diffraction analysis (XRD) with a Philips X-ray diffractometer, model PW1730, with a Cu target and Ni filter. The XRD patterns were obtained at room temperature with goniometric range of 2θ (5–80°), a scanning rate of 0.005°.s-1 and a step size of 0.02°. The microstructure of the fractured surfaces of the as-sintered specimens was examined with a scanning electron microscope (SEM-Jeol JSM-T20). The Vickers hardness of the sintered samples was measured with a hardness tester (Omnimet automatic MHK system Model Micro Met 5114, Buehler USA). The composite samples were polished down to 0.25-mm surface finish with diamond paste. Indentations were made on the polished surfaces with a load of 5 kg and 15 sec dwell time. 30 indents were made for each sample and average hardness was calculated according to the following equation (1) [15]: $HV = 1.8544 \left(\frac{P}{d^2}\right)$ (1)

Where p: is the load and d: is the length of the impression diagonal.

Bending strength was measured in a three point bending test on a universal testing machine (Model LLOYD LRX5K of capacity 5K N) at a crosshead speed of 1mm/min, and support distance of 25 mm. At least 10 specimens were measured for each data point. The fracture toughness was determined with the (single- edge v notched beam SEVNB) technique [16]. For the SEVNB method, ground and polished rectangular specimens (3 x 4 x 45 mm³) were notched on the surface (3 x 45 mm²) using a diamond charged cutting wheel, perpendicular to the length of the rectangular bars. The depth of the notches was approximately 0.7 mm, i.e. 20% of the height of the specimen and the sharpened notch root radius of the specimen is approximately 18 µm in accordance with DIN 51109. The fracture toughness was determined by applying the following equations (2) [17]:

$$K_{lc} = \left[\frac{L_{max}}{(t(h^{\frac{1}{2}})}\right] \times \left[\frac{(L_o - L_i)}{h}\right] \times \left[\frac{3}{h} R_M(\frac{d}{h})^{\frac{1}{2}} / 2(1 - (\frac{d}{h})^{\frac{3}{2}}\right]$$
(2)

Where $R_{\rm M}$ is from eq. (3) $R_{M} = [1.9887 - 1.326 (\frac{d}{h}) - [3.49 - 0.68(\frac{d}{h}) + 1.35(\frac{d}{h})^{2}](d/h) (1 - (\frac{d}{h})^{2})/(1 + (\frac{d}{h}))$ (3)

Where, L_{max} is the maximum load, L_o and L_i are the outer and inner roller spans; respectively, t and h are the thickness and height of the specimen, d is the depth of the sharpened notch.

III. Results and Discussion

III.1. Physical properties

The verification parameters of the prepared composites in terms of bulk density and apparent porosity as a function of firing temperature and CeO_2 content are given in Table (2). This Table shows the effect of sintering temperature on the studied bodies bulk density and apparent porosity (C1 = pureZTA, C2 = 95 ZTA-5 wt% CeO₂, C3 = 90 ZTA-10 wt% CeO₂, C4 = 85 ZTA-15 wt% CeO₂, C5= 80 ZTA-20 wt% CeO₂). The Table (2) indicates that as the firing temperature increases from 1600°C up to 1700°C the bulk density is sharply increased with a decrease of apparent porosity. On further increase of firing temperature up to 1675°C the increase in the bulk density and the decrease in the apparent porosity was slowdown. On the other hand, firing the samples at 1700°C led to apparent porosity and bulk density decrease, except C1 samples with the lowest CeO₂content. The physical properties revealed that the addition of CeO₂ improved the densification behavior and decrease the maturing temperature of the studied composites.

Table 2a. Bulk density of ZTA with various amounts of ceria addition at different sintering temperatures.

corra addition at anter ent sintering temperatures.								
SI. No.	Sample No.	Bulk density (g/cm ³) Temp. (°C)						
		1600	1625	1650	1675	1700		
1	ZTA-0	2.996	3.251	3.552	3.678	3.818		
2	ZTA-5	3.191	3.344	3.605	3.795	3.650		
3	ZTA-10	3.255	3.458	3.689	3.823	3.450		
4	ZTA-15	3.467	3.580	3.750	3.752	3.505		
5	ZTA-20	3.728	3.568	3.741	3.783	3.622		

Ta	ble	2b. 4	Apparent	po	rosity	of ZTA	A with	various	amounts
	of	ceria	addition	at	differe	ent sint	ering	tempera	tures.

SI. No	Sample	% of Apparent porosity					
110.	110.	1600 1625 1650 1675 1700					
1	ZTA-0	30.977	22.878	16.450	5.349	1.89	
2	ZTA-5	28.015	20.785	16.525	5.824	0.93	
3	ZTA-10	29.210	20.591	15.871	6.433	0.12	
4	ZTA-15	26.055	19.914	16.549	11.78	0.15	
5	ZTA-20	20.586	22.047	21.281	12.40	6.10	

III.2.Phase Composition

XRD diffraction patterns of the sintered samples sintered at 1675°C are shown in Fig. (1). Starting from 10 wt % CeO₂ addition the presence of cerium aluminate phase (CeAl₁₁O₁₈) was evident. Its content increases with the increase in the CeO₂ content. It is well known that the reduction of CeO₂ to Ce₂O₃ is an easy reaction. CeAl₁₁O₁₈ is formed as a result of the reaction of Ce₂O₃ and Al₂O₃ at high temperature (between 1200- 1400°C) according to the following equation [18]:

$$Ce_{2}O_{3} + 11Al_{2}O_{3} \xrightarrow{1400^{0}C} Ce_{2}O_{3}Al_{2}O_{3} + 10Al_{2}O_{3}$$
$$Ce_{2}O_{3}Al_{2}O_{3} + 10Al_{2}O_{3} \xrightarrow{1500^{0}C} Ce_{2}O_{3}.11Al_{2}O_{3}$$

The figure also, indicates the presence of α - alumina, while CeO₂ was indicating in XRD patterns of samples containing high CeO₂ content (10, 15 and 20 wt % CeO₂). On adding 5 wt % CeO₂ the diffraction line of tetragonal zirconia phase at (101) is shifted to the lower Bragg angle. It points to an increase in the lattice dimensions. According to Rejab *et al* [19] statement the increase in the lattice dimension is due to the formation of Ce⁴⁺ solid solution in zirconia. 5 and 10 wt % CeO₂ addition to ceria stabilized zirconia/ alumina bodies led to the formation of new phase; cerium zirconate; with ceria and zirconia equal proportions; $Zr_{0.5}$ Ce_{0.5} O₂. On the other hand the increase of ceria addition up to 15 and 20 wt % led to the formation of cerium zirconate phase that have higher content; $Zr_{0.4}$ Ce_{0.6} O₂. The formed $Zr_{0.4}$ Ce_{0.6} O₂phase is existed when the Ce⁴⁺ solubility in ZTA exceeds the solubility limits; i.e. when CeO₂ content is high.



Fig 1. XRD patterns of ZTA samples doped with different cerium oxide ratio fired at 1675°C.

III.3. Microstructure

Figure (2a-e) indicates the change that occurred in the microstructure of the sintered ZTA bodies when different CeO₂ additions were incorporated into the batch. Figure (2a) shows that zirconia particles are well distributed within the matrix. Zirconia grains are partially agglomerated and mostly located in the grains triple junction. Zirconia present in the triple point of the alumina particles inhibits the alumina grains growth. Pinning of the alumina grain boundaries with zirconia fine particles led to the inhabitation of the alumina grain growth [20, 21]. With the addition of CeO₂ from 5 up to 20 wt%, two new phases are starting to form. Tiny white crystals are shown in Fig. (2b, c and d) are pointed to the formation of cerium hexaaluminate (CeAl₁₁O₁₈).





Fig 2. SEM micrograph of C1 (a), C2 (b), C3 (c), C4 (d) and C5 (e) samples fired at 1675°C.

III.4. Mechanical Properties. III.4.1. Bending Strength.

A three point bending test was carried out according to ASTMC1161 (1990) on different batches starting from pure ZTA containing 0 wt % CeO₂ up to that containing 20 wt % CeO₂. The mole percentage of CeO₂ affects the bending strength of the sintered specimens. Fig. (3) illustrates that the addition of 5 wt % CeO₂ does not affect the bending strength of the sintered bodies. The addition of 10 and 15 wt % CeO₂ decreases the bending strength and further addition of 20 wt % CeO₂ significantly reduces the bending strength. The all results of mechanical properties which involve binding strength, Vickers hardness and fracture toughness are tablet in Table (3).

Table 3 . Mechanical properties of ZTA with various amounts of ceria addition sintering at 1675°C.

SI. No.	Sample	Bending Strength (MPa)	Hardness (HV)	Fracture Toughness (MPa. m ^{1/2})
1	ZTA-0	175.152	1508.75	7.97
2	ZTA-5	173.1	1176	7.54
3	ZTA-10	142.023	1200	7.39
4	ZTA-15	137.772	907.6	6.96
5	ZTA-20	111.068	848	6.82



Fig 3. Effect of CeO₂ content on the binding strength of composites sintered at 1675°C.

3.4.2. Vickers Hardness.

Vickers hardness behaves similar to bending strength. It decreases with the increase in CeO₂ content, and the lowest hardness figures are that belonging to the bodies containing the higher CeO₂wt % (20 wt %). The decrease in bending strength and Vickers hardness is attributed to the formation of cerium hexaaluminate. The formation of elongated CeAl₁₁O₁₈ particles in the bodies containing 20 wt % CeO₂ negatively affected the mechanical properties [14], shown in Figure (4).



Fig.4. Effect of CeO₂ content on the Vickers Hardness of composites sintered at 1675°C

III.4.3. Fracture Toughness.

Toughening mechanism of zirconia is clarifying the cause of mechanical properties failure of ZTA/ Ce composites with the increase in CeO₂ content. CeO₂ performs an important role in enhancing the stability of ceria/ zirconia solution in ZTA/ Ce composites. It is noticed that ZrO₂ and CeO₂ are present in equal proportions in batches containing 5 and 10 wt % CeO₂; the formula is $Zr_{0.5}$ Ce_{0.5} O₂. Increasing CeO₂ percentage up to 15 and 20 wt % led to the formation of cerium zirconate phase rich in Ce in comparison to Zr; $Zr_{0.4}$ Ce_{0.6} O₂. Figure (5) shows the relation between CeO₂ content and the sintered samples fracture toughness. The decrease in the fracture toughness with the increase in CeO₂ is due to the decrease in the zirconia tetragonal phase content of the composites. XRD patterns indicate the formation of cerium hexaaluminate in the sintered composite containing CeO₂. It is content increases with the increase in the CeO_2 . The formation of $CeAl_{11}O_{18}$ has a destructive effect on the fracture toughness [22].



Fig 5. Effect of CeO₂ content on the fracture toughness of composites sintered at 1675 °C.

IV. Conclusion

The effect of ceria addition on the physical, microstrucural and mechanical properties of ceria stabilized ZTA were studied. The presence of $Ce_2Zr_3O_{10}$ phase proved the exceeding limit of CeO_2 addition in ZTA composite. The highest values for fracture toughness and Vickers hardness were recorded of ZTA sample without ceria addition (ZAT-0) which produced 7.97 MPa.m^{1/2} and 1508 HV, respectively. The decreased mechanical properties for composites (ZAT-5, 10, 15& 20) are found to be due to the presence of cerium hexaaluminate (CeAl₁₁O₁₈) and cerium zirconate (Ce₂Zr₃O₁₀), which reduced the Vickers hardness and fracture toughness of the overall ceramics.

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