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PRODUCTION OF CALCIUM ALUMINATE CEMENT DOPED ZIRCONIA

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ABSTRACT

This study is aimed to investigate the solid state reaction using monoclinic zirconia (m-ZrO_2) and calcium aluminate cement (CA), as starting materials. Various compositions, containing different proportions of CA (5 - 15 mass % CA in ZrO_2), were reaction sintered at 1300 - 1500ºC. Crystalline phase formation and densification of CaO stabilized ZrO_2 composites were investigated by X-ray diffraction (XRD) analysis, density and shrinkage measurements. Scanning electron microscopy (SEM) was used to examine the microstructure. Mechanical characterization was carried out by three-point flexural test measurements.

As a result, sintering of mixtures of m-ZrO_2 with CA as a source of CaO at 1300 - 1500°C was effective to produce Ca stabilized ZrO_2 composites. XRD results indicated that during sintering, calcium coming from calcium aluminates decomposes and reacts with zirconia forming a tetragonal zirconia (t-ZrO_2) structure.

Keywords: CA Cement, Zirconia, Stabilization, XRD.

INTRODUCTION

Pure zirconia exhibits three polymorphs depending on temperature: monoclinic (m) up to 1170°C, tetragonal (t) to 2380°C, and cubic (c), beyond this temperature [1 - 6]. The phase transformations between these different polymorphs are very important for the processing and mechanical properties such as fracture toughness, strength, etc. of zirconia ceramics. It is well known in the literature that the t→m phase transformation in pure undoped zirconia during cooling, is a reversible athermal martensitic transformation, associated with a large temperature hysteresis (around 200°C for undoped zirconia) and a finite amount of volume change (4 - 5 %) [2, 4 - 7], being the most destructive phase transformation [8]. Stresses generated by this expansion originate cracks in pure zirconia ceramics that, after sintering at temperatures between 1500 and 1750°C, break into pieces at room temperature [5]. The feasibility of the stabilization of the t-phase at room temperature by adding to zirconia small amounts of CaO, was showed by Ruff et al. [9]. In tetragonal zirconia ceramics the toughening is due to the transformation of precipitates, in reticular form [1]. The toughening mechanism is associated with the stress-induced tetragonal to monoclinic phase transformation and high fracture toughness. It is noteworthy to point out that the different results within the existing works, published by diverse researchers, concerning magnesia or calcium stabilized ceramics, the magnesium or calcium starting material is used in "oxide" state, when mixed in situ with ZrO_2 powders.

Calcium has been used commercially to stabilize pure zirconia. For the calcium doped zirconia, CaO addition is in the range of 7.5 - 8.7 mol % in ZrO_2 and, for commercial alloys, 8.4 mol % (4.0 mass %) has been most common [10]. Standard materials with partial stabilization contain approximately 5 mol % CaO, while for full stabilization 20 mol % is required.

In several methods, Ca stabilized ZrO_2 can be prepared from mechanical alloying using high-energy ball-milling of pure ZrO_2 [11].

In this work, the formation of Ca stabilized ZrO_2 material with potential applications in biologic and dental applications, pure ZrO_2 with addition of different proportions of calcium aluminate cement (5 - 15 mass % CA in ZrO_2), was investigated. Thus, CaO was introduced in the form of high alumina cement, and the effect of important factors, such as chemical composition, sintering temperature on reaction, densification and microstructure was examined.

EXPERIMENTAL

Materials

Pure zirconia (m-ZrO_2) of commercial grade with a mean particle size $d_{50} = 2.21$ µm was employed as reactant. Particle size distribution is narrow with particle sizes in a range of $d_{90} = 9.54$ µm and $d_{10} = 0.52$ µm. A commercial calcium aluminate cement (CA), used in the refractory industry was employed as the second reactive (Secar 71, Kerneos, France). Table 1 shows the main chemical composition of this raw material, which was obtained from its product data sheet.

From these two raw materials a series of mixtures of different chemical composition were prepared varying between 5 and 15 mass % of CA in ZrO_2.

6.5 mm x 6.5 mm x 58.5 mm prismatic bars were shaped using uniaxial pressing (20 MPa). The compacts were identified according to the CA mass content in respect to ZrO_2: 5, 10 and 15 mass % of CA and were named as: ZrC5, ZrC10 and ZrC15. Reaction sintering was made with an electric furnace (SiC) in air atmosphere at different temperatures (1300 - 1500°C), using heating and cooling rates of 5°C min^{-1}. The soaking time was of 4 h.

Characterization

Crystalline phases were analyzed by X-ray diffraction (XRD) on a Panalytical X-Pert diffractometer, equipped with Cu-Kα radiation. A scan speed of 0.1 2 θ min^{-1} was employed in the 20 - 80° 2θ range.

The XRD analysis showed that the initial phase composition changed after sintering. As will be discussed below, the main transformation was the formation of t-ZrO_2. Linear shrinkage of the composites was geometrically determined as a function of the sintering temperature. The bulk densities and porosites of the sintered samples were determined by the Archimedes principle with distilled water as the medium. The bending strength, σ_f, was determined by three-point bending tests The specimens were tested at room temperature using a three point support with a span of 40 mm in a universal

Table 1. Chemical composition of the CA cement used.

Chemical Composition	(%)
Al_2O_3	68
CaO	30
Na_2O	0.5
SiO_2	0.2-0.6
Fe_2O_3	0.1-0.2
TiO_2	0-0.4

Table 2. Chemical composition of ZrO_2 used.

Chemical Composition	(%)
SiO_2	0.24
Al_2O_3	0.23
Fe_2O_3	0.044
ZrO_2-HfO_2	98.08
TiO_2	0.137
L.O.I	0.6

testing machine (Schimadzu AG-IS). The specimens were loaded to failure with a cross-head speed of 0.05 mm min^{-1}. A scanning electron microscope (SEM) (Jeol JSM 6400), equipped with an energy dispersive X-ray spectrometer (EDS), was used to characterize the microstructure of the sintered specimens.

RESULTS AND DISCUSSION

Influence of the sintering temperature and CA content on the phase transformation

Figs. 1 - 4 show the XRD patterns of the compacts ZrC5, ZrC10 and ZrC15, sintered at different temperatures.

For the sintered ZrC10 and ZrC15 (Fig. 1) a significant increase in the t-ZrO_2 content was observed in comparison with that of the 5 mass % composition. Besides, the m-ZrO_2 content was considerable. The t-ZrO_2 volume fraction increased with the increasing sintering temperature (Fig. 4). The content of CA_2 was related to t-ZrO_2 formation, so both phases had more intense reflections up to 1500°C (Fig. 4).

Fig. 4 shows the superposed diffractograms of ZrC15 at different temperatures. At 1300°C the main crystalline phase was m-ZrO_2, accompanied with a low content of tetragonal (t-ZrO_2) zirconia. The analysis of the principal reflections along the 25 - 32 2θ degree (zone of the more intense peaks of ZrO_2 polymorphs) indicated the presence of t-ZrO_2. Bruni et al. investigated the mineralogical composition of calcium aluminate cement and concluded that the major components of calcium aluminate cement (Secar 71) are monocalcium aluminate (CA) and monocalcium dialuminate (CA_2), 25% and scarce amounts of Al_2O_3 [12]. In our study, small peaks of CA_2 were also present.

When the addition of CA was 15 mass % (ZrC15), the t-ZrO_2 formation was favored even at 1300°C (Fig.4). With further increase in temperature (1300 - 1500°C), an increase of CA_2 and a decrease in the m-ZrO_2 content took place. High formation of t-ZrO_2 at 1500°C was also observed.

XRD results indicated that during sintering, calcium coming from decomposition of calcium aluminates reacts with zirconia to form a solid solution with a tetragonal structure. The t-ZrO_2 formation depended on CA concentration and the sintering temperature.

At low CA additions (5 - 10%), the m-ZrO_2 was the

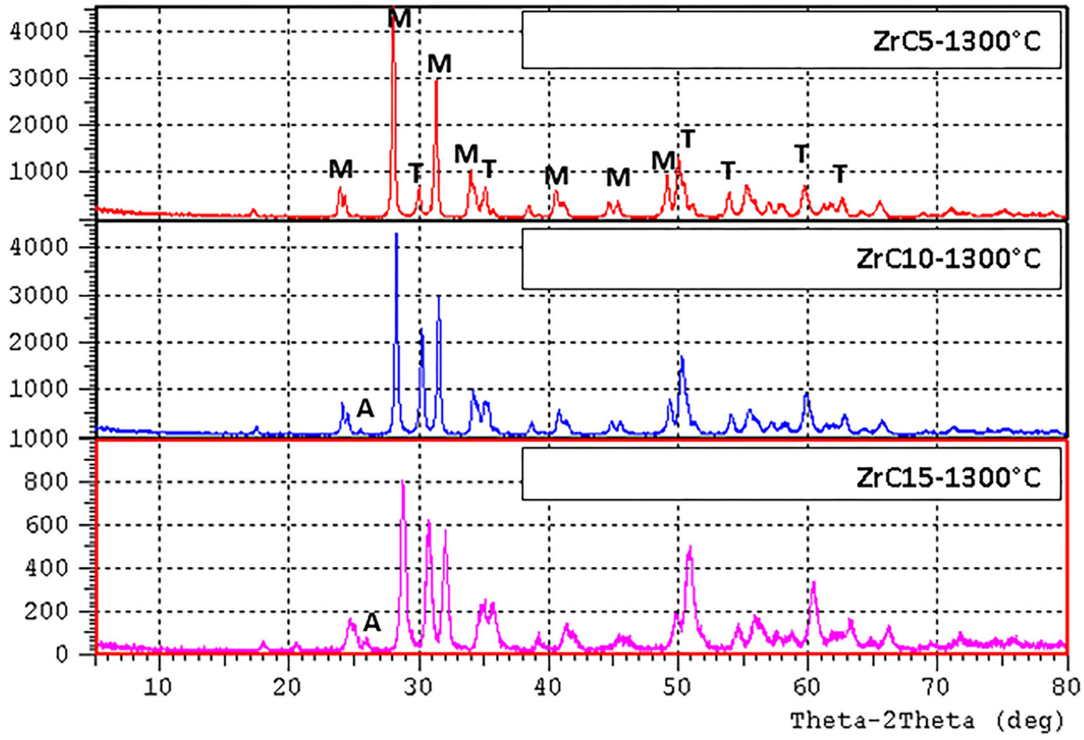

Fig. 1. XRD patterns of ceramics with 5-10-15 mass % CA in ZrO_2, sintered at 1300°C (M: m-ZrO_2; T: t-ZrO_2; A: $CaAl_4O_7$).

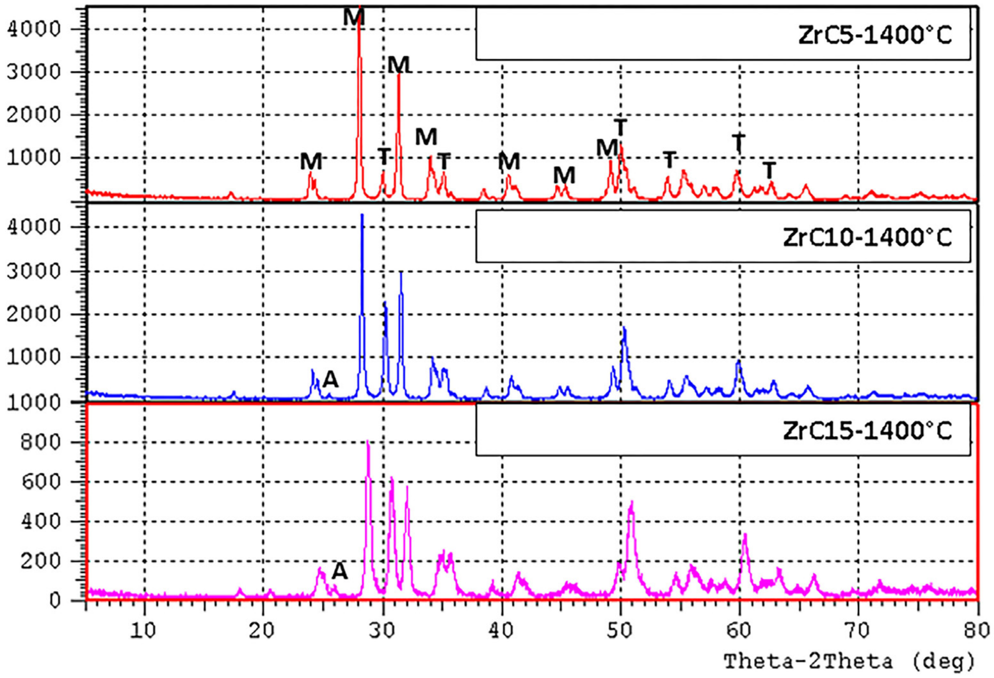

Fig. 2. XRD patterns of ceramics with 5-10-15 mass % CA in ZrO_2, sintered at 1400°C (M: m-ZrO_2; T: t-ZrO_2; A: $CaAl_4O_7$).

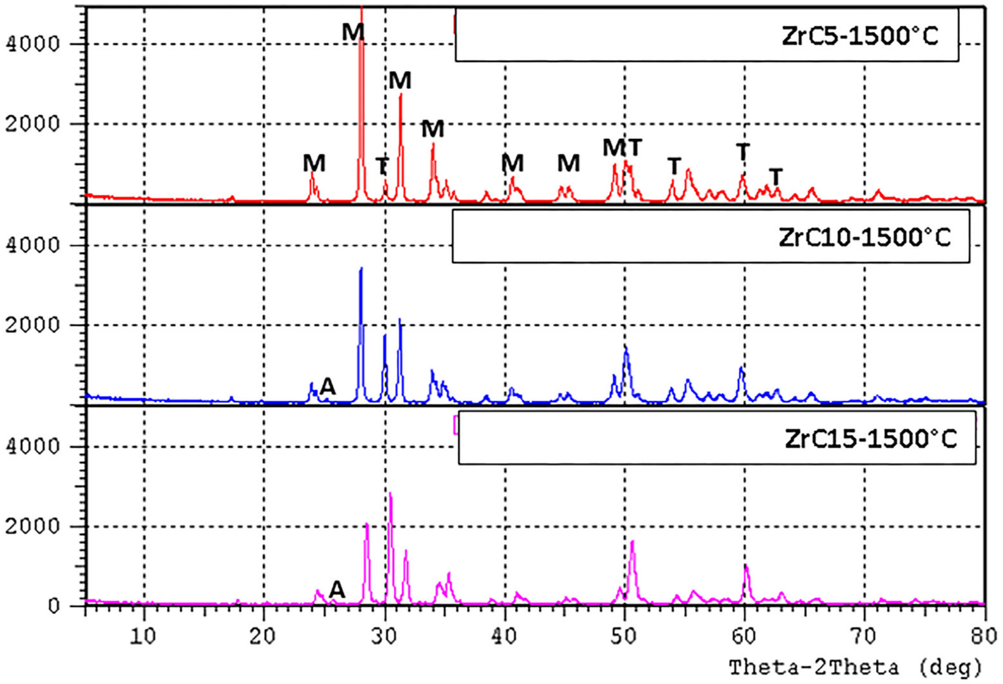

Fig. 3. XRD patterns of ceramics with 5-10-15 mass % CA in ZrO_2, sintered at 1500°C (M: m-ZrO_2; T: t-ZrO_2; A: $CaAl_4O_7$).

principal phase and the sintering temperature slightly influenced the t-ZrO_2 formation. For the ZrC15 composition, t-ZrO_2 strongly increased at 1500°C. Therefore, the sintering temperature seems to be the principal processing parameter in t-ZrO_2 formation.

The phase diagram of the CaO-Al_2O_3-ZrO_2 system was first reported by Berezhnoi and Kordyuk [13]. They determined a single-phase region of the liquid and the

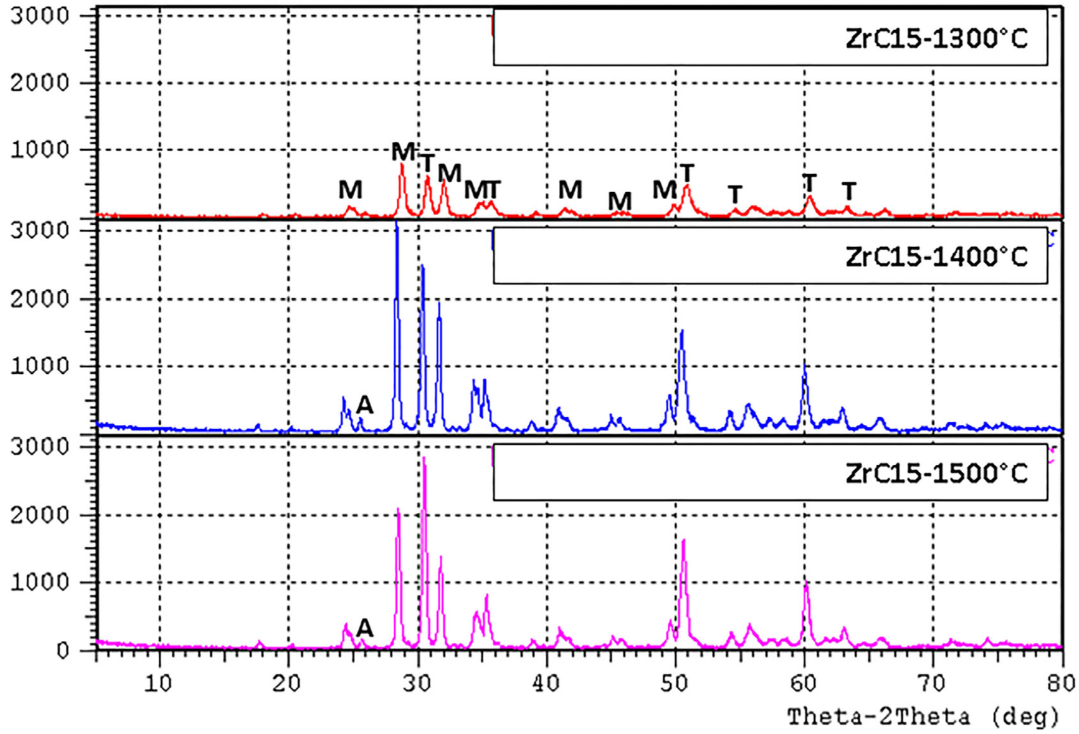

Fig. 4. XRD patterns of ceramics with 15 mass % CA in ZrO_2, sintered at different temperatures (M: m-ZrO_2; T: t-ZrO_2; A: $CaAl_4O_7$).

stoichiometric composition of a ternary compound as $Ca_7A_{16}ZrO_{18}$ (C_7A_3Z), with a melting point 1550°C. Espinosa and White [14], however, reported that the ternary compound is $Ca_{13}Al_{12}Zr_2O_{35}$ ($C_{13}A_6Z_2$) and that it decomposes into $CaZrO_3$ (CZ) plus liquid by a peritectic reaction at 1540°C. This compound appears for high CaO content and establishes a compatibily triangle CZ-$C_{13}A_6Z_2$-C [15, 16]. However, in our study, because of low CaO content, the calcium zirconate phases mentioned above were not detected.

Sintering and microstructure of ZrC5-15 composites

Variation of bulk density and shrinkage of ZrC5-5 compacts with sintering temperatures are shown in Table 3 and Table 4, respectively.

The bulk density dependence on the sintering temperature slightly varied with chemical composition.

The bulk density of all materials sintered at 1300°C remained lower than 4.00 gr cm^{-3}. The bulk densities of ZrC5 compacts significantly increased from 3.68 at 1300°C to 4.35 at 1400°C, respectively and then, a further increase to 4.99 was obtained at 1500°C. The bulk density of the ZrC15 sample reached up to 4.63 by

Table 3. Bulk density values of ceramics vs. sintering temperatures for different mass % CA in ZrO_2.

Sintering Temperature (°C)	Composition	Bulk Density (g cm^{-1})
1300	ZrC5	3.68
	ZrC10	3.58
	ZrC15	3.14
1400	ZrC5	4.35
	ZrC10	4.07
	ZrC15	3.92
1500	ZrC5	4.99
	ZrC10	4.79
	ZrC15	4.63

Table 4. Linear sintered shrinkage of ceramics vs. sintering temperatures for different mass % CA in ZrO_2.

Sintering Temperature (°C)	Composition	Linear Shrinkage (%)
1300	ZrC5	3.13
	ZrC10	2.79
	ZrC15	2.92
1400	ZrC5	8.01
	ZrC10	7.77
	ZrC15	7.73
1500	ZrC5	12.41
	ZrC10	12.11
	ZrC15	12.79

sintering at 1500°C. The denser composite (Bulk density = 4.99) was produced by sintering at 1500°C. Therefore, densification slightly decreased with increasing the content of CA in the starting composition.

As shown in Table 4, there are small differences in the shrinkage between samples sintered at 1300°C. The shrinkage varied between 3.13 % and 2.92 % for ZrC5 to ZrC15, respectively, indicating the initial sintering condition. Shrinkage of ZrC5 and ZrC15 composites sintered at 1400°C reached 8.01 % and 7.73 %, respectively. This agrees well with the increase in densification. The increase in the sintering temperature promoted the neck formation which is associated to a reduction in porosity, whereas shrinkage remained nearly constant to 12 % for the higher CA additions. Comparatively, the ZrC10 and ZrC15 compositions with high ZrO_2 content consolidated by dry pressing in a low packing density of solids and consequently, a slightly lower bulk density resulted even after sintering at 1500°C. The high ZrO_2 content and low packing density of the particles inhibited full densification and resulted in a high pore volume at 1500°C. Pores consisted of interparticle voids, coming from non-uniform packing of ZrO_2 aggregates. Contrarily, high proportion of CA resulted in a wider particle size distribution, in which finer particles fill the interstices left between coarse CA particles. Therefore, a slight increase of the solid packing density of the dried compact is possible. In addition, formation of a liquid phase probably occurred when the temperature approximated to 1500°C and caused the significant shrinkage and the improvements in densification of ZrC15 composite.

The SEM images of the samples, sintered at different temperatures are shown in Fig. 5. The fine aggregates and coarse particles present in the starting ZrO_2 and CA powders, respectively, remained in the sintered composite. It is very clear that the grain size has a significant dependence on temperature. Composites contained significant amount of pores (in dark color) as sintering of highly aggregated powder provided a highly porous ceramic.

Table 5 shows the evolution of open porosity with increasing sintering temperatures. The data show a reduction of porosity with sintering temperature, as expected.

Table 5. Open porosity, determined by the Archimedes method vs. temperature for different wt. % CA content.

Sintering Temperature (°C)	Composition	Open Porosity (%)
1300	ZrC5	32.60
	ZrC10	37.06
	ZrC15	45.18
1400	ZrC5	23.18
	ZrC10	28.51
	ZrC15	32.00
1500	ZrC5	10.76
	ZrC10	13.97
	ZrC15	12.41

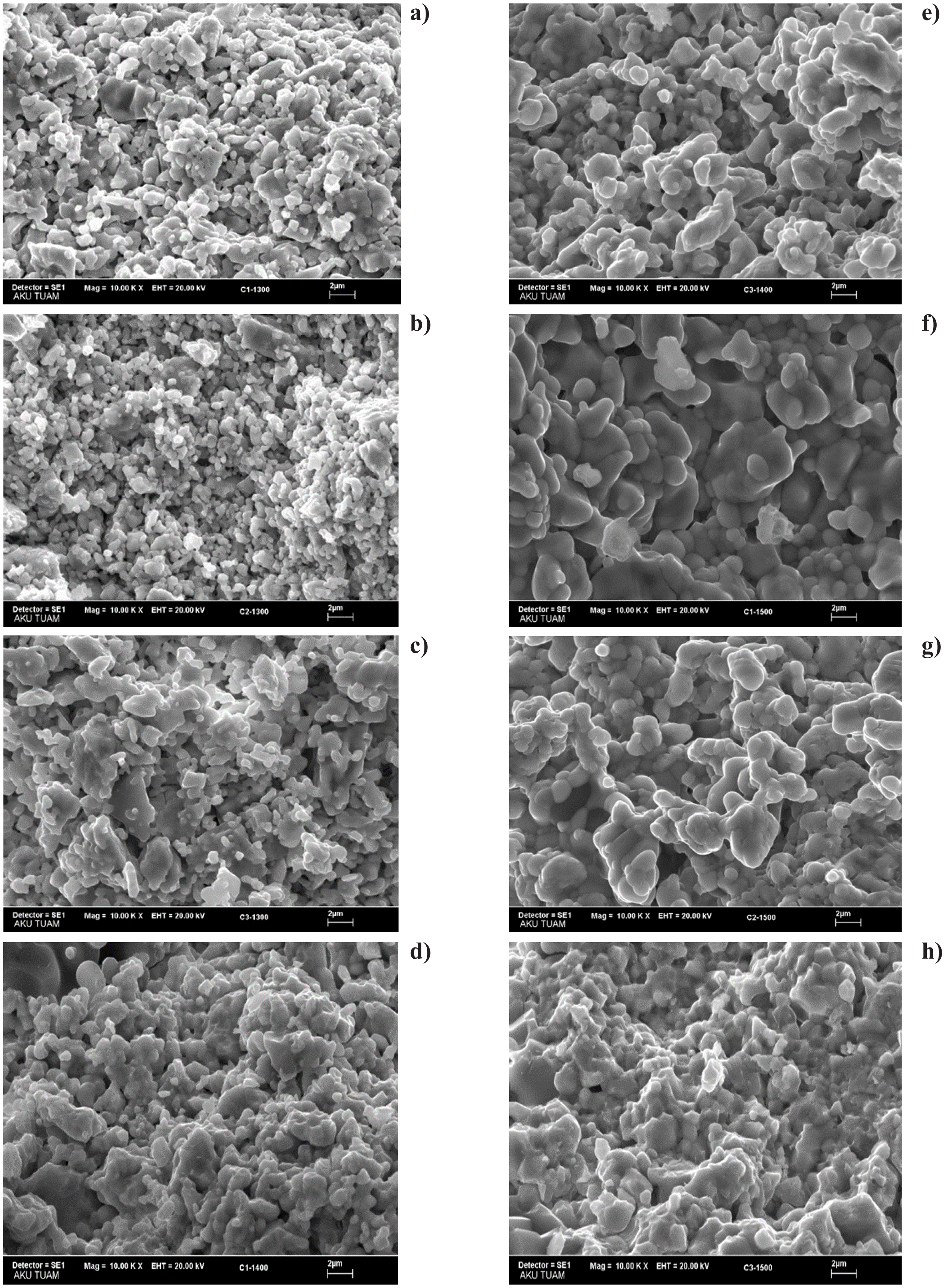

Fig. 5. SEM micrograph of composites with 5-10-15 mass % of CA, sintered at different temperatures.

Table 6. Three point bending strength vs. temperature for different mass % CA content.

Sintering Temperature (°C)	Composition	Three point bending strength (MPa)
1300	ZrC5	25.38
	ZrC10	28.49
	ZrC15	15.55
1400	ZrC5	54.85
	ZrC10	68.00
	ZrC15	44.38
1500	ZrC5	85.55
	ZrC10	93.75
	ZrC15	68.43

Mechanical properties of ZrC5-15 composites

The results of the three point bending strength tests of the samples, after sintering at 1300, 1400 and 1500°C for 4 h, are provided in Table 6.

As shown in Table 6, the bending strength values of the samples increase with the increasing of the sintering temperature for all samples. Bending strength values of the ZrC10 samples are higher than those of the ZrC5 and ZrC15 samples. In general, sintered samples with higher relative density exhibit greater strength and fracture toughness, although one to one correspondence does not exist in this regard. Increasing the CA amount from 10 mass % to 15 mass % negatively affected the mechanical properties.

CONCLUSIONS

Sintering of mixtures of m-ZrO_2 with calcium aluminate CA as a source of CaO at 1300 -1500°C was effective to produce Ca stabilized ZrO_2 composites.

XRD results indicated that during sintering calcium, coming from decomposition of calcium aluminates, reacts with zirconia forming a tetragonal structure (t-ZrO_2).

The t-ZrO_2 formation depended on the CA concentration and the sintering temperature. The ceramics containing 5 -15 mass % CA sintered up to 1500°C are composed by a combination of monoclinic and t-ZrO_2 phases with a low proportion of calcium dialuminate CA_2 ($CaAl_4O_7$). The stabilization was partial and the m-ZrO_2 predominated.

The sintering temperature slightly influenced the t-ZrO_2 formation. The maximum conversion to t- ZrO_2 was observed for 15 mass % CA doped samples at 1500°C.

The transformation to t-ZrO_2 for the ZrC15 sample was the highest by sintering at 1500°C. The densification gradually increased with temperature and is improved at 1500°C.

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