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The influence of firing temperatures on the phase formation, microstructure and mechanical properties of alumina zirconia composite ceramics

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This research prepared composite ceramics between Al_2O_3 (6 mol% MgO); AM and ZrO_2 (4 mol% Y_2O_3); ZY with *50:50* ratio. The samples were sintered under two-step method with four different sintering temperature conditions. It was found that the densities and shrinkage values tended to slightly increase with the lower T_2 temperature for the length of holding times. XRD patterns showed a combination main phase between Al_2O_3 and ZrO_2. Rietveld refinement was used to calculate the percentage of phase composition. All of samples were reveled weight percentage of main composition as m-ZrO_2 c-ZrO_2 t-ZrO_2 and r-Al_2O_3 in different sintering conditions. Rietveld analysis of data revealed a high ratio of t-ZrO_2, c-ZrO_2 phases from the two stage sintering condition with T_1 temperature at 1600 °C for 60 min and T_2 temperature at 1450 °C for 10 h, and T_1 temperature at 1600 °C for 60 min and T_2 temperature at 1500 °C for 5 h. SEM micrographs revealed grain shape and size of grains. The average grain size of AM as 0.863-1.156 μm and ZY was 0.622-0.902 μm:, the size of grain tended to increase with high T_2 temperature for the length of holding time. EDX identified large grains corresponding to the Al_2O_3 phase and small round oval shapes corresponding with the ZrO_2 phase. The mechanical properties were measured by Vicker and Knoop hardness calculate the fracture toughness value. It was found that the optimum mechanical properties were obtained from composite ceramic with sintering conditions temperatures of T_1 temperature at 1600 °C for 60 min and T_2 temperature at 1450 °C for 10 h; this resulted in the highest of fracture toughness value of about 0.32 GPa·m$^{1/2}$. The optimal two stage sintering conditions were obtained from a high ratio of t-ZrO_2 and c-ZrO_2 phases with fine grain size.

Keywords : ZrO_2, Al_2O_3, Mechanical properties, Two stage sintering, Rietveld method.

Introduction

In order to improve the fracture toughness of Al_2O_3 ceramics, a second phase is usually introduced into them, so that the second phase is filled at the grain boundary of alumina, which is conducive to preventing the extension of fracture lines and improving the fracture toughness of alumina ceramics [1, 2]. The fracture toughness of Al_2O_3 ceramics has been improved by adding ZrO_2 as the second phase and sintering to form intergranular or intragranular structure. Alumina-zirconia composite is a common second-phase toughened ceramic material. As an important engineering material, it is widely used in structural ceramics applications because of its unique mechanical and chemical properties [3, 4]. It is well known that the properties of sintered ceramics are mainly dependent on the initial powder properties. Work by Jilin Hu et al. [5] confirmed that high-quality composite powder can be used to prepare high-performance multi phase ceramics. Among dopants used in Al_2O_3, magnesium oxide (MgO) has an important

effect on mechanical properties since it can reduce the sintering temperature and grain size [6, 7]. Other work [8] has revealed that small amounts of magnesia (≤0.70 wt.%), when added to zirconia-toughened alumina, enable it to become a promising material for machining applications. Zirconia in the tetragonal form at room temperature which has the best mechanical properties among all forms and provides toughening mechanisms associated with the phase transformation from t-ZrO_2 to m-ZrO_2 under stress [9, 10]. Many reports have reported attempts to synthesize a metastable tetragonal phase formation in zirconia at low temperature [11-13]. Zirconia stabilized with Y_2O_3 has the best properties for mechanical device applications. Stabilizing oxides (e.g., Y_2O_3) are used to stabilize cubic and tetragonal zirconia forms at room temperature. The mechanical properties of ZrO_2 ceramics with 4 mol% Y_2O_3 addition depend strongly on the microstructure as well as composition as reported by Rittidech et al. [14]. The mechanism of t-ZrO_2 to m-ZrO_2 transition is typical of partially stabilized zirconia and frequently supported by many studies of the transformation strength process, which has been widely, discussed [15, 16]. The alumina-zirconia system (AZx with 15-50 mol% ZrO_2) is interesting to study [17, 18]. The ceramic composite between AM

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and ZY at a ratio of *50:50* was therefor selected for investigation due to its good properties and reduced production costs. The process of heat treatment is important in preparation of ceramics. The microstructure of Al_2O_3-ZrO_2 composite ceramics can be controlled by two ways i.e., either by using additives to prohibit the grain growth, used for obtaining highly dense ceramics, or it can be controlled by using novel processing techniques to modify the microstructure. Two-stage sintering process is one of the ways of eliminating grain growth in the final stage of sintering reported by Chen and Wang [19]. Two stage sintering methodologies involve sintering with thermal pretreatment at a high sintering temperature for short holding times, followed by a second stage at lower temperature for long holding times. The first-stage high temperature sintering step helps eliminate supercritical pores while the second-stage low temperature sintering step suppresses grain growth [19]. However, different Al_2O_3 and ZrO_2 contents of composite ceramics will be suitable for two stage sintering using different conditions. The *0.50*AM-*0.50*ZY composite ceramics sample were investigated to find optimal two stage sintering conditions, which are revealed producing appropriate composite ceramics.

Recently, composite ceramics between Al_2O_3 using addition of 6 mol%MgO and ZrO_2 addition of 4 mol%Y_2O_3 with *50:50* ratio under four different firing conditions (TS-*1*) T_1 temperature at 1650 °C for 60 min and T_2 temperature at 1500 °C for 5 h, (TS-*2*) T_1 temperature at 1650 °C for 60 min and T_2 temperature at 1500 °C for 10 h, (TS-*3*) T_1 temperature at 1600 °C for 60 min and T_2 temperature at 1450 °C for 10 h, and (TS-*4*) T_1 temperature at 1600 °C for 60 min and T_2 temperature at 1500 °C for 5 h were prepared by solid state reaction using two stage sintering method. The influence of firing conditions on bulk densification, percentage of shrinkage, phase formation, crystal structure calculated by Rietveld refinement, microstructure and microhardness is also studied.

Experimental

The composite ceramic alumina zirconia was used as matrix powders to which Al_2O_3 was added MgO 6.0 mol% to form AM and ZrO_2 was added Y_2O_3, 4.0 mol% to form ZY. The powder of AM : ZY at *50:50* ratio was mixed in varying proportions and then wet ball milled for 24 h. After ball-milling, drying in electronic furnaces and sieving with 120 mesh, the resulting powders were annealed at 1200 °C, with dwell times of 120 min and heating/cooling rates of 10 °C/min. The composite powders were then pressed at 3 MPa to form pellets having 1.5 cm diameter using a hydraulic press and sintered in an alumina crucible under two stage sintering with 4 different conditions. These conditions were (TS-*1*) (1) T_1 temperature at 1650 °C for 60 min and T_2 temperature at 1500 °C for 10 h, (TS-*2*) (2) T_1

temperature at 1650 °C for 60 min and T_2 temperature at 1500 °C for 5 h, (TS-*3*) (3) T_1 temperature at 1600 °C for 60 min and T_2 temperature at 1450 °C for 10 h, and (TS-*4*) (4) T_1 temperature at 1600 °C for 60 min and T_2 temperature at 1500 °C for 5 h. The sintering experiments were carried out in an electrical furnace (Nabertherm, Germany). The bulk densities of sintered sample were calculated using Archimedes' method. Phase identification was then performed using an X-ray diffractometer (XRD; Bruker model D8 advance). Subsequently, Rietveld refinement of the XRD patterns of all samples was performed using TOPAS software. Microstructural analysis was performed by using Scanning Electron Microscopy (SEM) (JEOL JSM-840A) of sintered samples on a polished surface. The microhardness of the bulk ceramics was measured using a micro scan from Vickers and Knoop (FM-700e type D, Future Tech., Japan).

Results and Discussion

The x-ray diffraction patterns (XRD) of *0.50*AM-*0.50*ZY composite ceramics with two stage sintering different conditions are given in Fig. 1. XRD patterns consist of two main phases of alumina and zirconia. Apart from the alpha (α)-Al_2O_3 and monoclinic (*m*), tetragonal (*t*), cubic (*c*) zirconia were found. The main reflections in the pattern form around 2θ=25, 30, 35, 43, 50, 57 and 59° that closely match the characteristic reflections of Al_2O_3-ZrO_2 [20-22]. The XRD patterns of sintering condition of TS-*3* and TS-*4* clearly revealed the tetragonal phase and cubic phase of ZrO_2 by the presence of 2θ as 30° and the splitting of peaks around 2θ as 35 and 50°. Full pattern matching refinement of XRD patterns was performed using the TOPAS program based on the Rietveld method. This obtained more detailed information on crystallographic spectra of *0.50*AM-*0.50*ZY composite ceramics with different sintering condition and selected samples with sintering condition of the TS-*3* as shown in the XRD refinement pattern in
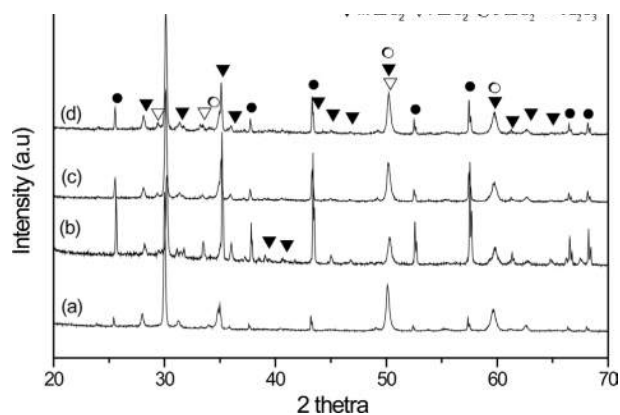

Fig. 1. XRD patterns of *0.5*AM-*0.5*ZY composite ceramics with different two stage sintering conditions (a) TS-*1* (b) TS-*2* (c) TS-*3* (d) TS-*4*.
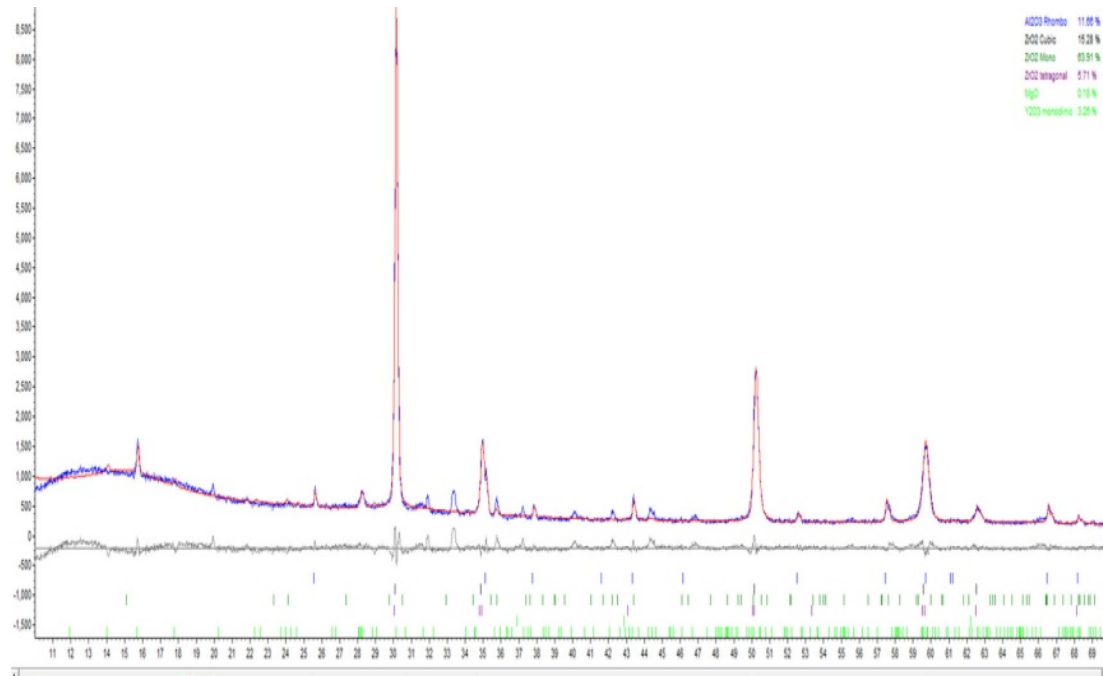
Fig. 2. Rietveld refinement of *0.5*AM-*0.5*ZY composite ceramics with two stage sintering of TS-*3* condition

Fig. 2. The fitted patterns were in good agreement with the respective experiment data, denoted by GOF factors listed in Table 1. The lattice parameter of the AM is showed to be in the range of 0.4558-1.3020 nm, while the ZY phase consists of three different crystallographic system; m-ZrO_2, t-ZrO_2 c-ZrO_2. It was found that two stage sintering condition by the lower T_2 temperature for the length of holding times were obtained the high percentage of phases content of t-ZrO_2, c-ZrO_2. Table 1 shows the relationships between the crystallographic and

Table 1. Parameters obtained from Rietveld analysis and densities, percentage of shrinkage of *0.5*AM-*0.5*ZY composite ceramics with different two stage sintering conditions.

Two stage sintering condition	Phase present	Lattice parameter				Phase content (%)	GOF	Density (g/cm³)	Shrinkage (%)
		a (nm)	b (nm)	c (nm)	β (°)				
1	Al_2O_3	0.4560	0.4560	1.3020		51.06			
	m-ZrO_2	0.5052	0.5140	0.5132	98.51	15.55			
	t-ZrO_2	0.3752	0.3752	0.5101		6.86	1.90	4.33	9.04
	c-ZrO_2	0.5120	0.5120	0.5120		18.74			
2	Al_2O_3	0.4558	0.4558	1.3017		58.96			
	m-ZrO_2	0.5200	0.5129	0.5044	98.30	18.40			
	t-ZrO_2	0.3735	0.3735	0.5018		7.37	2.59	4.12	8.86
	c-ZrO_2	0.5125	0.5125	0.5125		15.89			
3	Al_2O_3	0.4652	0.4652	1.3009		49.58			
	m-ZrO_2	0.5814	0.5107	0.5450	97.69	14.32			
	t-ZrO_2	0.3650	0.3650	0.5101		14.89	2.17	4.50	10.05
	c-ZrO_2	0.5132	0.5132	0.5132		21.87			
4	Al_2O_3	0.4681	0.4681	1.3018		48.92			
	m-ZrO_2	0.5732	0.5462	0.4415	98.63	12.23			
	t-ZrO_2	0.3637	0.3637	0.5129		19.9	2.32	4.41	10.10
	c-ZrO_2	0.5140	0.5140	0.5140		12.18			

Table 2. Average grain sizes and crystalline size of *0.5*AM-*0.5*ZY composite ceramics with different two stage sintering conditions.

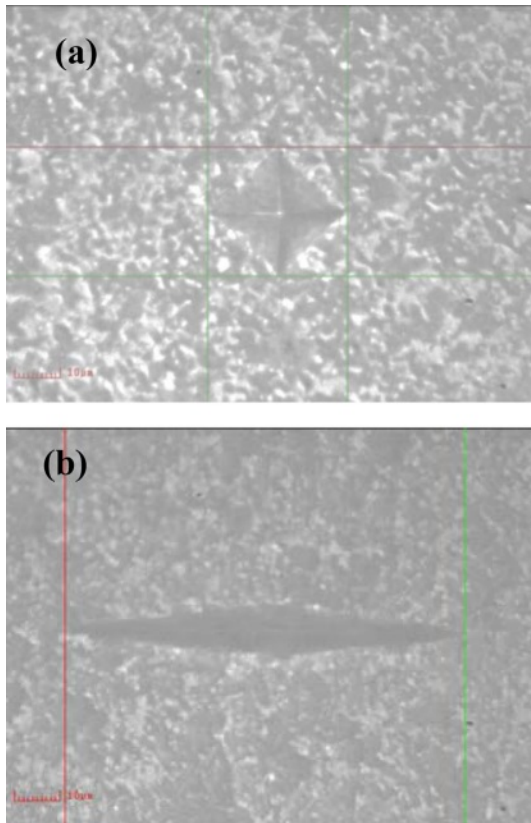| Two stage sintering condition	Average grain size AM (μm)	Average grain size ZY (μm)	Crystalline size AM (μm)	Crystalline size ZY (μm)
1	1.156	0.902	0.811	0.784
2	0.984	0.865	0.792	0.712
3	0.863	0.634	0.758	0.694
4	0.875	0.622	0.779	0.632

physical properties of *0.50*AM-*0.50*ZY with different two stage sintering conditions. Densities of sintered sample were determined using the Archimedes principle. Table 1 contains data about the densities, percentage of shrinkage of *0.50*AM-*0.50*ZY composite ceramics with different two stage sintering condition. It was observed that the density was between 4.12-4.50 g/cm^3. The optimal density was obtained in the sample with the two stage sintering condition of TS-*3* (T_1 temperature at 1600 $^{\circ}$C for 60 min and T_2 temperature at 1450 $^{\circ}$C for 10 h) and TS-*4* (T_1 temperature at 1600 $^{\circ}$C for 60 min and T_2 temperature at 1500 $^{\circ}$C for 5 h). The promotion of densification by the addition of yttria in zirconia and magnesia in alumina under two stage sintering is reflected by the lower temperature required to achieve a high final density than when using undoped and conventional sintering. The crystalline sizes of AM and ZY phases calculated from the XRD patterns are summarized in Table 2. The crystalline sizes of AM were in the range 0.863-1.156 μm and for ZY they were in the range 0.622-0.902 μm. Fig. 3(a)-(d) shows the SEM/EDX micrographs of as-received *0.5*AM-*0.5*ZY composite ceramics with different two stage sintering condition. The microstructure of the sintered *0.5*AM-*0.5*ZY composite ceramics with different two stage sintering condition is showed in Fig. 3, where the ZY phase has a smaller spherical grain shape, while the AM phase is larger and darker grains agreement with the other research [20, 23, 24]. The presence of AM and ZY grain in the specimens was confirmed by EDX analysis (as shown by arrows in Fig. 3(c)). Microstructural characteristics in Fig. 3(c)-(d) were observed, i.e., uniform sized grains with well-packed and continuous grain structure while, the samples in Fig. 3(a)-(b) had a large grain size with low well-packed consistent with bulk density results. SEM results confirmed the small grain size from two stage sintering conditions of TS-*3* and TS-*4* as revealed by high fraction contents of *t*-ZrO$_2$ and *c*-ZrO$_2$ by Rietveld results. Almost no abnormal grain growth appeared. This supported previous research, in which the composite ceramics between alumina and zirconia restrained abnormal grain growth in alumina-based materials [21]. By applying the linear intercept method [25] the grain sizes in SEM micrographs were estimated for these samples as shown in Table 2. It can be seen that *0.5*AM-*0.5*ZY composite ceramics with
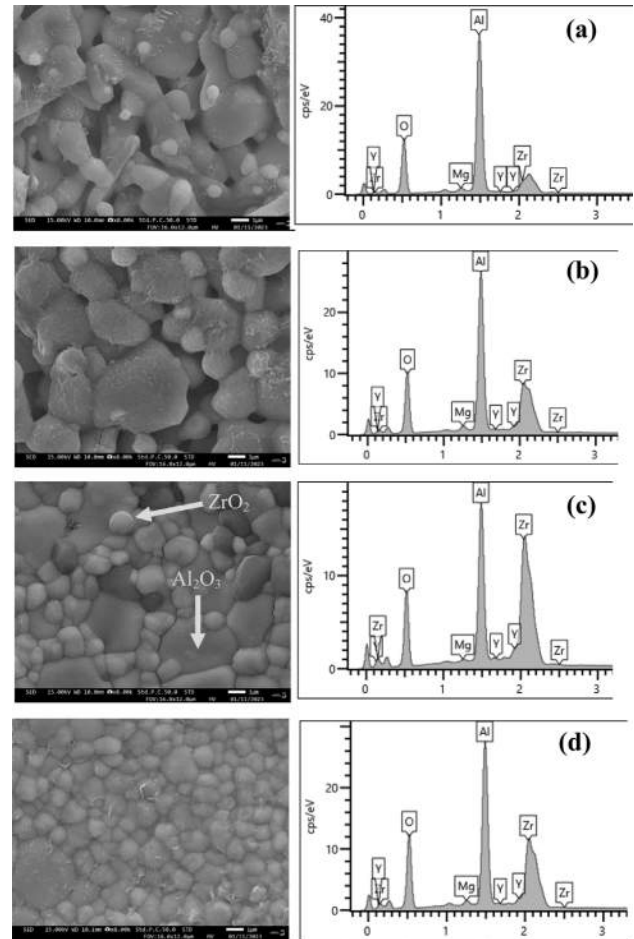
Fig. 3. SEM/EDX micrographs of *0.5*AM-*0.5*ZY composite ceramics with different two stage sintering conditions (a) TS-*1* (b) TS-*2* (c) TS-*3* (d) TS-*4*
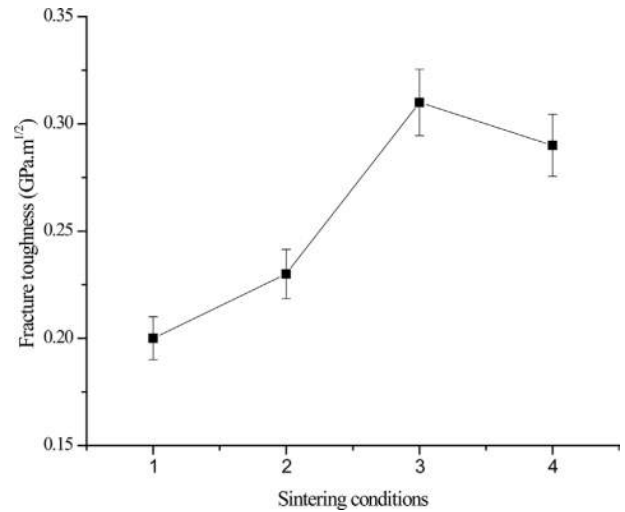
different two stage sintering condition showed average grain sizes for AM in the range 0.863-1.156 μm, while the average grain sizes of ZY was 0.622-0.902 μm. After display a comparison of the grain sizes in Al$_2$O$_3$-ZrO$_2$ (Y$_2$O$_3$) composite ceramics after conventional sintering [26], Al$_2$O$_3$-ZrO$_2$ (Y$_2$O$_3$) composite ceramics without MgO addition after two stage sintering [20] and *0.5*AM-*0.5*ZY composite ceramics with different two stage sintering condition, it was found that the sizes of grains in *0.5*AM-*0.5*ZY composite ceramics with different two stage sintering condition was smaller than in ceramics from the other two cases. The main reason for the

Table 3. Chemical compositions of *0.5*AM-*0.5*ZY composite ceramics with different two stage sintering conditions.

Two stage sintering condition	Compositions (at%)				
	Al(K)	Zr(K)	Mg(K)	Y (K)	O(K)
1	31.33	28.20	1.07	0.66	30.64
2	29.02	30.98	0.98	0.72	31.41
3	29.80	31.12	0.96	1.01	34.38
4	30.84	30.95	0.78	1.23	33.57

Fig. 4. Indentation of microhardness of *0.5*AM-*0.5*ZY composite ceramics with two stage sintering of TS-*3* condition (a) Vickers (b) Knoop.

Fig. 5. The relationship between fracture and different two stage sintering conditions *0.5*AM-*0.5*ZY composite ceramics.

application of two stage sintering is inhibition of grain growth in the final stage sintering by the application of the second, low temperature, heating step. Moreover, MgO addition in alumina is also an important factor in controlling grain size as reported in the other works [7, 14]. The EDX analysis and chemical compositions for *0.5*AM-*0.5*ZY composite ceramics with different two stage sintering conditions are shown in Table 3. The mechanical properties of *0.5*AM-*0.5*ZY composite ceramics with two sintering different conditions were investigated by measuring microhardness by Knoop and Vickers techniques and then calculating the fracture toughness values. The selected samples with two sintering conditions of TS-*3* are shown as indentation of Vickers and Knoop hardness micrographs in Fig. 4(a-b). Figure 5 shows the relationship between fracture toughness

values and the two different sintering conditions. It was found that the fracture toughness values increased with lower T_2 temperature during holding times. The sample of *0.5*AM-*0.5*ZY composite ceramics with two sintering conditions of TS-*3* had a high fraction of t-ZrO_2, c-ZrO_2 phases. These results confirm that increases in hardness were due to the small grain size and lower value of the crystalline size, corresponding to densities and phase analysis. The fracture toughness values of all compositions was higher than that of the Al_2O_3-ZrO_2 with only doped Y_2O_3. The highest value for fracture toughness was demonstrated by *0.5*AM-*0.5*ZY composite ceramics with two sintering conditions of TS-*3*, which corresponds to the highest percentage fraction in the tetragonal phase and cubic phase by XRD. It had high densification and optimal microstructure revealed by SEM.

Conclusions

The *0.5*AM-*0.5*ZY composite ceramics with four different two sintering conditions were successfully prepared. The influence of heat treatment was investigated by characterization of densification, phase analysis and mechanical properties. The key parameters that controlled the phase formation, microstructure, mechanical properties was various four sintering

conditions. It was found that the lower T_2 temperatures (holding times) resulted in optimal characterization of samples. The *0.5*AM-*0.5*ZY composite ceramics with two sintering conditions of TS-*3*:T_1 temperature at 1600 °C for 60 min and T_2 temperature at 1450 °C for 10 h had optimal densification, the highest microhardness and fracture toughness. These samples had a high percentage fraction of *t*-ZrO, *c*-ZrO$_2$ phase composition, and they showed a fine grain size and small crystallize size of the AM phase and ZY phases.

Acknowledgements

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