Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Study on mechanical properties of hot pressing sintered mullite-ZrO_2 composites with finite element method

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ARTICLE INFO

Keywords:
Mullite
ZrO_2
Hot pressing
Mechanical properties
Finite element analysis
Grains and interfaces

ABSTRACT

In this study, mullite–zirconia (ZrO_2) composites were fabricated by hot pressing sintering method. The effects of sintering temperature and holding time on the microstructures, phase compositions and mechanical properties of the composites were investigated. The results indicated that the size of t-ZrO_2 grain varies with sintering temperature and holding time, and the maximum flexural strength of 674.05 MPa and fracture toughness of 12.08 MPa $m^{1/2}$ are obtained when the sintering temperature is 1500 °C with holding times of 20 and 60 min, respectively. Finite element method was employed to analyze the relationship between grain size and mechanical properties of mullite–ZrO_2 composites for the first time. The results showed that the maximum stress on mullite–ZrO_2 interface increases with the growth of t-ZrO_2 grain size, which enhances the generation and propagation of cracks on grain boundaries significantly and degrades the flexural strength and fracture toughness of the mullite–ZrO_2 composite ceramics.

1. Introduction

Mullite ($3Al_2O_3{\cdot}2SiO_2$) ceramics are widely used as traditional refractory materials and high-temperature engineering ceramic parts because of their excellent properties such as high melting point, outstanding high-temperature strength, high creep resistance and chemical stability, low thermal expansion coefficient [1,2]. However, mullite has a low fracture toughness (~ 2 MPa $m^{1/2}$) at room temperature and is susceptible to flaw [3]. In addition, mullite is difficult to be sintered compactly [4]. These shortcomings limit its applications in advanced structural ceramics. To improve the fracture toughness of mullite, some toughening agents such as ZrO_2 [5], SiC [6] and Al_2O_3 [7] were introduced into mullite ceramics. Among these agents, ZrO_2 has attracted particular attentions because of its efficient toughening function through the generation of surface compressive and stress-induced transformation toughening [8], ferroelastic domain reorientation [9], and microcrack toughening mechanism [10].

Mullite–ZrO_2 composites have been fabricated by methods of sol–gel [11], co-precipitation [12], plasma-spark [13], laser solidification method [14], hot-pressing sintering [15], microwave sintering [16] and reaction sintering [17]. Among these methods, hot-pressing sintering has been widely employed for fabricating dense mullite compacts at a relatively low temperature [18] with promoted growth of mullite equiaxial grains [19]. In addition, CaO [20], MgO [21] and TiO_2 [22] were usually added to reduce sintering temperature, improve sintering speed and densification of mullite–ZrO_2 ceramics. Columnar mullite was frequently formed in liquid phase sintering process when CaO or MgO was added, which was prone to enlarge inherent flaw size because the geometries of columnar mullite cannot be matched readily [20,21]. However, the addition of TiO_2 did not encounter the problems discussed above because TiO_2 exhibited a solid solution reaction with ZrO_2, Al_2O_3 and mullite [23,24], which could reduce the formation of glassy phase, promote the growth of mullite equiaxial grains and even stabilize t-ZrO_2 phase [25,26] in mullite–ZrO_2 ceramics.

In this study, SiO_2, Al_2O_3 and ZrO_2 were employed as the main raw materials to fabricate mullite–ZrO_2 composite ceramics by hot-pressing method. TiO_2 was introduced as a sintering additive. The effects of sintering temperature and holding time on the microstructures and mechanical properties of the mullite–ZrO_2 ceramics were studied. Moreover, finite element model was established to analyze the relationship between grain size and the maximum stress on mullite–ZrO_2 interface for the first time.

2. Experimental

2.1. Material preparation

SiO_2 (500 nm, 99.9% purity), Al_2O_3 (200 nm, 99.99% purity), ZrO_2

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https://doi.org/10.1016/j.ceramint.2018.01.146
Received 3 January 2018; Received in revised form 14 January 2018; Accepted 17 January 2018

(400 nm, 99.9% purity) and TiO_2 (50 nm, 99.9% purity) powders were selected as the raw materials. The mixture powders of 8.71% SiO_2, 30.89% Al_2O_3, 59.41% ZrO_2 and 0.99% TiO_2 were ball-milled for 24 h at 300 r min^{-1} with a mass ratio of ball: powder: ethanol = 3: 1: 0.8. The milled powders were then dried via a vacuum dry evaporator at 60 °C and screened through a 100-mesh steel sieve, which were placed into graphite dies with a diameter of 42 mm. The dies loaded with mixture powders were hot-pressing sintered at 1450–1600 °C in a furnace (HIGH, MULTI 10,000, Fujidempa Co. Ltd., Japan) for 1 h under 30 MPa pressure with a heating rate of 10 °C min^{-1}. Later, sintered compacts were cut and polished into bars with height × width × length = 3 mm × 4 mm × 40 mm (International Organization for Standardization, ISO 14704: 2000) and 2 mm × 4 mm × 30 mm (American Society for Testing and Materials, ASTM E399) for flexural strength test and fracture toughness test, respectively. The powders were also sintered for different holding times (1, 20, 60 and 120 min) to investigate the effects of holding time after the optimal sintering temperature was determined.

2.2. Characterization

The hardness of ceramic samples was measured using a Rockwell hardness tester (HRS-150, HuaYin, China). The relative density of ceramics was calculated according to Archimedes' principle. A universal testing machine (AGS-10KNG, Shimadzu, Japan) was applied to measure the flexural strength and fracture toughness of ceramic specimens via three-point bending method and single-edge notched beam method, respectively. Spans of 30 mm and 16 mm and speeds of 0.5 mm min^{-1} and 0.05 mm min^{-1} were applied for flexural strength test and fracture toughness test, respectively. Formula (1) and (2) were used to calculate the flexural strength [27] and fracture toughness [28], respectively:

$$\sigma = \frac{3FL}{2BH^2} \tag{1}$$

$$K_{IC} = \frac{3FLa^{1/2}}{2BH^2} \times \left[1.99 - \frac{a}{H}(1 - \frac{a}{H})(2.15 - 3.93\frac{a}{H} + 2.7\frac{a^2}{H^2})\right] / \left[(1 + 2\frac{a}{H})(1 - \frac{a}{H})^{3/2}\right] \tag{2}$$

where σ is flexural strength, K_{IC} is fracture toughness, F is breaking load, L is the span length, a is notch depth, B is sample width and H is sample height. The composition of ceramics was determined using X-ray diffraction (XRD, D8 Advance, Bruker, Germany). The microstructures of the fracture surface of samples were characterized by scanning electron microscopy (SEM, SU8010, Hitachi, Japan). Ansys software was used for simulative calculation of the ceramic samples based on finite element model.

3. Results and discussion

3.1. Influence of sintering temperature

The XRD patterns of fabricated ceramics are shown in Fig. 1. It can be seen that the major phases in ceramics are mullite (PDF#15-0776) and t-ZrO_2 (PDF#50-1089). A small amount of m-ZrO_2 (PDF#37-1484) phase is presented in all samples, but Al_2O_3 (PDF#10-0173) and $ZrSiO_4$ (PDF#06-0266) phases exist only in the sample sintered at 1450 °C, which disappear when the annealing temperature further rises. Thus, 1500 °C is determined to be the energy-efficient sintering temperature for fabricating mullite–ZrO_2 composites with relatively less impurities in our study.

Fig. 2 shows the SEM images of fracture surfaces of ceramic samples sintered at 1450–1600 °C. At 1450 °C, pores (indicated by yellow dashed circle) are observed in the sample (Fig. 2a), and the pore number reduces with the rise of sintering temperature (Fig. 2b–d). As shown in

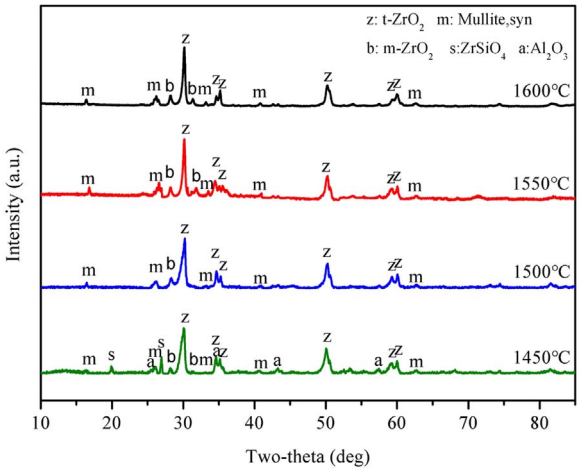

Fig. 1. XRD patterns of the ceramic samples sintered at different temperatures for 60 min.

the inset of Fig. 2a, pores are normally distributed within dark-grey areas. The dark-grey areas result from mullite phase while the white-grey areas result from t-ZrO_2 phase since the atomic numbers of Si and Al component elements in mullite phase are less than that of Zr element in t-ZrO_2 phase. The grain size (denoted by yellow double-sided arrows) increases as the sintering temperature rises from 1500 °C to 1600 °C (Fig. 2b–d). Some cavities (denoted by yellow one-way arrows) exist in the samples sintered at 1500 °C and 1550 °C, hinting a pull-out fracture mechanism. When the ceramic is sintered at 1600 °C, many cracks (indicated by hollow one-way arrows) remain in dark-grey areas and on interfaces between dark-grey and white areas (Fig. 2d). The generation and propagation of these cracks should be caused by the abnormal growth of grains, which will result in the poor mechanical performances of ceramics. The existence of cavities (generated by the pull-out of grains) and cracks on heterophase boundaries reveals that the bonding forces of atoms on grain boundaries is weaker than those of atoms within grains.

Fig. 3 shows the variations of flexural strength, fracture toughness, Rockwell hardness and relative bulk density with sintering temperature. The flexural strength and fracture toughness initially increase when temperature rises from 1450 °C to 1500 °C and then decrease as temperature further rises (Fig. 3a). The largest flexural strength of 596.32 MPa and fracture toughness of 12.08 MPa $m^{1/2}$ are achieved at the sintering temperature of 1500 °C. Fig. 3b illustrates that the Rockwell hardness and relative bulk density of ceramic samples sintered at 1450–1600 °C are higher than 85.9 HRA and 97.5%, respectively. Both the Rockwell hardness and relative bulk density initially increase and then decrease with temperature increasing, and the highest Rockwell hardness of 91.13 HRA and relative bulk density of 98.64% are obtained at 1550 °C. The sample sintered at 1450 °C has poor mechanical properties and low density, which should be ascribed to the presence of pores and impurity phases in the sample. While the degradation of mechanical performance and density at 1600 °C can be attributed to abnormal growth of grains, as is discussed in Fig. 2.

3.2. Influence of holding time

Fig. 4 shows the XRD patterns of ceramic samples sintered for different holding times. Mullite and t-ZrO_2 are dominant phases in all samples, but Al_2O_3 and $ZrSiO_4$ phases exist when holding time is too short (e.g. 1 min) and disappear when holding time expands to 20 min and more. The influence of holding time on the microstructures of the ceramic samples is depicted in Fig. 5. It can be found that there are many pores (indicated by yellow dashed circle) in the sample sintered for 1 min (Fig. 5a). But pore number reduces significantly when holding time increases to 20 min (Fig. 5b) and 60 min (Fig. 5c), and pore even