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Microstructure and mechanical behaviour of SrO doped Al_2O_3 ceramics

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ABSTRACT

Microstructure and mechanical behaviour of the SrO doped Al_2O_3 ceramics have been studied with a dopant concentration levels of, 0 ppm (AS0), 1000 ppm (AS1), 3000 ppm (AS3), and 5000 ppm (AS5), respectively. High density (~99.1%) and finer grain size (~3.4 μm) have been obtained for the Al_2O_3 ceramics at an optimum dopant concentration of 5000 ppm SrO (AS5) attributed to the important effects of in-situ formed strontium hexaluminates ($SrAl_{12}O_{19}$). Controlled grain growth behaviour in SrO doped Al_2O_3 (AS5) may be ascribed to the zener pinning stresses and solute drag effect actuated by the grain boundary phase $SrAl_{12}O_{19}$ with platelet morphology. Improved densification behaviour in SrO doped Al_2O_3 (AS5), presumably because of the lower interfacial energy of newly formed $Al_2O_3/SrAl_{12}O_{19}$ interfaces and key benefits of secondary phase ($SrAl_{12}O_{19}$) inhibited grain growth mechanism. The activation energy for densification in SrO doped Al_2O_3 (AS5) is found to be 550 ± 30 kJ/mol, which is higher compared to undoped Al_2O_3 and the estimated activation energies have been phenomenonlogically correlated to the lower energy of $Al_2O_3/SrAl_{12}O_{19}$ interfaces. Improved mechanical properties in terms of fracture toughness (~3.7 MPa. $m^{1/2}$), strength (~890 MPa) and hardness (~13.8 GPa) in optimum SrO doped Al_2O_3 (AS5) ceramics are triggered by a combination of toughening mechanisms primarily including $SrAl_{12}O_{19}$ platelet grain bridging, crack deflection, grain pullout, and crack tip healing.

1. Introduction

Engineering properties of the polycrystalline Al_2O_3 ceramics strongly dependent on the microstructural control in terms of density, grain size, and homogeneity [1]. For many years the effect of various chemical additives and dopants on microstructural evaluation of the Al_2O_3 ceramics have been studied extensively since they act as a secondary phase and refine the microstructural characteristics [2]. These dopants generally fall into two categories in accordance to their morphology. They are dispersed particulates (e.g. ZrO_2, SiC) and platelet morphologies (e.g. hexaluminates) derived from the reaction between such a dopant (e.g. SrO, CaO, LaO) and the matrix phase (Al_2O_3) [3]. It is a well-established fact that doping Al_2O_3 with ZrO_2 has surprising and salient effects on macroscopic properties and microstructure evaluation. Numerous studies demonstrated that ZrO_2 addition should be a minimum of 5 vol% to obtain improved toughness combined with the desired microstructural features [4]. In a recent article, 5 wt% ZrO_2 doped Al_2O_3 ceramics were sintered at 1550 °C and densified to 98% of the theoretical density with a grain size of 0.8 μm and fracture toughness of 4.8 MPa. $m^{1/2}$ [5]. Tuan and co-workers determined that the addition of 1 vol% ZrO_2 into Al_2O_3, densified the ceramics nearly to theoretical density with a grain size of 3.8 μm but reduced the fracture toughness to 4.2 MPa. $m^{1/2}$, has been noticed at slightly higher sintering temperatures [6]. Indeed, the fracture toughness yielded at 1 vol % of ZrO_2 doping was found to be 80% of the toughness obtained at 5 vol% ZrO_2 doped Al_2O_3 and the current works substantially correlated the evolved microstructures with the attained mechanical properties. The results of these studies clearly elucidated that the amount of dopant plays a decisive role in determining microstructural development and mechanical properties. However, such kinds of investigations are rather limited in platelet structure reinforced alumina based ceramics.

Recently, there has been a great deal of effort to develop in-situ platelet structures like hexaluminates incorporated Al_2O_3 based ceramics by the addition of dopant CaO, pertaining to their high degree of mechanical responses [7]. The dopant SrO (5 – 20 vol%) is of particular interest due to the formation of strontium hexaluminates with a nominal composition of $SrO.6Al_2O_3$ which have a characteristic feature of strong anisotropic growth results in a grain morphology of platelet structure, improved the mechanical properties including strength and toughness without compromising the hardness [8]. Cutler et al. suggested that 2 wt% SrO doped Ce-TZP/Al_2O_3 ceramics lead to a fracture toughness of 14 MPa. $m^{1/2}$ [9]. Similar experimental investigations on Ce-TZP/Al_2O_3 ceramics have reported that doping with 0.5 wt% (5000 ppm) of SrO stimulated a dramatic improvement in mechanical

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properties including fracture toughness of 12.5 MPa. $m^{1/2}$, strength of 570 MPa, and hardness of 11 GPa, respectively [10]. However, attainment of high fracture toughness, strength and hardness becomes a smart choice for structural application [11]. A recent study by Vishista and Gnanam proposed that the addition of 5 wt% SrO to Al_2O_3 inhibited the densification but resulted in a fracture toughness and hardness of nearly ~4 MPa. $m^{1/2}$ and ~15 GPa, respectively [12]. It is worthy to mention that no previous study has investigated the role of SrO concentration below 5000 ppm (i.e. < 0.5 wt%) on microstructural development in Al_2O_3 in terms of densification and grain growth phenomenon, and consequent effects on the mechanical properties.

In the current study the influence of SrO doping on the microstructure evaluation and mechanical behaviour of Al_2O_3 ceramics have been investigated in detail at a dopant concentration level of 5000 ppm. Three dopant concentrations viz., 1000 ppm, 3000 ppm, and 5000 ppm SrO have been selected and referred as AS1, AS3, and AS5, respectively, followed by undoped Al_2O_3 referred as AS0. Additionally, activation energy determination for densification in SrO doped Al_2O_3 system combined with a hypothesis illustrating the phase formation mechanism of $SrAl_{12}O_{19}$ have been presented.

2. Experimental procedure

Commercially available high purity alumina powder (AKP-5N, 99.99%, Sumitomo, Japan) with a particle size of about 120 nm was used as the starting material. High density poly ethylene (HDPE) and high purity alumina laboratory ware was preferred to avoid SiO_2 impurities. The lab ware was cleaned with aquaregia (3:1 HCl: HNO_3) and solvent (distilled water) prior to use. A stock solution of high purity strontium nitrate was prepared in aqueous media. Calculated amounts of aliquot were added to the alumina slurry prepared by dispersing the high purity alumina in distilled water to make 1000 ppm (AS1), 3000 ppm (AS3), and 5000 ppm (AS5) SrO doping. This mixture was ball milled in an acid-washed Nalgene bottle and dried under a heat lamp. The dried powder was calcined at 600 °C for 2 h to remove residual organics. This approach is expected to have yielded a uniform coating of SrO on alumina particles. The calcined powders were sieved, loaded into a steel die and pressed uniaxially at 200 MPa into cylindrical discs of 25 mm in diameter and 5 mm in thickness. The green samples were sintered at 1600 °C for 1 h in air in a box furnace with $MoSi_2$ heating elements. The sintered compacts were cleaned by ultrasonication in acetone followed by deionized water. Density of the sintered specimens was measured using Archimedes' principle. The relative density was calculated as the ratio of sintered density to its theoretical value. Theoretical densities of the α-Al_2O_3 and $SrAl_{12}O_{19}$ are 3.98 g/cm^3 and 3.95 g/cm^3, respectively.

Phase identification measurements were performed on a Bruker X-ray powder diffractometer with Co-Kα radiation (λ = 1.79°A) in the range of 20–80° at a scan speed of 2°/min and a step size of 0.02°. The sintered surfaces were polished using diamond media and thermally etched at 1400 °C for 1 h. Microstructural characterizations of the etched surfaces were studied using a field emission scanning electron microscope (Nova NanoSEM FEI 450, Netherlands) equipped with EDS attachment. Grain size measurements were obtained by a linear intercept method. At least 500 grains were counted for each sample and a stereographical correction factor of 1.56 was used to determine the average grain size [13]. Dilatometry measurements for activation energy calculation were performed on Netzsch dilatometer (DIC 402 C, Germany) at different heating rates of 5 °C/min, 7.5 °C/min, 10 °C/min, and 15 °C/min. Compressive strength of the sintered cylindrical samples (L/D ≥ 1.5) with a size of 10 mm in diameter (D) and 19 mm in thickness (L) was tested by a universal testing machine (HK 10-S, Tinius Olsen, UK) under a loading rate of 1 kN/min. Vikers hardness was measured on a Leco Hardness tester under load 49 N and 10 s dwell. Fracture toughness was determined by the indentation method. The hardness (H_V) and fracture toughness (K_{IC}) were calculated using Eqs. (1) and (2), respectively [14,15]:

$$H_V = 0.18544 \times \frac{P}{d^2} \times 10^{-2} \quad (1)$$

$$K_{IC} = 0.016 \times \left(\frac{E}{H_V}\right)^{1/2} \times P \times \left(\frac{d_c}{2}\right)^{-3/2} \times 10^3 \quad (2)$$

Where, P, d, E, d_c, are the indentation load (N), average diagonal length (mm), elastic modulus (GPa), and average crack length (mm), respectively. Elastic modulus was calculated from the rule of mixtures to determine the toughness. The average values of the sintering and mechanical characteristics were calculated using a minimum number of five specimens for every experimental composition. At least six measurements for each specimen were considered to determine the mean values of hardness and toughness.

3. Results and discussion

3.1. Phase analysis and formation mechanism of the strontium hexaluminate ($SrAl_{12}O_{19}$)

X-ray patterns of the undoped Al_2O_3 (AS0) and SrO doped Al_2O_3 (AS1, AS3, AS5) sintered at 1600 °C for 1 h. are shown in Fig. 1, demonstrating that strontium hexaluminate ($SrAl_{12}O_{19}$) is the only crystalline phase in alumina matrix appeared at dopant levels of 3000 ppm (AS3) and 5000 ppm (AS5) SrO. Strontium hexaluminate is a grain boundary complexion or grain boundary phase as like similar hexaluminates, can have a nominal composition of SrO.6 Al_2O_3 (commonly referred as $SrAl_{12}O_{19}$) formed by the reaction between one mole of SrO and six moles of Al_2O_3. The increase in intensity of the hexaluminate peak with increasing SrO concentration from 3000 ppm (AS3) to 5000 ppm (AS5) corroborates this observation. The relative phase amount of hexaluminate in AS5 systems is found to be 2.6 vol%, calculated using a method reported by Evans et al. [16]. Despite strontium hexaluminate, no other crystalline phases in SrO–Al_2O_3 system are detected in the XRD patterns of sintered specimens and this phenomenon can be explained by two effects. Firstly, lower dopant concentrations facilitate the solely formation of strontium hexaluminates since it is the alumina rich compound in SrO-Al_2O_3 system. Secondly, improved homogentiy of dopant in the alumina matrix attributed to molecular precursor approach, reduced the non-stoichiometry effects and actuated the formation of strontium hexaluminates [17].

Molecular homogentiy and the inter diffusion kinetics of SrO and

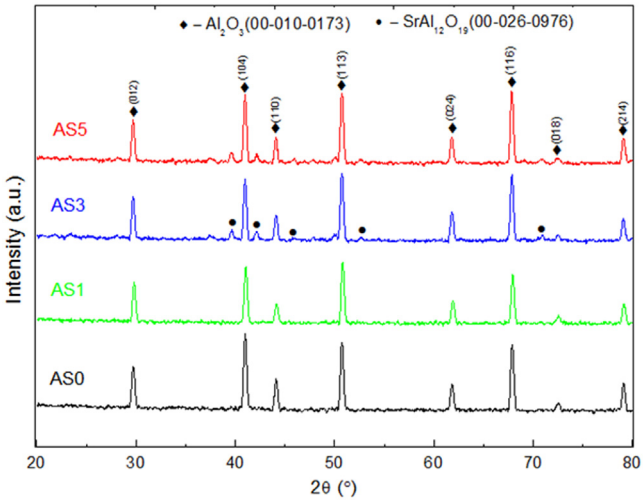

Fig. 1. X-ray patterns of the undoped (AS0) and SrO doped Al_2O_3. Formation of strontium hexaluminate ($SrAl_{12}O_{19}$) in 3000 ppm (AS3) and 5000 ppm (AS5) SrO doped specimens can be observed.