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Viewpoint Paper

Effect of Gd_2O_3 on the thermal conductivity of ZrO_2–4 mol.% Y_2O_3 ceramics fabricated by spark plasma sintering

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Abstract—Porous and dense ZrO_2–4 mol.% Y_2O_3 ceramics were fabricated by spark plasma sintering at 1100 and 1500 °C. The porosity of the ceramics sintered at 1100 °C increased with the addition of $\sim$0–5 mol.% Gd_2O_3. In contrast, the ceramics sintered at 1500 °C showed full density regardless of the amount of Gd_2O_3 addition. The fluorite-type $Gd_2Zr_2O_7$ phase was formed as the second phase in the tetragonal ZrO_2 matrix. The thermal diffusivity and thermal conductivity of sintered ZrO_2–4 mol.% Y_2O_3 decreased with increasing Gd_2O_3 addition.

Keywords: ZrO_2–4 mol.%Y_2O_3; Gd_2O_3; $Gd_2Zr_2O_7$; Thermal conductivity; Fluorite structure

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1. Introduction

The thermal efficiency of gas turbine engines at the highest operating temperatures is significantly improved by employing ceramic-based thermal barrier coatings (TBCs), which are deposited on bond-coat coated superalloy turbine airfoils by means of electron beam physical vapor deposition (EB-PVD) [1–3] or by air plasma-sprayed coating [4,5]. The use of TBCs in aircraft engines is receiving much attention because of the resulting engine efficiency and prolonged operational life. The state-of-the-art material for these TBCs, partially stabilized zirconia of ZrO_2–4 mol.% Y_2O_3 (YSZ), exhibits outstanding properties, such as low thermal conductivity, low Young's modulus and a relatively high thermal expansion coefficient [6–8]. However, YSZ has limited temperature capability due to accelerated sintering and phase transformation during prolonged use at the operating temperatures of gas turbine engines. In order to meet the demands of this environment, much effort has been given to the development of new coating materials for advanced TBC applications [9,10].

In particular, studies on ZrO_2 coatings with doping of rare earth oxides, such as Gd_2O_3, La_2O_3, Sm_2O_3 and Nd_2O_3, have recently reported low thermal conductivity and improved phase stability at high temperatures >1200 °C [11–15]. Addition of these oxides to ZrO_2 resulted in the formation of zirconates (e.g. $La_2Zr_2O_7$, $Gd_2Zr_2O_7$, $Sm_2Zr_2O_7$ and $Nd_2Zr_2O_7$) with a pyrochlore or fluorite structure. Among interesting TBC candidates, $Gd_2Zr_2O_7$ has some favorable properties, including lower thermal conductivity ($1.6\ W\ m^{-1}\ K^{-1}$), a relatively high thermal expansion coefficient ($11.6 \times 10^{-6}\ K^{-1}$), elastic modulus (205 GPa), and phase stability up to its melting point (2300 °C), suggesting that it might be a superior TBC material [16–18]. Many reports on $Gd_2Zr_2O_7$ have focused on the microstructure, corrosion resistance and thermal properties of TBCs of $Gd_2Zr_2O_7$ zirconate [16,17,19].

However, the influence of a porous and dense microstructure and Gd_2O_3 addition on the thermal conductivity of sintered ZrO_2 ceramics, which are used for coating ingots of EB-PVD for TBC application, has not been

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investigated. For this reason, in this work, we focussed on the fabrication of porous and dense ZrO_2 at different sintering temperatures. This work describes the influence of Gd_2O_3 addition on the thermal conductivity of ZrO_2–4 mol.% Y_2O_3 ceramics fabricated by spark plasma sintering (SPS).

2. Experimental procedure

Commercial starting powders of ZrO_2–4 mol.% Y_2O_3 (TZ4Y, Tosoh Co.) and Gd_2O_3 (Rare Metallic Co.) were used for fabricating the present samples. The mean particle sizes of the starting powders are shown in Table 1. The additions of Gd_2O_3 in the ZrO_2 matrix are 0, 1, 3 and 5 mol.%. Mixed powders were prepared by ball milling using high-purity ZrO_2 balls, 5 mm in diameter, in polyethylene pots with an isopropyl alcohol solution for 24 h. After mixing, the slurries were dried at 50 °C. The dried mixed powders were then sieved using 300 mesh sieves to obtaining homogeneous granulation.

The mixed powders were then put into a 30 mm diameter graphite mold. A thin graphite sheet 0.2 mm thick was pre-set into the inner wall of the graphite mold for lubricating and filling the gap between the punches and die, and the mold assembly was wrapped using a thick sheet of carbon fiber to maintain homogeneous heating during sintering. The assembly of the graphite mold and mixed powders was set into the SPS apparatus (Syntex, Inc., Japan). Sintering temperatures of 1100 and 1500 °C under a vacuum of 10^{-2} Pa were used. Sintering was conducted for 20 min at each sintering temperature under a pressure of 30 MPa. After sintering, the sintered samples were cooled to room temperature.

Any contamination on the surface of samples was removed using a diamond grinding wheel. All the samples were ground and polished down to 1.0 μm diamond grit to obtain a fine surface. Sintered samples were cut into square shapes of 10 mm × 10 mm and 2 mm thickness. The relative density and porosity of the samples were determined by water immersion using the Archimedes method.

Phase analysis of the sintered samples was performed using X-ray diffraction (XRD; JDX-3500, JEOL Co., Japan) with Cu K_α radiation. The microstructure was observed by scanning electron microscopy (SEM; JSM-7001F, JEOL Co., Japan) and transmission electron microscopy (TEM; Tecnai G2 F30, FEI, USA). Prior to SEM, the samples were sputter-coated with platinum to avoid charging effects under the electron beam. To make cross-sectional foils for TEM analysis, 300 μm slices of the materials were cut into small pieces, polished with a tripod polisher down to 20 μm thickness, and then ion-milled with Ar ion at an acceleration of 5 kV. Thin foils were examined in a transmission electron microscope equipped with an energy dispersive spectroscopy (EDS) analyzer.

The thermal diffusivity of the sintered samples was measured by the laser flash method [20] using a thermal analyzer (LFA 457 Micro Flash, Netzsch, Germany). For the measurement, both the front and back sides of the samples were coated with a thin graphite layer to allow the sample to absorb the incident laser beam and emit black-body radiation to the IR detector.

The laser flash method relies on the generation of a thermal pulse on one face of a thin sample and the recording of the temperature history on the opposite face. The thermal diffusivity can be determined from the time required to reach one-half of the peak temperature in the resulting temperature rise curve on the rear surface [21].

The specific heat capacity was characterized from the laser flash analysis by comparing the relative temperature rise of the sample with that of the reference sample of alumina. The thermal conductivity (k) can be calculated by the following equation:

$$k = \alpha \cdot C \cdot \rho, \tag{1}$$

where α is the thermal diffusivity, C is the specific heat and ρ is the density of the sample.

3. Results and discussion

3.1. Fabrication of Gd_2O_3-doped YSZ samples

Figure 1 shows the relative density of sintered YSZ ceramics as a function of Gd_2O_3 addition. The densities of all YSZ samples sintered at 1100 °C decreased with increasing Gd_2O_3 addition and showed between ~72–85% of theoretical density. On the other hand, YSZ samples sintered at 1500 °C were dense regardless of the amount of Gd_2O_3 addition during solid reaction sintering.

Figure 2 shows the typical microstructure of the fracture surface for sintered YSZ samples. The grain size of YSZ samples sintered at 1100 °C revealed a fine microstructure between ~50 and ~900 nm grain size with little grain growth, and pore clustering increased with increasing Gd_2O_3 addition. In contrast, the microstructure of YSZ samples sintered at 1500 °C was dense without pore clustering, and the grain size increases from ~200 nm to ~5 μm with increasing Gd_2O_3 addition.

In particular, the microstructure in Figure 2f and h consists of larger grains. Figure 2f mainly shows intergranular fracture, whereas transgranular fracture is dominant for Figure 2h. The other samples show a mixed type of transgranular and intergranular fracture. The clear difference in the microstructures of the present samples due to the sintering temperature as well as Gd_2O_3 addition can affect the thermophysical properties, as explained in the next section.

The XRD results for the Gd_2O_3-doped YSZ ceramics are shown in Figure 3. This indicates that the phase of YSZ for all samples is tetragonal. The near peak of the $Gd_2Zr_2O_7$ phase was overlapped with tetragonal ZrO_2 peaks. The relative peak of the $Gd_2Zr_2O_7$ phase becomes higher with increasing Gd_2O_3 addition. In general, $Gd_2Zr_2O_7$ can exist as a crystalline pyrochlore phase of an intermediate compound or a fluorite phase of a cubic structure [22,23] formed by a solid reaction between Gd_2O_3 and ZrO_2 in the ZrO_2–Gd_2O_3 binary system. The pyrochlore structure in $Gd_2Zr_2O_7$ is an ordered variation of the more common disordered-fluorite structure, where the cations (Gd, Zr) and the oxygen vacancies occupy special positions in pyrochlore, while they occupy random sites in fluorite [24]. It was reported