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Feature Article

Densification behaviour and microstructural development in undoped yttria prepared by flash-sintering

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Abstract

Conventional sintering of undoped Y_2O_3 requires temperatures above 1400 °C for a few hours. We show that it can be sintered nearly instantaneously to nearly full density at furnace temperature of 1133 °C under a DC applied field of 500 V/cm. At 1000 V/cm sintering occurs at 985 °C. The FLASH event, when sintering occurs abruptly, is preceded by gradually accelerated field-assisted sintering (FAST). This hybrid behaviour differs from earlier work on yttria-stabilized zirconia where all shrinkage occurred in the flash mode. The microstructure of flash-sintered specimens indicated that densification was accompanied by rapid grain growth. The single-phase nature of flash-sintered Y_2O_3 was confirmed by high-resolution transmission electron microscopy. The non-linear rise in conductivity accompanying the flash led to Joule heating. It is postulated that densification and grain growth were enhanced by accelerated solid-state diffusion, resulting from both Joule heating and the generation of defects under the applied field.

Keywords: Yttria; Flash-sintering; Electron microscopy; Diffusion

1. Introduction

Yttria (Y_2O_3) ceramics have special chemical and physical properties such as high resistance to halogen-plasma corrosion[1] and thermal stability.[2–4] At the same time they are difficult to sinter. Conventional sintering requires very high temperatures typically >1400 °C, and a vacuum or hydrogen atmosphere.[5–12]

New techniques that use electrical fields have shown that ceramics can be sintered quickly at low temperatures. Collectively these methods are called field-assisted sintering techniques (FAST).[13–16] For instance, direct current (DC) electrical fields of approximately 20 V/cm lower the sintering temperature of 3 mol% yttria-stabilized tetragonal zirconia polycrystal (3Y-TZP) from about 1400 °C to 1300 °C.[17,18] Spark plasma sintering, in which pulsed electric current and compressive stress are applied, has produced dense, translucent polycrystalline Y_2O_3 at 1050 °C and a heating rate of 2 °C/min.[19,20] More recently, it has been shown that nanocrystalline 3Y-TZP can be sintered at 850 °C within 5 s under an electric field of 120 V/cm.[21] This phenomenon is called FLASH-sintering. The nature of flash-sintering where densification occurs in just a few seconds under a threshold condition of temperature and applied field, is fundamentally different from FAST. In the latter case fields lead to a gradual enhancement in the sintering without any change in specimen conductivity. Flash-sintering, on the other hand, is accompanied by a non-linear increase in conductivity.[17,21] Flash-sintering has been demonstrated in several ceramics including cubic zirconia,[22,23] cobalt manganese oxide (Co_2MnO_4),[24] Mg-doped alumina (Al_2O_3),[25] strontium titanate ($SrTiO_3$)[26] and, most recently, silicon carbide (SiC).[27]

In the present study we demonstrate that DC fields greater than 300 V/cm can trigger the flash-sintering in undoped Y_2O_3. Dense polycrystals are obtained at 985 °C under a field of 1000 V/cm in less than 10 s.

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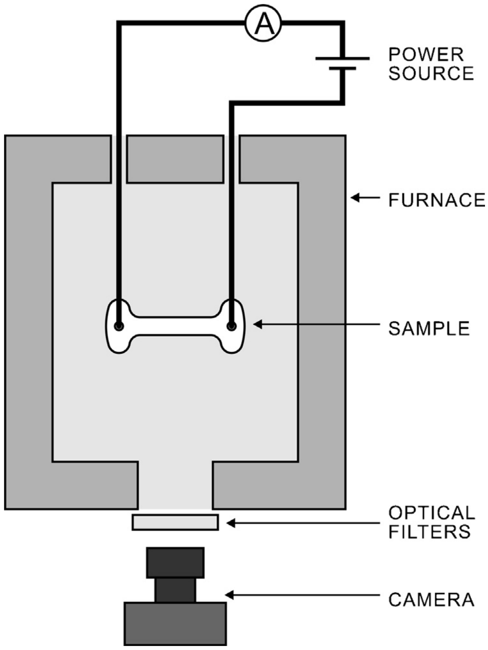

Fig. 1. Schematic of the present sintering experiments. Two platinum wire electrodes were used to apply the field as well as to suspend the sample in the furnace. A camera from underneath measures the shrinkage as a function of time.

2. Experimental procedure

2.1. Material

Commercially available, high-purity Y_2O_3 powder (BB-type; 99.9% purity, Shin-Etsu Rare Earth, Japan) with a manufacturer-specified average particle size of 20 nm and a BET multi-point specific surface area of 37.0 m^2/g was used. The maximum impurities determined by inductively coupled plasma atomic emission spectrometry are CaO < 10 ppm, Fe_2O_3 < 5 ppm, Dy_2O_3 < 30 ppm, Ho_2O_3 < 30 ppm, Er_2O_3 < 30 ppm, and Yb_2O_3 < 30 ppm. The powders were uniaxially pressed into dog bone-shaped specimens[25] having a relative density of 53.0%. The gage section had a length of 20 mm and a rectangular cross section of 3.5 mm × 1.0 mm.

2.2. Sintering experiments

A schematic of the sintering experiments apparatus is shown in Fig. 1. A dog bone-shaped specimen is suspended into the centre of a tubular furnace by two platinum wires attached to the handles of the dog bone specimen. The field is applied via the platinum electrodes. A CCD camera records the sample dimensions through a series of optical filters positioned at the bottom end of the tube.[22] The furnace temperature was measured in the vicinity of the specimen.

A constant voltage was applied to the specimen, while the furnace temperature rose at a heating rate of 10 °C/min. The applied field ranged from 75 V/cm to 1000 V/cm, and the current limit at the power supply was set to 60 mA. The voltage supply and furnace were turned off 3 min after the flash event. The linear shrinkage strain was determined by $\varepsilon = \ln(l/l_0)$, where l_0 is the initial gage length and l is the time-dependent gage length as the specimen sinters.

In order to examine the effect of the current limit on the microstructure, sintering experiments were carried out at the current limits of 5 mA, 15 mA and 30 mA under an applied field of 500 V/cm. Flash-sintering was observed at all current levels; in these experiments the power supply, and the furnace, were switched off 10 s after the onset of the flash.

In a separate experiment, Joule heating of the specimen was measured with a pyrometer. In this case a smaller horizontal furnace was used. The field and the current settings were 500 V/cm and 60 mA.

Note that in constant heating rate experiments, the time and furnace temperature are proportional to each other. The results are presented by plotting the linear shrinkage strain as a function of the furnace temperature.

2.3. Electrical conductivity of conventionally sintered Y_2O_3

In flash-sintering, the conductivity of the specimen changes in a non-linear way. In order to obtain a baseline behaviour, we measured the electrical conductivity of dense, conventionally sintered Y_2O_3 by the two-terminal alternating current (AC) impedance method.[28] The detailed fabrication procedure for conventional sintering of Y_2O_3 polycrystals has been described elsewhere.[29] Briefly, the Y_2O_3 powder was cold-isostatically pressed into a disc shape, and the green body was sintered at 1600 °C for 3 h in air. The relative density of the sintered body was 96%, and the average grain size was 1.8 μm.[29] The specimens for the impedance measurements were 9.3 mm in diameter (electrode area) and 1.4 mm in thickness. Platinum paste electrodes were applied on each electrode area by firing at 930 °C for 15 min. The impedance spectra were obtained in air at temperatures ranging from 750 to 1000 °C from 0.1 to 12 MHz at an applied voltage of 1 V using an impedance analyzer (Solartron SI 1260; Toyo Corporation, Japan). A resistance-heated furnace operating under zero-crossing power controls was employed. The Z' and Z'' values in the complex impedance spectrum (Cole–Cole plot) are normalized by multiplying by the thickness and dividing by the electrode area.

2.4. Microstructure characterization

The densities of the sintered bodies were measured by the Archimedes method. Theoretical density of Y_2O_3 is assumed to be 5.03 g/cm^3.[30] The microstructure of the sintered bodies was characterized by scanning electron microscopy (SEM, SU-8000; Hitachi, Japan) and high-resolution transmission electron microscopy (HRTEM, JEM-ARM200F; JEOL, Japan). TEM specimens were prepared using standard techniques involving mechanical grinding to a thickness of less than 0.1 mm, and ion beam milling to an electron transparency at about 4 kV.