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Superplasticity of zirconia–alumina–spinel nanoceramic composite by spark plasma sintering of plasma sprayed powders

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Abstract

Zirconia 3 mol% yttria–alumina–alumina magnesia spinel nanoceramic composite was synthesized by spark plasma sintering of plasma sprayed particles. For compacts sintered from high energy ball milled powders, superplasticity was observed at temperatures between 1300 and 1450 °C and at strain rates between 10^{-4} and 10^{-2} s^{-1}, while for those without high energy ball milling, deformation at the same temperature and strain rate range did not show superplastic behavior. Also, the apparent activation energy (945 kJ/mol) of the high energy ball milled batch was much higher than that of the same composite processed from nanopowder mixtures (621 kJ/mol). The flow stresses were also higher at the same temperatures and strain rates. The difference may be related to the unique low angle grain boundaries in the grains that nucleated and grew from the metastable phase inside the plasma sprayed agglomerate at elevated temperatures. Such boundaries were not intrinsically easy to slide.

Keywords: Nanoceramics; Superplasticity; Plasma spray; Spark plasma sintering (SPS); Low angle grain boundary; High energy ball milling (HEBM)

1. Introduction

Superplasticity was first widely studied in metals and alloys. The constitutive relationship for superplastic deformation usually takes the form of the Mukherjee–Bird–Dorn equation [1]:

$$\dot{\varepsilon} = A\frac{D_0 G b}{kT}\left(\frac{b}{d}\right)^p\left(\frac{\sigma}{G}\right)^n \mathrm{e}^{-Q/RT} \qquad (1)$$

in which G is the elastic shear modulus, b the Burger's vector, k the Boltzmann's constant, T the absolute temperature, d the grain size, p the grain-size dependence coefficient, n the stress exponent, Q the activation energy, D_0 the diffusion coefficient and R the gas constant. The inverse of n is termed the strain rate sensitivity m. Grain-boundary sliding is generally the predominant mode of deformation during the superplastic flow. Plastic deformation by grain-boundary sliding is generally characterized by $n = 2$ (or $m = 0.5$) and an apparent activation energy that is typically either equal to that for lattice diffusion or for grain-boundary diffusion.

From Eq. (1), it is clear that at a constant temperature and stress, high strain rate is more easily realized in specimens with smaller grains. With the development of ceramic processing, the particle sizes are now made increasingly smaller into the nanometer range and so is the probability of realizing increasingly finer grain sizes in dense compacts. Superplasticity in ceramics has also been studied since the first observation of fine-structure superplasticity in yttria-stabilized tetragonal zirconia (YTZP) by Wakai et al. [2]. A number of fine-grained polycrystalline ceramics have also demonstrated superplasticity, such as YTZP [3], magnesia-doped alumina [4], and alumina reinforced YTZP [5]. Unfortunately, the superplastic temperatures were typically above 1450 °C and the strain rates were relatively low (10^{-4} s^{-1} or lower). Recently, Kim et al. [6] realized a high strain rate of 0.1 s^{-1}

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in zirconia with 3 mol% yttria–alumina–alumina magnesia spinel (ZAM) triphase composite (volume ratio 4:3:3), but at a rather high temperature of 1650 °C.

More recently, superplasticity of the ZAM triphase ceramic composite at temperatures as low as 1300 °C was demonstrated in samples processed by spark plasma sintering (SPS) [7]. Because of rather low sintering temperature (1150 °C) and very short sintering time (3 min), the grain sizes of the three phases were between 50 and 100 nm. Superplastic behavior between 1300 and 1450 °C were observed with an apparent activation energy of 622 kJ/mol. Three binary systems of the triphase composite were also investigated to compare the sliding characteristic of three individual interfaces (zirconia–alumina, alumina–spinel and zirconia–spinel) [8]. It was concluded that in the triphase ceramic composite, zirconia–alumina and zirconia–spinel contributed more to the superplasticity (with the activation energies of 597 and 522 kJ/mol respectively). Although alumina–spinel was not superplastic, spinel played a roll in hindering the grain growth of the other two phases.

The above ceramic composites were processed by mechanically mixing nanoparticles and subsequent sintering. A new parallel process to make monolithic nanoceramic composites [9] is plasma spraying of spray dried aggregates of a mixture of different ceramic particles, followed by sintering of the plasma sprayed powders. The advantage of this method is that the nanophases in plasma sprayed powders are more uniformly distributed. This is due to high nucleation rates and limited grain growth of each phase from the liquid state in the unique plasma melting and fast quenching process [10]. Another advantage is that starting materials are not necessarily nanoparticles. A typical spray dried particle composed of an aggregate of micrometer sized primary particles consisting of all components in the composite. In most cases, the plasma sprayed particles have large strain energies and usually contain metastable and even amorphous phases [10], which have a considerable driving force to form an equilibrium state and thus can help in consolidation. Duan et al. studied the phase transformations in the consolidation by SPS of plasma sprayed metastable Al_2TiO_5 powder and of mixtures nano-Al_2O_3, TiO_2 powder with and without MgO additive [11]. This paper will discuss the consolidation of zirconia–alumina–spinel nanoceramic composite processed from plasma sprayed powders and high temperature deformation. Comparison will be made to the nanoceramic composite of the same composition processed from mechanically mixed commercially available nanoparticles.

2. Experimental procedures

2.1. Spray drying and plasma spraying

High purity starting powders for spray drying are TZ3Y (Tosoh, Japan), alumina (Baikowski Malokoff Inc., Malokoff, TX) and alumina magnesia spinel (Baikowski International Corp., Charlotte, NC). The average particle sizes are in either submicron meter or nanometer range. The powders were mixed in water (50 vol.% solid loading) and ball milled for 24 h. A Niro 2M spray drier (Niro Inc., Columbia, MD) was used to spray dry the slurry. The resulting agglomerate was sieved and only sizes between 35 and 75 μm was used as input of plasma spray. Plasma spraying was carried out using a Sulzer-Metco 9MP gun. The carrier gas was argon and the primary and secondary gases were respectively hydrogen and nitrogen. The current and voltage were 750 A and 65 V respectively. Plasma melted particles were quenched in a water bath. The process is discussed in detail elsewhere [10].

2.2. High energy ball milling (HEBM)

Two batches of plasma sprayed powders were made for subsequent sintering. One (PS-HEBM-SPS) was first high energy ball milled for 24 h in a SPEX 8000 mixer mill (SPEX CertiPrep, Metuchen, NJ) with a tungsten carbide (WC) ball in a WC vial. One weight percentage polyvinyl alcohol (PVA) was added as a dry milling agent to prevent severe agglomeration. A heat treatment in air at 350 °C for 3 h after HEBM removed the PVA from the powder mixture. After sieving to remove the particles over 100 μm, the powders were unidirectionally pressed at 35 MPa in a graphite die (∼20 mm in diameter) to form the green compacts. The other batch was directly consolidated without HEBM.

2.3. SPS

SPS is a new sintering method with moderate pressures and comparatively low temperatures [12]. Spark plasma is generated between the particles by electrical discharge at the onset of on–off DC pulsing. The on–off DC pulses may also result in spark impact pressure, Joule heating and electrical field diffusion. SPS can rapidly consolidate the green compact to nearly theoretical density. In SPS, rapid heating rate (normally a few hundreds °C/min), moderate pressure and short sintering time (min) makes it possible to consolidate fully dense ceramics while retarding grain growth.

In this study, a Dr. Sinter 1050 (Sumitomo Coal Mining Co., Japan) was used to sinter the green compacts to full density. The heating rate was 300 °C/min from room temperature to 600 °C and then in 2 min the samples were ramped to 1150 °C. After holding at 1150 °C for 3 min, the power was shut down and the samples were cooled in vacuum. A unidirectional pressure of 63 MPa was applied during sintering and an optical pyrometer focusing on the graphite die monitored the temperatures. The final densities of sintered compacts were measured by the Archimedes method with deionized water as the immersion liquid. The theoretical densities were calculated by the rule of mixtures.