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Spark plasma sintering of ZrB_2 powders synthesized by citrate gel method

Hasan Gocmez[a], Mustafa Tuncer[a,*], Iurii Bogomol[b]

[a] Department of Material Science and Engineering, Dumlupınar University, Kutahya, Turkey
[b] Department of High-temperature Materials and Powder Metallurgy, National Technical University of Ukraine, Igor Sikorsky Kyiv Polytechnic Institute, Kyiv, Ukraine

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ABSTRACT

The densification behavior of nanocrystalline zirconium diboride (ZrB_2) powders with nickel (5 vol%) is reported by spark plasma sintering (SPS) technique. SPS experiments were performed at 1600 and 1900 °C with 65 MPa pressure and 1 min holding time. A maximum relative density around 95% was obtained after SPS processing of ZrB_2 at 1900 °C while the density of ZrB_2 sample sintered at 1600 °C reached 88% of the theoretical density. Hardness and fracture toughness values are 11 GPa and 4.11 MPa m$^{1/2}$ for the sample sintered at 1600 °C and 13.7 GPa and 2.65 MPa m$^{1/2}$ for the sample sintered at 1900 °C, respectively.

1. Introduction

Zirconium diboride has high hardness with strength, good oxidation and chemical attack resistance, good electrical and thermal conductivity. These properties make ZrB_2 good candidate for application such as atmospheric re-entry, hypersonic flight, rocket propulsion, high-temperature electrodes and crucibles for molten metal contact [1–4].

On the other hand, one of the difficulties for ZrB_2 is to obtain full densified body because of having highly covalent bond characteristics and low diffusion coefficient. Therefore, the densification of ZrB_2 requires either high temperature sintering (2100–2300 °C) or external pressure assisted sintering methods or the addition of sintering aids when it is compared with other advanced ceramic powders [5–7]. Some of the methods are used to densify ZrB_2 include pressureless sintering (PS), flash sintering, lazer sintering, hot pressing (HP), spark plasma sintering (SPS) as well as the usage of sintering aids with any of these methods [8–20]. Each technique has its own advantages and disadvantages, which leads to form various microstructure and final properties of sintered materials. At this point, SPS with a high heating rate and short dwelling time at low sintering temperatures presents advantages compared to the conventional sintering methods. Recently, SPS has gained interest for sintering ultra-high temperature ceramics. SPS is direct or pulsed direct current assisted sintering technique which is performed under uniaxial pressure. In addition, using sintering additives combined with the advantage of SPS would help to improve densification and final properties of the ZrB_2-based materials. As a result, SPS processing promises materials with fine microstructure and better properties at reduced sintering temperatures in a short time.

In the present study, microstructure and mechanical properties (hardness and toughness) of gel synthesized nanocrystalline ZrB_2 ceramics with the addition of 5 vol% nickel were examined by using spark plasma sintering method [2,4–7].

2. Experimental

Nanocrystalline ZrB_2 powders were synthesized by gel method described in our previous publication [21]. Nickel powders (Alfa Asear, −325 mesh, 99.8%) were introduced as a sintering additive. ZrB_2–5 vol % Ni powders were wet ball-milled in ethanol for 24 h., and dried in an oven for 24 h at 80 °C. Densification of ZrB_2 powders were performed by computer controlled SPS instrument ERAN 2/1 at 1600 °C (labeled as Z16) and at 1900 °C (labeled as ZB19) with a heating rate of 450 °C min^{-1}. As prepared powders were placed in a graphite die with a diameter of 10 mm and a pulsed current was applied through die under the pressure of 65 MPa. The sample was held under these conditions for 1 min and then the pressure was quickly released and the power was turned off. Temperatures were measured by using a pyrometer inserted on the surface of the graphite die cylinder.

The microstructural characterizations of sintered ceramics were done by scanning electron microscopy (SEM, Jeol 6335F). After sintering, the densities of the samples were measured by Archimedes' method with water as a liquid medium. Relative density calculation based on the theoretical density of 6.1 and 8.9 g/cm^3 for ZrB_2 and metallic nickel, respectively. The hardness of the specimen was determined using a static microhardness tester (Future-tech). In preparation for hardness measurements, specimens were mounted in epoxy resin prior to grinding and polishing. In order to eliminate any surface

* Corresponding author.
E-mail address: mustafa.tuncer@dpu.edu.tr (M. Tuncer).

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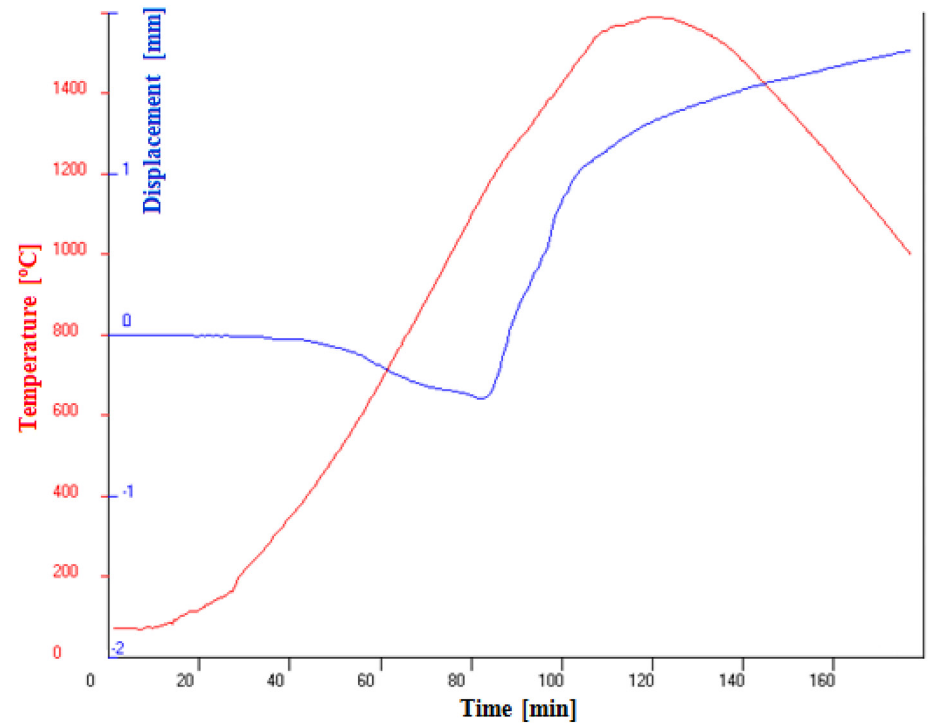

Fig. 1. Displacement of the total height of the graphite mold assembly during SPS process of ZB16 sample (red solid: temperature profile, blue solid: displacement). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

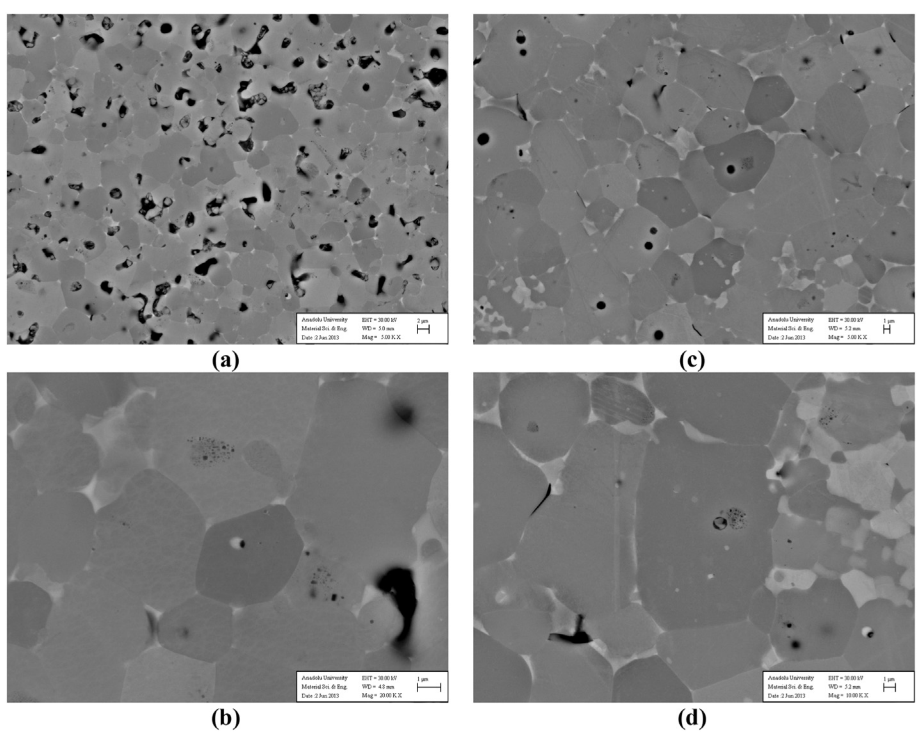

Fig. 2. SEM micrograph of the samples; (a) and (b) SPS at 1600 °C, (c) and (d) SPS at 1900 °C.

Table 1
The density and mechanical properties of spark plasma sintered samples.

Material	Relative density [%, ρ_{th}]	Vickers hardness [H_v, GPa]	Indentation toughness [K_{IC}, $MPa{\cdot}m^{1/2}$]
ZB16	88	11	4.11
ZB19	95	13.7	2.65

damage, grinding was performed using 2400 and 4000 papers and followed by a polishing process, which was carried out with 6, 3 and 1 mm diamond lap wheels. Vickers hardness measurement was carried out at 9.8 N load with a loading time of 15 s. The fracture toughness (K_{1C}) of sintered pellets was determined by using Anstis equation with direct crack measurement using the crack length near the Vicker's indentation [22]. A value of 490 GPa, which is the elastic modulus of