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Short communication

Enhanced microstructural and mechanical gradients on silicon nitride ceramics

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Abstract

Continuous in situ functionally graded silicon nitride materials with outstanding gradients in their morphological and mechanical characteristics are developed using the spark plasma sintering technique with an asymmetric setting of punches and die, and placing an electrical insulator barrier between the top punch and the ceramic powder compact. Temperature gradients well above 150 °C are created across the specimen inducing significant variations through the specimen thickness (3.5 mm) in phase transformation (78%) and grain size (240%). Hardness and toughness gradients of 2.0 GPa mm^{-1} and 1.2 MPa $m^{1/2}$ mm^{-1}, respectively, are attained.

Keywords: A. Sintering; B. Microstructure-final; C. Mechanical properties; D. Si_3N_4; Functionally graded materials (FGM)

1. Introduction

Functionally graded materials (FGMs) have attracted a wide interest during the last years, as confirms the continuous increase of publications on this topic since the 90s, with a total number of ~6000 published papers, ~10% of them corresponding just to the last year (data from Web of Science Core Collection). FGMs, consisting on graded compositions and/or microstructures [1,2], cover numerous applications [3,4], from wear and corrosion resistant components to electronics devices, or even biomaterials. However, the scarce trade of FGMs seems to be related to the fabrication process, usually costly and awkward, thus burdening the transference to a larger scale manufacturing. Furthermore, the poor reliability as consequence of the residual stress build up along the graded structure is also a handicap. To circumvent these troubles, and focusing on silicon nitride (Si_3N_4) as a major engineering ceramics [5–7], one-step approach to develop continuous in situ functionally graded Si_3N_4 was proposed by present authors in a recent work [8]. The graded Si_3N_4 was processed from a sole homogenous powder and using the spark plasma sintering (SPS) as densification technique. SPS, a pressure-assisted pulsed direct current sintering process [9,10], allowed creating a temperature gradient of up to 150 °C within the ceramic powder compact by varying the contact sections between the plungers and the die in the SPS machine. As result, gradual $\alpha \rightarrow \beta$-Si_3N_4 phase transformation and grain growth were produced along the specimen, leading to continuous hardness and fracture toughness gradients of 30% and 60%, respectively, when a set point temperature of 1650 °C was selected for the SPS controller [8]. Besides, samples showed a gradient on the shear elastic coefficient, which depended on the α-Si_3N_4 phase transformation [11]. The proposed method greatly simplified the preparation of FGMs compared to the common stacking process of few layers of different compositions or grain sizes [4], and thus can make easier the scaling up towards mass production systems. In addition, it would substantially reduce the nucleation of residual thermal stresses within the component.

Interestingly, most of the research conducted on FGMs using SPS is focused on intermetallics and metal matrix composites, graded ceramics becoming a small group of materials including bio- [12] and ultra-high-temperature ceramics [13,14]. To the best of our knowledge, very few works [8,15] report continuous gradients in the properties of the FGM, in particular, the referred previous work by Belmonte et al. [8] on Si_3N_4 and the works by Hulbert et al. [15] on graded boron carbide–aluminum

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composites. In both studies the gradients were obtained using an asymmetric setting of the punches and the die into the SPS, controlling the temperature at the bottom of the powder compact. However, the punches arrangements were different, and while in the former work the bottom punch was completely enclosed into the die that leaned on the spacer [8], in Hulbert's work the distance between the die and the spacer was kept in the range 3–5 mm [15]. In a SPS system, the current distribution mainly depends on the die geometry and the electrical conductivity of the powder compact. In the case of insulator powders such as Si_3N_4, the graphite elements (spacers, punches and die) are Joule-heated by the pulse direct current, and the ceramic powders are heated through the die. Thus, the punches and die setting becomes a key factor in the temperature distribution.

By taking advantage of SPS technique the goal of the present work is to move a step forward in the manufacture of FG–Si_3N_4, developing materials with largest microstructural and mechanical gradients than those attained previously, getting these features in thinner specimens. In this way, the asymmetric setting of the SPS configuration is modified by placing an electrical insulating barrier, such as boron nitride (BN), between the top punch and the ceramic powder to promote a larger current density gradient and, hence, larger temperature variations across the specimen.

2. Material and methods

The Si_3N_4 powder composition, consisting of α-Si_3N_4 (93 wt%, SN-E10 grade, UBE Industries) and Al_2O_3 (2 wt%, SM8, Baikowski Chimie) plus Y_2O_3 (5 wt%, Grade C, H.C. Starck GmbH & Co.) used as sintering additives, was attrition milled in ethanol for 2 h. Afterwards, the solvent was removed from the suspension in a rotary-evaporator, and the resulting mixture was oven dried at 120 °C, and sieved through a 63 µm mesh. 4 g of the ceramic powders composition were placed into a graphite die of 20 mm diameter, and uniaxially pressed at 20 MPa. The die was then asymmetrically arranged (Fig. 1) to modify the spatial distribution of the effective current intensity per unit area through the system. In this way, the bottom punch was completely enclosed into the die (50 mm diameter), which was in electric contact with the bottom spacer, whereas the upper punch (20 mm diameter) was partially introduced into the die (Fig. 1b). In addition, a BN spacer of 1 mm thickness was placed between the top punch and the ceramic powder compact. The SPS (Dr. Sinter, SPS-510CE) tests were performed under 6 Pa of vacuum atmosphere, using a set point temperature of 1650 °C, a holding time of 5 min, and heating rates of 133 °C min^{-1} between 600 and 1400 °C and 50 °C min^{-1} from the latter temperature up to 1650 °C to avoid temperature overshooting. A uniaxial pressure of 50 MPa was applied during the first minute of the heating process and maintained during the heating–holding cycle, decreasing it to 20 MPa on the cooling step. The current was shut off at the end of the holding time, reaching cooling rates of ~300 °C min^{-1}. Discs of 20 mm in diameter and ~3.5 mm in thickness were obtained and labelled as BN-FGM. The results were compared to those previously reported for FG-Si_3N_4 [8] equally processed and sintered except for the inclusion of a BN spacer. This material was labelled as STD–FGM in the present paper. Top and bottom identifications on the specimens referred to the corresponding upper/lower graphite punches.

Elastic modulus (E), hardness (H), and fracture toughness (K_{IC}) were determined using instrumented indentation (Zhu 2.5, Zwick/Roell, Germany), Vickers diamond indenters, and peak loads of 49 N for E and H measurements, 196 and 490 N for K_{IC}. Miranzo et al.'s expression [16] was used to assess K_{IC}. At least five well-defined indentations were considered for each material.

3. Results and discussion

Fig. 2a illustrates the electrical resistance (R) evolution versus the SPS running time for both settings. As expected, higher R values were recorded for BN-FGM mounting, especially during the initial 200 s, with a maximum R of 10.2×10^{-3} Ω that is 30% larger than the value for STD–FGM set-up ($R = 7.8 \times 10^{-3}$ Ω). For longer times, the resistance decreased for both settings to around 2×10^{-3} Ω, although the R value for the BN-FGM system always appeared slightly higher than for STD–FGM one.

The optical image of the STD–FGM cross-section (Fig. 2b) exhibited a homogeneous dark-grey color along the specimen associated with its complete densification. However, the BN-FGM material presented a thick dark-grey area (Fig. 2c) at the

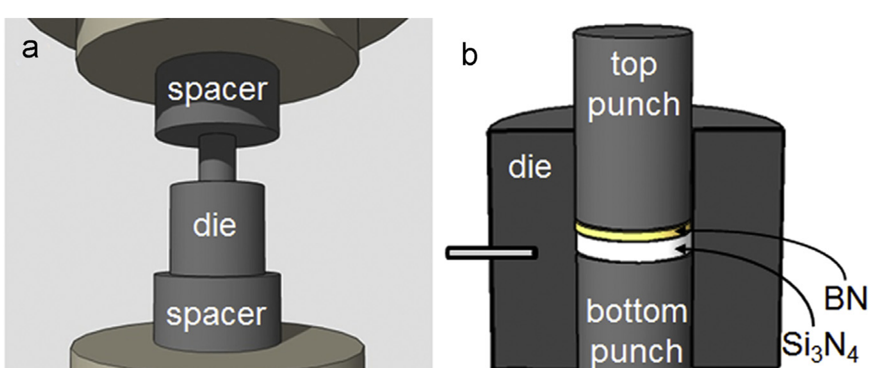

Fig. 1. Sketch showing the asymmetric SPS graphite die and punch set-up: (a) overall view and (b) cross-section.