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ScienceDirect

Ceramics International 42 (2016) 3836–3848

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of pressure and temperature on densification, microstructure and mechanical properties of spark plasma sintered silicon carbide processed with β-silicon carbide nanopowder and sintering additives

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Received 16 September 2015; received in revised form 30 October 2015; accepted 7 November 2015
Available online 26 November 2015

Abstract

The effects of applied pressure and temperature during spark plasma sintering (SPS) of additive-containing nanocrystalline silicon carbide on its densification, microstructure, and mechanical properties have been investigated. Both relative density and grain size are found to increase with temperature. Furthermore, with increase in pressure at constant temperature, the relative density improves significantly, whereas the grain size decreases. Reasonably high relative density (~96%) is achieved on carrying out SPS at 1300 °C under applied pressure of 75 MPa for 5 min, with a maximum of ~97.7% at 1500 °C under 50 MPa for 5 min. TEM studies have shown the presence of an amorphous phase at grain boundaries and triple points, which confirms the formation of liquid phase during sintering and its significant contribution to densification of SiC at relatively lower temperatures ($\leq$1400 °C). The relative density decreases on raising the SPS temperature beyond 1500 °C, probably due to pores caused by vaporization of the liquid phase. Whereas β-SiC is observed in the microstructures for SPS carried out at temperatures $\leq$1500 °C, α-SiC evolves and its volume fraction increases with further increase in SPS temperatures. Both hardness and Young's modulus increase with increase in relative density, whereas indentation fracture toughness appears to be higher in case of two-phase microstructure containing α and β-SiC.

Keywords: C. Mechanical properties; D. SiC; SPS; Densification; Microstructure

1. Introduction

Silicon carbide (SiC) is an attractive non-oxide ceramic material, because of its unique combination of low density (3.21 g/cm^3) and excellent mechanical properties such as good hardness (HV 24.5–28.2 GPa), flexural strength (440–500 MPa), elastic modulus (440–475 GPa), high thermal conductivity (~41 W/m °C) and high oxidation resistance [1,2]. These properties make SiC a potential candidate material for numerous applications such as protective armors, aluminum electrolysis cell, as well as nuclear fuel coating for next generation fusion reactors [1–7]. Nevertheless, the incessant demand for materials with superior properties for strategic and high performance applications requires the properties of SiC to be continuously upgraded. A promising route to improve the mechanical properties (e.g. hardness and fracture toughness) of SiC is to retain nanometric ($<$100 nm) or submicrometer grain size after sintering [7]. It is necessary to mention here that fracture toughness improvement also depends upon other factors like grain morphology and other microstructural features capable of obstructing crack growth. However, consolidation of ceramic nanoparticles possessing high surface area to obtain densified products is challenging due to (i) difficulty in compaction caused by large interparticle friction, and (ii) possibility of rapid grain growth. It is well known that the presence of coarse grains deteriorates both strength and fracture toughness [8]. In order to restrict grain growth, low temperature sintering techniques involving shorter durations are promising.

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http://dx.doi.org/10.1016/j.ceramint.2015.11.048
0272-8842/

In this context, SPS offers an effective approach as lower temperatures (100–200 °C lower than that for conventional sintering) and shorter durations compared to other sintering methods are required to consolidate the nanopowders by this process to yield dense ceramic compacts with fine grain sizes [9–11].

Recent studies on SPS-ed SiC have focused on (i) consolidation of nanosized β-SiC powder to obtain fine grain size [12–14] as well as (ii) understanding the effects of sintering additives on microstructure and properties of sintered product [15]. Yamamoto et al. obtained 98% dense SiC compact with grain size ≤100 nm using SPS, where mechanically alloyed β-SiC powder was used as the starting raw material [16]. There are already reports in the literature on the nanostructured SiC prepared by SPS using Al-based compounds as sintering additives [17,18]. Guillard et al. have shown the effect of temperature, dwell time and applied pressure on the densification behavior of sub-micrometer size SiC powder compact using SPS [19]. In another study, Carlson et al. investigated the effect of essential parameters such as temperature, time, pressure, and load removal on densification, grain size, and crystal structure of additive-free β-type nano-SiC [20]. A maximum relative density of 70.9% and grain size of 133 nm were obtained upon SPS at temperature, pressure and time of 1700 °C, 50 MPa, and 1 min, respectively. No change in crystal structure was observed even at a temperature of 1800 °C, under applied pressure of 50 MPa and zero min dwell time [20].

It is well known that applied pressure and temperature are two critical parameters for SPS, which need to be properly controlled in order to tailor the sintered compact microstructure for achieving desirable properties for different types of applications [21,22]; however, there are no comprehensive reports on such studies for nanocrystalline SiC using sintering activators. Therefore, the present work was carried out with the specific objective of studying the influence of applied pressure and sintering temperature on the development of microstructure and concomitant mechanical properties of SiC by SPS, where carbon (C) and boron carbide (B_4C) were used as sintering additives. It has been shown that C reduces the surface native oxide silica (SiO_2) encapsulating the SiC particles by carbothermal reduction and thereby enhances the bulk self-diffusion of SiC and promotes its sintering [23,24,25]. Earlier studies have also confirmed that addition of small amount of B_4C promotes densification of SiC either by forming liquid phase at elevated temperature [15,26] or by solid state sintering mechanism [27,28]. Therefore, considering the effectiveness of C and B_4C for the densification of SiC, they have been chosen as sintering activators in this study. The mechanical properties evaluated for the SPS processed SiC has been also compared with those of a solid state sintered SiC (SSiC, α-type) pellet produced through pressureless sintering of α-SiC powder.

2. Experimental procedure

2.1. Raw materials

The primary raw material used in this study was commercially available silicon carbide (SiC) powder (Inframat Advanced Materials, USA) having particle size in nanometric range ($D_{50} \approx 40$ nm) and ~99% purity, with the major impurities being free Si < 0.25%, free C < 0.75%, as well as trace amounts of the elements Ca, Ti and Mn. Phenolic resin (ABR Organics Limited, India, Grade: ABRON 100 WS) with net C content of 40 wt% was used as the source of carbon along with B_4C ($D_{50} \approx 0.7$ μm) obtained from Electro-Abrasives Corporation, NY,USA. Commercial RTP α-SiC powder (Grade: SIKA DENSITEC 15) used for sintering without applying pressure was obtained from Saint-Gobain (Norway). This powder contained B and C as sintering aides.

2.2. Powder processing

2.2.1. Hydrofluoric (HF) acid treatment of SiC powder

The as-received SiC powders were treated with 5% (w/w) HF ethanolic solution to reduce the oxygen content through dissolution of the surface oxide (SiO_2) layer, which is known to act as a diffusion barrier during sintering. The presence of stable oxide at the surface also lowers the driving force for sintering [29].

2.2.2. Powder premix preparation

The acid-treated SiC powder was mixed in absolute ethanol and deagglomerated for 30 min using a probe ultrasonicator (Model: Vibrosonics 750 W, Sonics, USA) in presence of ~4 wt% polyethylene imine dispersant. Required quantity of B_4C powder (1 wt%) was added to SiC and mixed in a horizontal roller mill for 24 h. Required amount of resin was added 2 h prior to completion of the mixing process, in order to obtain the desired carbon content (3 wt%) in the starting composition. Subsequently, the powder was dried at ~70 °C with continuous stirring to ensure homogeneity in the powder mix, and then sieved through a 60 BSS mesh.

2.2.3. Sintering

Sintering of SiC powder was carried out in an SPS apparatus (Model: DR SINTER 1050, SPS Syntex Inc., Japan) under argon atmosphere at different conditions, being shown along with respective sample codes in Table 1. Further in the text, the samples processed at varying pressures and temperatures have been marked as SC-P and SC-T, respectively. A constant pulse current with on:off ratio of 12:2 was applied throughout the sintering cycle. The temperature was monitored by a radiation pyrometer focussed at a circular hole on the die wall. A graphite die with inner diameter of 15 mm was used for all the runs.

During SPS, the applied voltage and pulsed DC current play a significant role in rapid consolidation of the samples [30]. Both current and voltage were increased rapidly in the initial stage of heating cycle in order to reach 570 °C, at which the pyrometer starts reading the temperature. Thereafter, both the current and voltage were increased linearly with time to maintain the required heating rate (~100 °C/min) till the final sintering temperature was reached. In the subsequent dwelling stage, both current and voltage were reduced. In the present study, voltage of ≈4–6 V and current of ≈3000–4500 A