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Pressureless sintered silicon carbide with enhanced mechanical properties obtained by the two-step sintering method

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Abstract

The Two-step sintering (TSS) method was applied to the pressureless sintering of commercial silicon carbide powder doped with boron and carbon. The microstructural and mechanical properties of TSS-SiC were compared to those of sintered SiC obtained with the conventional thermal cycle (CS-SiC). TSS-SiC was densified (97.7% T.D.) at 2050 °C instead of 2200 °C needed for CS-SiC (97% T.D.). Furthermore, TSS-SiC showed finer microstructure and enhanced mechanical properties. In particular, flexural strength of the TSS-SiC materials greatly increased up to 556 MPa, much higher than 341 MPa reached by CS-SiC.

Keywords: A. Sintering; C. Mechanical properties; D. SiC

1. Introduction

Silicon carbide (SiC) is a very interesting ceramic material due to its properties like high hardness, low bulk density, high oxidation resistance which make SiC suitable for a wide range of industrial applications. Sintering of silicon carbide was first performed by Prochazka [1] by using boron and carbon through a solid state mechanism (BC-SSiC). This process is normally performed at 2150–2200 °C and densification is enhanced through the reduction of the superficial energy of the grains promoted by boron [2] and the reaction between carbon and the silica film [2–4] located on the SiC particle surface.

The additives most widely used are boron and carbon and they normally cause an exaggerated grain growth due to the high sintering temperature needed to reach high sintered density. Pressureless sintering of BC-SSiC at lower temperature would be desirable in order to limit the grain growth, but it is still an unresolved issue. Coarse microstructure affects the mechanical properties and several sintering methods have been already tested with BC-SSiC in order to reduce the grain size and to improve the mechanical properties by using simultaneous pressure application during sintering (hot pressing, hot isostatic pressing and spark plasma sintering) [5–9] also with different additives (Al-B-C) [10] or through liquid phase mechanism (metal and rare-earth oxides) [11]. The main problems of the pressure-assisted sintering processes are high production costs and limitation in the product size and shape complexity which can limit the industrial applicability. Two-step pressureless sintering process can be proposed both to overcome these limitations and to reduce the sintering temperature in order to obtain high strength BC-SSiC ceramics with fine microstructure.

The two-step sintering method (TSS) proposed by Chen and Wang [12] is based on the heating of the sample to a high temperature T_1 followed by a rapid cooling down to a lower temperature T_2 and then held at T_2 for a long period. The main characteristic of this method is that the grain boundary diffusion of the sample is maintained avoiding at the same time the grain boundary migration. Therefore, the grain growth associated to the final step of the sintering process is completely suppressed. Several studies focused on this method are available. Chen and Wang [12] firstly applied this method in Y_2O_3 ceramics, whereas different authors were able to obtain $BaTiO_3$ [13], ZnO [14, 15], ZrO_2 [16–19], Al_2O_3–ZrO_2

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[20], Al_2O_3 [21, 22] and SiC [23] ceramics. In particular, Lee et al. [23] obtained nanostructured SiC ceramics with a two-step liquid phase sintering process based on hot pressing with alumina, yttria and calcia as sintering aids. To our knowledge this is the only study focused on the TSS method applied to SiC, whereas there are no studies on the applicability of the TSS method on the pressureless sintering of the SiC-B-C system. On the basis of these considerations, the study reported in this paper was aimed to show that the two-step sintering method can be used to manufacture pressureless-sintered BC-SSiC ceramics at temperature lower than 2150–2200 °C. In addition, further scope was the evaluation of the effects of the TSS method on the mechanical properties.

2. Experimental procedure

Commercially available α-SiC (UF15 Premix, H.C. Starck, Germany) was used as starting powder. This is a ready-to-press powder with the appropriate amount of organic binder and sintering aids (boron and carbon). The main physical and chemical characteristics of the powder are reported in Table 1. Discs with diameter 35 mm and thickness 3 mm were prepared by uniaxial pressing at 60 MPa followed by cold isostatic pressing at 200 MPa. Sintering was performed in a graphite resistance high temperature furnace in flowing argon at 1 atm. The temperature of the conventional sintering (CS) was set at 2200 °C for 1 h, whereas TSS was conducted at 2100 °C (T_1) and 2050 °C (T_2) for a period of time up to 7 h.

Samples density (CS-SiC and TSS-SiC) were determined by the Archimedes method (ASTM C373). The microstructures of the polished and chemically etched (Murakami′s etching) samples were observed using scanning electron microscopy (SEM-LEO 438 VP). X-ray patterns (XRD) were collected with a Philips powder diffractometer with a Bragg–Brentano geometry and equipped with a copper anode operated at 40 kV and 30 mA (step 0.02°, time 6 s). The phase analysis was carried out with the PC X′pert High Score software Version 2.2a (PANalytical B.V., Almelo, The Netherlands).

The flexural strength was determined by four-point bending tests. Ten samples as bars of $2 \times 2.5 \times 25$ mm^3 were prepared and tested in accordance with the standard ENV 843-1 (crosshead speed 0.5 mm/min, support span 20 mm).

Table 1
Chemical and physical properties of the commercial powder.

Properties	UF15 premix
Specific surface area (m^2/g)	14–16
Bulk density (g/cm^3)	0.72
Granule size (μm)	< 150
Particle size distribution d_{90} (μm)	1.3
d_{50} (μm)	0.6
d_{10} (μm)	0.25
Oxygen (wt%)	< 1.5
Boron (wt%)	0.5
Carbon (wt%)	3.0
Organic binder (wt%)	< 10

The fracture toughness was calculated by the Vickers indentation method on the basis of the equation proposed by Niihara et al. [24]:

$$K_{IC} = 0.203\ Ha^{1/2}(c/a)^{-3/2} \tag{1}$$

where H is the hardness, a is the impression radius and c is the crack length. The indentations were performed with a load of 98 N.

Finally, the elastic modulus was determined by applying the impulse excitation method in accordance with the standard EN 843-2. Each sample, supported at its nodes for the fundamental frequency of flexural vibration, was lightly struck by a small hammer in order to detect its natural frequency of vibration by a microphone (or a piezo transducer) coupled to a proper frequency analyser. In the experimental activity here described, a microphone was used, connected to the frequency analyser Grindo-Sonic System Mk5-Industrial (J.W. Lemmens N.V., Belgium).

The values of Young′s modulus were then calculated in accordance with the following equation:

$$E = 0.946\ (mf^2/b)(l/h)^3[1 + 6.585(h/l)^2] \tag{2}$$

where E is the dynamic Young′s modulus, m the mass of the test piece, b the width of the test piece perpendicular to the flexural mode vibration, h the thickness of the test piece in direction of flexural vibration, l the length of the test piece and f the fundamental frequency of flexural vibration.

3. Results and discussion

3.1. Density and microstructure

Microstructures of the samples obtained with both methods, CS and TSS, are reported in Fig. 1. CS-SiC sample shows an exaggerated grain growth with grains having length more than 100 μm and very high aspect ratio. On the contrary, the microstructure of TSS-SiC sample is mainly composed of equiaxed grains with some elongated grains with length of about 30 μm. The residual porosity is homogeneously distributed in the CS-SiC and TSS-SiC samples having very similar sintered density: 97% T.D. and 97.7% T.D., respectively (T.D. = 3.2 g/cm^3). Conventional sintering was also tested at temperature lower than 2200 °C in order to limit the grain growth, but the density was always less than the value obtained at 2200 °C. These results confirmed that the second step of the TSS method performed at lower temperature than CS (2050 °C instead of 2200 °C) leads to the same final densification with limited grain growth. Furthermore, there are no reports that SiC ceramics can be densified at 2050 °C using the pressureless sintering process, boron–carbon additives and starting powder of similar quality.

The lowering of the sintering temperature from 2200 °C (CS) to 2050 °C (TSS) also influences the content of the different α-SiC polytypes. The XRD patterns reported in Fig. 2 show some peaks with different intensities. The quantitative determination of the content of the 6H, 4H and 15R polytypes was carried out on the basis of the method proposed by Ruska et al. [25] (Table 2). TSS-SiC sample showed a lower content