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Flexural strength and toughness of liquid phase sintered silicon carbide

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Abstract

Liquid phase sintering process of silicon carbide allows the obtaining of a dense sample at lower temperature than the solid state process with reduced grain growth and improved mechanical properties. In this paper mechanical properties at RT (room temperature) and at high temperature of liquid phase sintered silicon carbide (LPSSC) was determined. Flexural strength measurements were conducted by means of four-point bend tests in the range RT–1400°C. Hardness and fracture toughness were determined by Vickers indentation method at different load. Flexural strength changed from 532 MPa at RT to 240 MPa at 1400°C. SEM analysis showed that this behaviour is due to superficial oxidation of SiC and formation of yttrium silicate which create bubbles and cavities.

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

1. Introduction

Silicon carbide (SiC) is widely used for structural applications thanks to its good mechanical properties (hardness, fracture strength) [1]. Furthermore it is well known that SiC showed high corrosion resistance and thermo-stability at high temperature [2]. These properties depend strictly on density and grain size [3] and because of the difficulty to obtain SiC parts with high density and small grain size, in recent years methods to sinter silicon carbide with the aim to improve its mechanical properties (fracture strength and toughness) were studied [4–6]. Omori and Takai [4] proposed to sinter silicon carbide via liquid phase using alumina and yttria as sintering-aids. Mulla and Krstic [7] and Do-Hyeong and Chong Hee [8] demonstrated that it is possible to obtain SiC parts with high density and high mechanical properties at a temperature below 2000°C. At this temperature, crystal structure transformation β-α is prevented. As a consequence exaggerated crystal growth due to this crystallographic changing is avoided and, thus, it is possible to obtain an improvement of mechanical properties.

In this paper mechanical properties of liquid phase sintered silicon carbide (LPSSC) were determined. Flexural strength tests were conducted at different temperature in the range RT–1400°C while hardness and toughness were determined at different loads. To explain flexural strength variation with temperature, corrosion behaviour of LPSSC at high temperature was investigated.

2. Experimental procedure

β-SiC powder (BF12, H.C. Starck — Germany) was wet-mixed in ethanol with 6%wt Y_2O_3 (purity 99.99%, Mandoval Ltd. England) and 4% wt Al_2O_3 (purity 99.99%, Baikalox SM8, Baikowski Chimie, France). In Table 1 are reported characteristics of SiC, alumina and yttria powders. Mixing was performed by Turbula mixer using a polyethylene bottle and SiC balls as grinding media. After drying and sieving, the powder was compacted by die pressing at 67 MPa and subsequently was pressed at 250 MPa by CIP.

The green body was put in a graphite crucible embedded with powder bed with the same composition of the pellet and covered with a graphite foil. Sintering was performed at 1875°C in a graphite elements furnace

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Table 1
Chemical and physical properties of SiC, alumina and yttria powders

Powder	Purity wt%	S.S.A. m^2/g	Particle size (μm)
β-SiC	⩾97.5	11.59	0.72
Y_2O_3	99.99		3.5–4.3
Al_2O_3	99.99	10	<0.3

in flowing Ar at 1 atm. The thermal cycle was characterised by the heating and cooling rate of 22°C/min and by dwell time of 0.5 h at sintering temperature. Density of the SiC sintered sample was determined using Archimede's method. Crystalline phases were identified by means of X-ray diffraction (Rigaku — Miniflex CuK_α 1.54 Å). Furthermore, the sintered sample was polished, plasma etched with HF and finally examined by SEM (Stereoscan 250-Cambridge).

Flexural strength was measured by four-point bend tests at a different temperature from RT to 1400°C. Samples as bars of 2×2.5×25 mm were prepared and tested in accordance with the standard EN 843-1. Five bars for each temperature were tested. Hardness and fracture toughness were determined by means of Vickers indentation method (Durimet-Leitz). Tests were conducted at different load within the range 2.9–196 N. Fracture toughness was calculated using the equation proposed by Niihara et al. [9]. Thermomechanical behaviour of LPSSC was investigated through SEM examination of a transversal section of samples tested at high temperature. Identification of corrosion products formed on the surface was performed by means of EDS microprobe (QX 2000 Link Analytical).

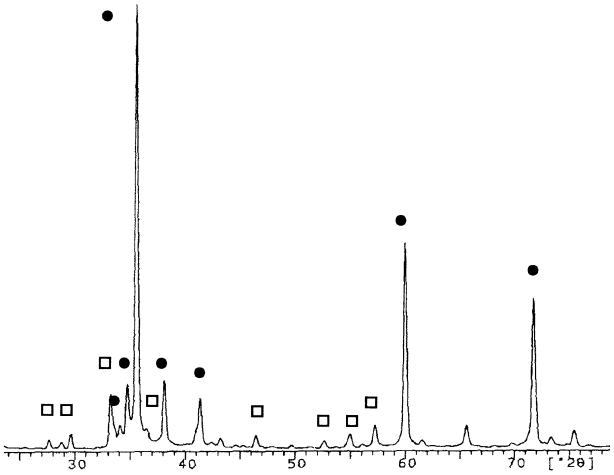


Fig. 1. X-ray diffraction pattern of the sintered sample (□ YAG, ● SiC).

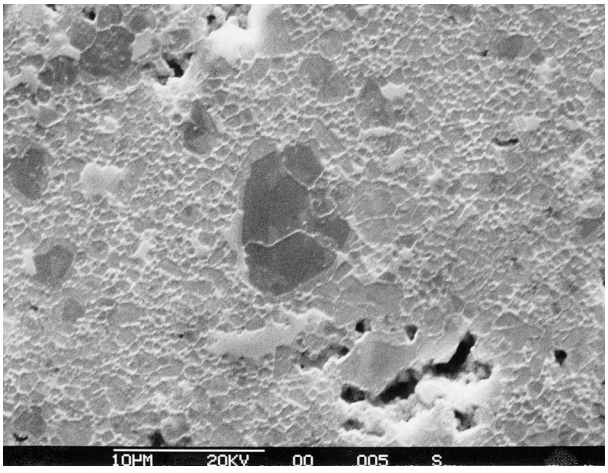


Fig. 2. Microstructure of the sintered sample. Black and grey phases are SiC, white phase is YAG.

3. Results and discussion

3.1. Density and microstructure

In Fig. 1 the X-ray diffraction pattern of the sintered sample is reported. It shows that YAG was formed as a liquid phase.

Density of the SiC sintered sample resulted in 96.3% T.D. Theoretical density, calculated by means of determination of secondary phase content following a method described elsewhere [10], resulted in 3.24 g/cm^3. SEM examination of plasma etched sintered sample revealed a fine microstructure with average grain size of 2–3 μm (Fig. 2).

Large pores are probably due to the loss of alumina and/or yttria during the sintering process in accordance with these reactions:

$$SiC(s) + Al_2O_3(s) \Longleftrightarrow Al_2O(g) + SiO(g) + CO(g) \quad (1)$$

$$SiC(s) + 2Y_2O_3(s) \Longleftrightarrow 4YO(g) + SiO(g) + CO(g) \quad (2)$$

Total weight loss associated to the sintering process was 5.4%. In literature several studies are reported concerning methods to reduce weight loss. For example Mulla and Krstic [11] proposed to sinter in CO atmosphere while Lee et al. [12] used YAG as a sintering aid. In our case, the presence of a powder bed having the same composition of sintered body, allows the control of reactions (1) and (2) and thus to reduce weight loss.

3.2. Hardness and fracture toughness

Hardness and fracture toughness (K_{Ic}) were determined at different load (Vickers indentation). K_{Ic} was determined using the equation proposed by Niihara et al. [9]:

$$K_{Ic} = 0.203 Ha^{1/2}(c/a)^{3/2} \quad (3)$$

where H is the hardness, a is the impression radius and c is the crack length.

Results are reported in Fig. 3 (hardness and toughness vs indentation load) and in Fig. 4 (crack length as function of indentation load). From Fig. 3 it is possible to see that hardness shows a slight decrease (from 25 to 21 GPa) when indentation load is increased while fracture toughness resulted in 5–6 MPa.m$^{0.5}$ independently of the load applied. Reporting crack length values as a function of indentation load (Fig. 4) and applying the least-square method, a straight line is obtained with a slope of 0.6973 which is very similar to the theoretical value of 0.67 proposed by Lawn et al. [13] with the following general equation:

$$K_{Ic} = \chi P/c^{2/3} \quad (4)$$

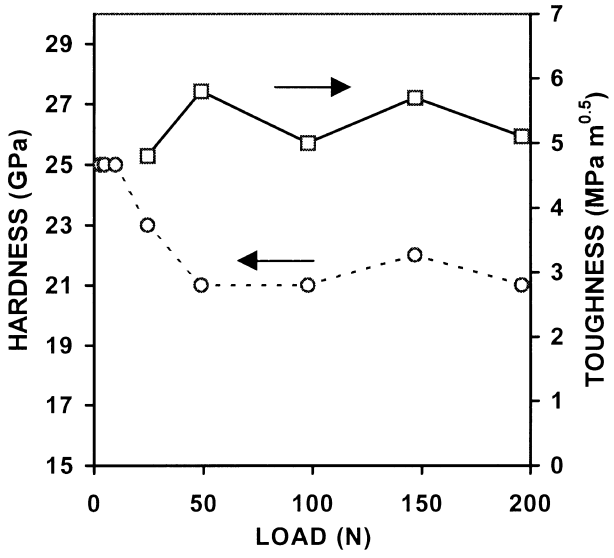


Fig. 3. Hardness and fracture toughness at different indentation load.

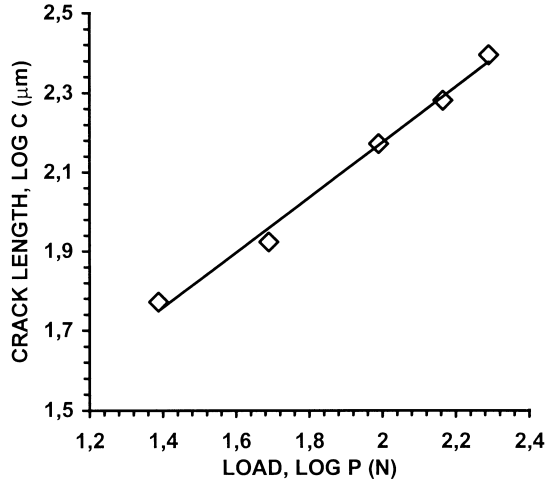


Fig. 4. Crack length as a function of indentation load.

where χ is a constant.

In our case Eq. (4) can be written as follows (function of straight line reported in Fig. 4):

$$\mathrm{Log}c = 0.6973\ \mathrm{Log}P + 0.7797 \quad (5)$$

Furthermore the value of the slope being so close to the theoretical indicates that radial cracks observed on the surface (Fig. 5a) correspond to the median crack [9,14].

The values determined of K_{ic} are higher than values obtained with SiC pressureless-sintered via solid-state [15,16]. As reported by Do-Hyeong and Chong Hee [8], crack deflection mechanism, due to the presence of grain boundary phase, is responsible for fracture toughness increasing in LPSSC. This mechanism was confirmed also in our case as is clearly show in Fig. 5b where it is reported typical crack deflection in sintered sample indented with a load of 24 N.

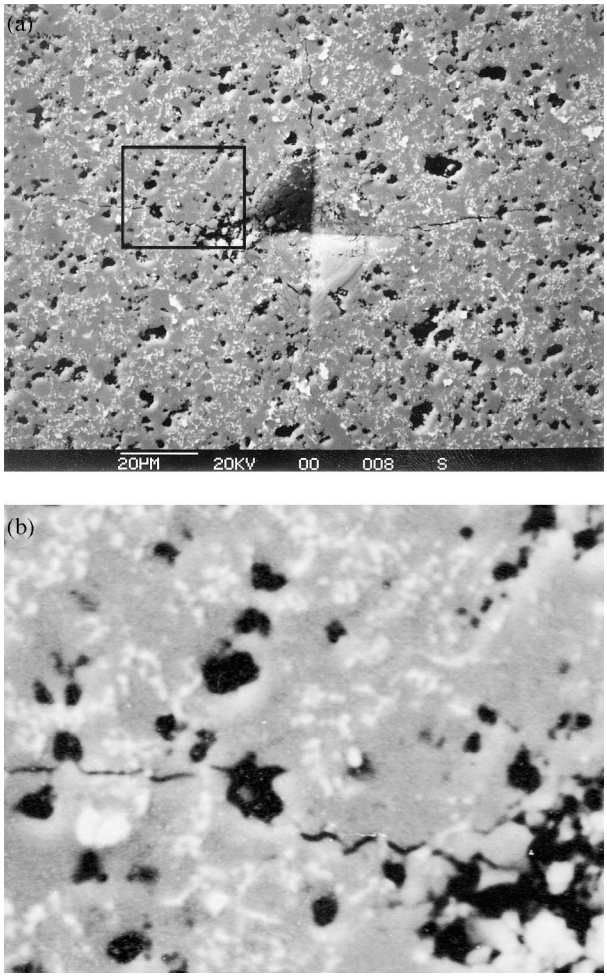


Fig. 5. SEM micrographs of (a) specimen surface indented at 24 N and (b) typical crack deflection for LPSSC (zone indicated with a rectangle in (a) at higher magnification (3000X).

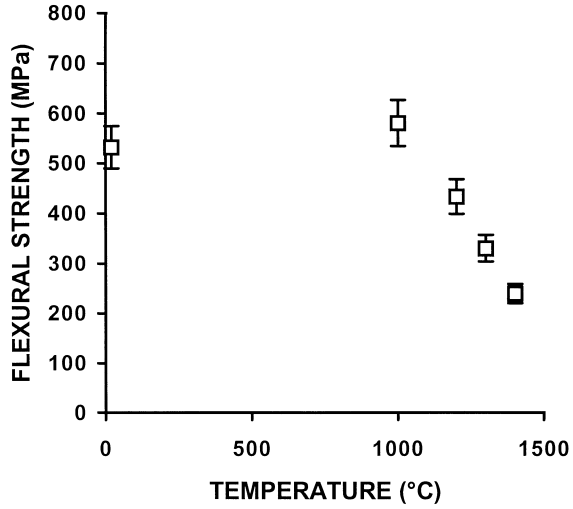


Fig. 6. Variation of flexural strength with temperature.

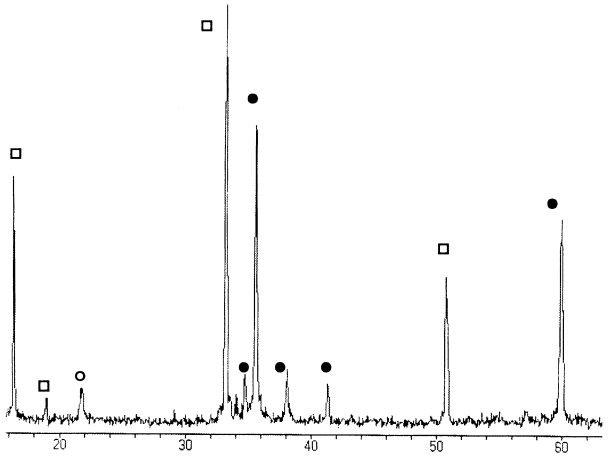


Fig. 7. XRD pattern of the sintered sample tested at 1400°C (□ γ-$Y_2Si_2O_7$, ○ SiO_2, ● SiC).

3.3. Flexural strength

Flexural strength (σ) variation with temperature is reported in Fig. 6.

At room temperature σ resulted 532 MPa. At 1200°C it begins to decrease and at 1400°C resulted in 240 MPa. This behaviour is due to oxidation of SiC with formation of silica which reacts with yttrium aluminate to form yttrium silicate. Possible reactions are:

$$SiC(s) + 3/2O_2(g) \Longleftrightarrow SiO_2(s) + CO(g) \quad (6)$$

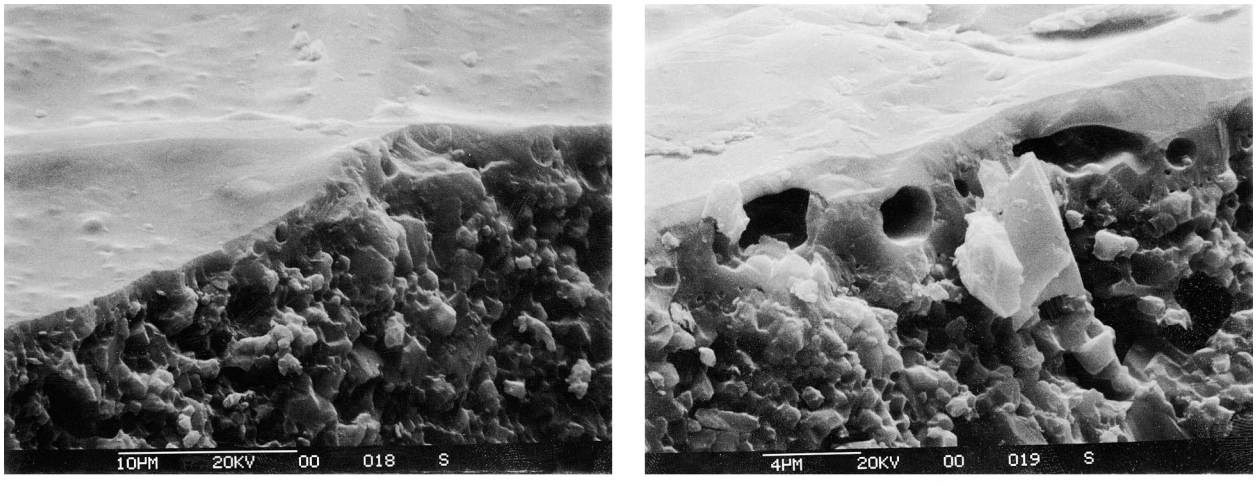
$$6\,SiO_2(s) + 2Y_3Al_5O_{12}(s) \Longleftrightarrow 3Y_2Si_2O_7(s) + 5Al_2O_3(s) \quad (7)$$

This mechanism was confirmed by means of XRD (Fig. 7) and SEM–EDS (Figs. 8 and 9) analysis of sintered sample tested at 1400°C. XRD spectrum reveals the presence of SiO_2 (α-cristobalite) and γ-$Y_2Si_2O_7$.

As reported by Drummond et al. [17] at 1400°C, polymorph γ of $Y_2Si_2O_7$ is thermodynamically favoured. Free alumina was not identified; probably its content is too low or is present as a solid solution. Alumina was detected by SEM–EDS analysis. In fact SEM images of Fig. 8a–b show that an oxidation layer of about 4 μm was formed.

This layer was composed of yttrium silicate (γ-$Y_2Si_2O_7$) and alumina/silica as revealed by EDS microprobe investigation (Fig. 9a–b). Below the superficial layer, was identified (Fig. 9c), a silica layer formed by means of reaction (6). The rest of the specimen was composed of SiC and YAG (Fig. 9d–e).

The large holes shown in Fig. 8b were due to reactions (6) and (7) and they permit the oxidation to proceed inside the specimen. This behaviour is different compared



(a) (b)

Fig. 8. SEM micrographs of the fracture surface of the specimen tested at 1400°C. In (a) are shown bubbles on the surface, while in (b) is shown the oxidation layer with large holes.

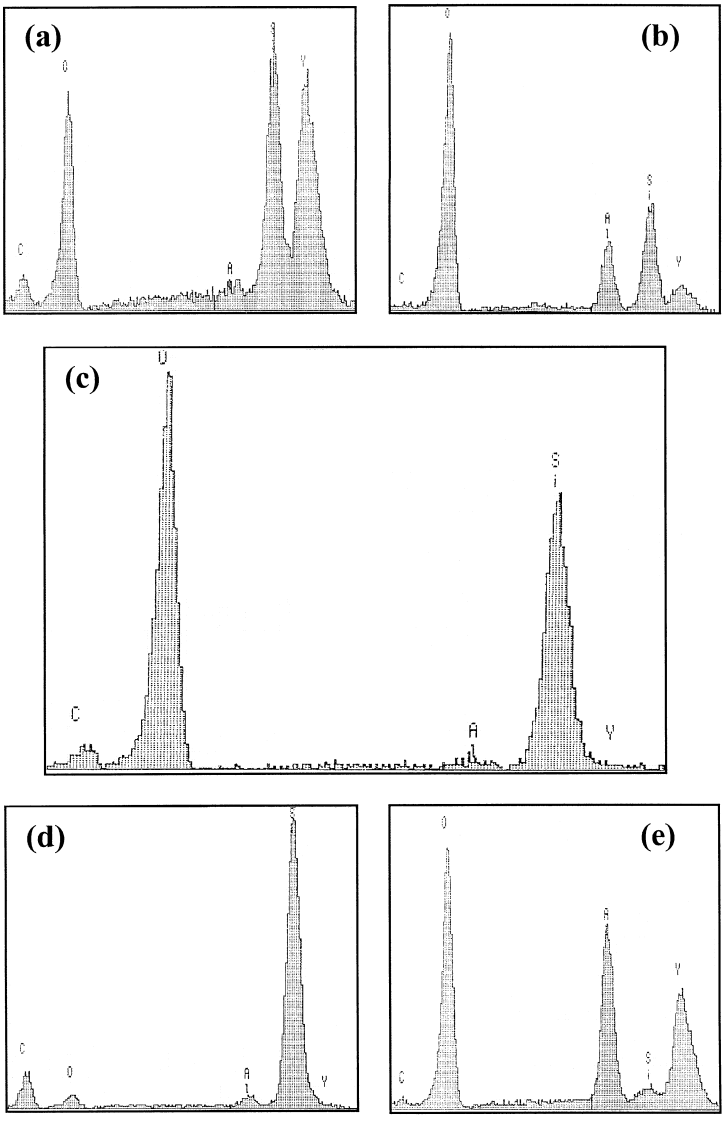


Fig. 9. Sintered sample tested at 1400°C: EDS spectra of (a) and (b) oxidation layer, (c) silica layer, (d) and (e) rest of specimen.

to SiC sintered via solid state. In this last case, oxidation leads to formation of a protective silica layer which reduces oxidation rate [18]. In the case of LPSSC, formation of a glassy-phase leads to creation of bubbles and holes that allow oxygen permeation through the oxidation layer. Thus, flexural strength variation with temperature depends on the formation rate of the glassy phase (γ-$Y_2Si_2O_7$).

4. Conclusion

Mechanical properties of the SiC powder sintered via the liquid phase were determined. Formation of a grain boundary phase (YAG) allows the obtaining of a sintered sample with high fracture toughness. The crack deflection mechanism was revealed as responsible for the toughening behaviour of LPSSC confirming the proposition by Do-Hyeong and Chang Hee [8]. Furthermore, the crack length increased with indentation load on the basis of the general equation proposed by Lawn et al. [13] which indicates that the cracks observed on the surface correspond to the median cracks.

Flexural strength at room temperature resulted higher than σ of SiC sintered with B and C as sintering aids. At 1400°C flexural strength value is reduced by 55% compared to the RT. This behaviour is due to oxidation of SiC; it proceeds through formation of cristobalite which reacts with YAG to form γ-$Y_2Si_2O_7$. Because of these reactions, bubbles and holes were formed and consequently oxidation is not stopped on the surface but proceeds inside the sintered specimen.

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