EFFECT OF ANNEALING ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF LIQUID-PHASE-SINTERED SILICON CARBIDE

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Abstract
The paper deals with the influence of annealing on the microstructure and mechanical properties (hardness, Young's modulus, fracture toughness, bending strength) of SiC based ceramics. By annealing, the microstructure of the studied materials was changed from fine globular (annealing at 1650°C/5 h) to coarse plate-like (annealing at 1850°C/5h). The annealing has no influence on the values of hardness and Young's modulus. By increasing the annealing temperature the fracture toughness values have been increased. The bending strength values of these materials have been degradated by the present defects in the form of pores and SiC agglomerates.
Keywords: SiC, annealing, microstructure, mechanical properties

INTRODUCTION

Silicon carbide has been recognised as an important structural ceramic because of its good combination of properties, such as high-temperature strength, resistance to wear and corrosion, and thermal shock resistance. However, the low fracture toughness [1] and extremely flaw-sensitive strength [2] of SiC at room temperature have made it unsuitable for use in many structural applications. SiC is a promising material for high temperature engineering applications, but it is difficult to densify without additives because of the covalent nature of Si-C bonding and low self-diffusion coefficient. Since the innovative approach initiated by Omori and Takei [3], who found that SiC could be fabricated at a relative lower temperature (1850°C to 2000°C) with a liquid oxide phase, a number of attempts have been made to improve the fracture toughness of silicon carbide. Liquid phase sintering (LPS) has been extensively applied in order to obtain dense ceramics with a controlled, fine-grained microstructure. For LPS-SiC various sintering additives have been reported such as Al_2O_3 [4,5], Al_2O_3-Y_2O_3 [6,7], yttrium-aluminum garnet (YAG) [8] and AlN-Y_2O_3 [9,10]. These additives form a liquid during sintering with SiO_2, which is the oxidized surface layer of SiC particles, and liquid promotes densification and microstructure development through grain rearrangement and solution-reprecipitation [11].

One promising method to increase the toughness of SiC is to develop in situ or self-reinforced materials trough $\beta \rightarrow \alpha$ phase transformation. The microstructure of LPS-SiC materials can be changed radically by varying the ratio of α-SiC to β-SiC in the starting powder and applying suitable post-sintering heat treatments. It was shown [12] that, in the case of compacts derived from α-SiC powder, the aspect ratio of the SiC grains changed only slightly during post-sintering heat treatments. In contrast, the use of β-SiC starting powders increases the aspect ratio as a result of anisotropic grain growth, which results in a microstructure with interlocking plate-like grains. The fracture toughness of LPS-SiC

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sensitively depends on the aspect ratio of the grains. Improved fracture toughness has been achieved through microstructure development of elongated or plate-like grains, which results in grain bridging [13-15] and crack deflection [16].

In this work, the influence of annealing on microstructure and some mechanical properties (hardness, Young's modulus, fracture toughness and bending strength) have been investigated.

EXPERIMENTAL PROCEDURE

Powder batches were produced using β-SiC powder (HSC-059, Superior Graphite). The sintering additives were Al_2O_3 (A 16 SG, Alcoa) and Y_2O_3 (grade C, H.C. Starck). A combination of 91 wt.% β-SiC powder with 3 wt.% Al_2O_3 and 6 wt.% Y_2O_3 was ball milled in isopropanol with SiC balls for 24 hours. The suspension was dried, subsequently sieved through 25 μm sieve screen in order to avoid hard agglomerates. The samples were hot pressed at 1850°C/1 h under mechanical pressure of 30 MPa in N_2 atmosphere. Hot pressed samples were subsequently annealed under various time/temperature conditions given in Table 1. After sintering and annealing the specimens were cut, polished to a 1 μm finish, and plasma etched.

The density was measured by Archimedes method in water. The phase identification of the sintered samples was performed by means of X-ray diffractometry (Philips X`Pert Pro) using CuKα radiation. The microstructures of polished and plasma-etched specimens were studied using scanning electron microscopy (JEOL JSM-7000F).

Hardness was determined by Vickers indentation (hardness testers LECO 700AT) under a load of 0.98 N to 98.1 N for 10 s and calculated by Eq. (1):

$$HV = \frac{1.8544 \text{ x } P}{d^2} \text{ (MPa)} \quad (1)$$

where HV - Vickers hardness, P- indentation load, d - average of the diagonal length of indent.

The dynamic Young's modulus was estimated by impulse excitation of vibration. Measurements were taken as a function of temperature between room temperature and 1000°C with the commercially available system (RFDA-HT 1750, IMCE, Belgium). The fracture toughness was determined by the Single Edge V- Notched Beam (SENVB) method [17]. Seven samples were tested for each annealing batch. In the case of a 4-point flexure with spans of 40 and 20 mm, the fracture toughness is then calculated by Eqs. (2) - (4):

$$K_{IC,SENVB} = \sigma\sqrt{aY} = \frac{F}{B\sqrt{W}} \cdot \frac{S_1 - S_2}{W} \cdot \frac{3\sqrt{\alpha}}{2(1-\alpha)^{1.5}} \cdot Y \quad (2)$$

$$Y = 1.9887 - 1.326\alpha - \frac{\left(3.49 - 0.68\alpha + 1.35\alpha^2\right)\alpha(1-\alpha)}{(1+\alpha)^2} \quad (3)$$

$$\alpha = \frac{a}{W} \quad (4)$$

where K_{IC} - fracture toughness, σ - fracture strength, F - fracture load, B - specimen thickness, W - specimen width, S_1 - outer span distance, S_2 - inner span distance, a - average V - notch length, α - relative V - notch depth, Y - stress intensity shape factor.

The strength was measured using specimens with dimensions of 3x4x45 mm, tested in the four point bending mode. The specimens were ground by 15 μm diamond wheel before testing. The two edges on the tensile surface were rounded with a radius about 0.15 mm in order to eliminate failure initiated from an edge of the specimen. The specimens were tested in a four point bending fixture (inner span of 20 mm and an outer

span of 40 mm) with the crosshead speed of 0.5 mm/min at ambient temperature and atmosphere. The flexural strength is then calculated by Eq. 5:

$$\sigma_B = \frac{3}{2} \cdot \frac{F(S_1 - S_2)}{b.h^2} \quad (5)$$

where b - sample width and h - sample height.

The characteristic flexural strength and Weibull modulus were computed using two-parameter Weibull distribution. Fractographic analysis of broken bend specimens was used to characterize the fracture origins, their location, size, shape and chemical composition.

RESULTS AND DISCUSSION

In Table 1 the density and phase composition after sintering and annealing are shown. The hot pressed sample without annealing had the highest density. The density was decreased from 3.220 to 3.189 g.cm^{-3} by increasing the annealing temperature. Phase analysis of the hot pressed SiC-HP and annealed materials SiC-AN1650 by XRD showed β-SiC as a major phase. The SiC-AN1850 material contained α-SiC as a major phase. The X-ray pattern of the sintered sample SiC-HP and annealed sample SiC-AN1650 showed that $Y_3Al_5O_{12}$ (YAG) was formed as a liquid phase. In the case of annealed sample SiC-AN1850 there was $Y_{10}Al_2Si_3O_{18}N_4$ formed as a main secondary phase. Traces of Y_2O_3 and C were found.

Tab.1. The density and phase composition of SiC after sintering and annealing.

Specimen	Conditions	Density [g.cm^{-3}]	Phase composition
SiC-HP	HP:1850°C/1h	3.220	SiC, $Y_3Al_5O_{12}$, C
SiC-N1650	HP:1850°C/1h+ AN:1650°C/5h	3.208	SiC, $Y_3Al_5O_{12}$, Y_2O_3
SiC-N1850	HP:1850°C/1h+ AN:1850°C/5h	3.189	SiC, $Y_{10}Al_2Si_3O_{18}N_4$, Y_2O_3, C

Figure 1a shows a representative SEM micrograph (plasma - etched) of sintered SiC-HP. The microstructures of hot pressed SiC-HP and SiC-AN1650 material annealed at 1650°C (Fig.1b) consist of fine submicron-sized equiaxed SiC grains with a low aspect ratio (1.03). The nearly equaixed nature of the SiC grains and the core-rim substructure within the SiC grains are evident (Fig.1d). No visible effect of the heat-treatment at 1650°C was found on the microstructure of the material. All the materials additionally contain an intergranular phase in the form of a very thin grain boundary films, and in the form of triple points, with a size up to circa 0.5 μm. The microstructure of the SiC material is significantly changed after post-sintering high temperature treatment at 1850°C, Fig.1c. It has bimodal distribution and consists of elongated SiC grains with higher aspect ratio (4.41) and with smaller SiC grains. The above results clearly demonstrate that β-α phase transformation is key for the growth of high aspect ratio SiC grains. During LPS, dissolution of SiC in the melt takes place, enabling the solution/precipitation sintering mechanisms. In micrographs of plasma – etched samples, the reprecipitation of material on the undissolved ,,cores" of the α-SiC grains is obvious [8]. In samples that are rich in β-SiC, the solution/precipitation process is accompanied by the phase transformation from β-SiC to α-SiC. The α-SiC grains exhibit anisotropic grain growth.

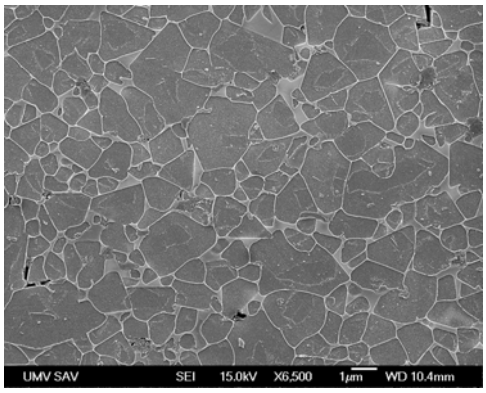

Fig.1a. SEM micrograph of sintered SiC (1850°C/1h).

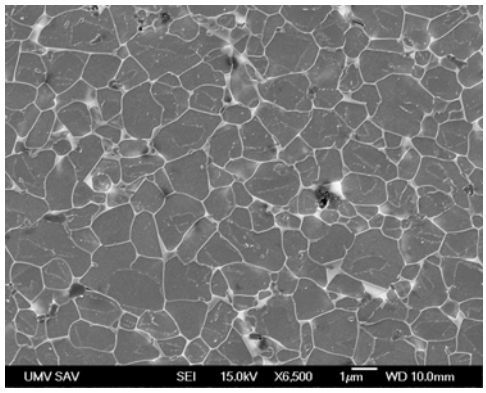

Fig.1b. SEM micrograph SiC annealed at 1650°C/5h.

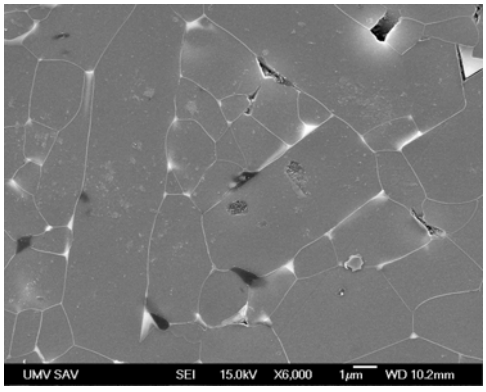

Fig.1c. SEM micrograph SiC annealed at 1850°C/5h.

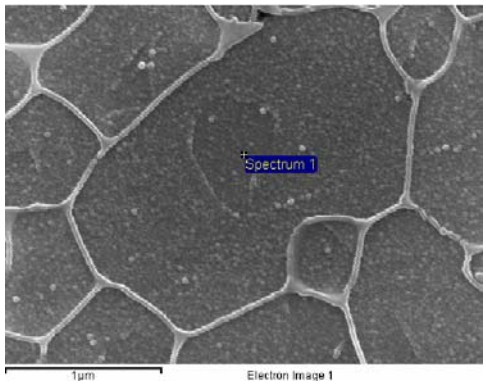

Fig.1d. „Core-rim“ structure of SiC grain in the hot pressed microstructure.

Tab.2. Mechanical properties of sintered and annealed SiC ceramics.

Material	HV 0.1 [GPa]	K_{IC} [MPa.m$^{1/2}$]	E [GPa]	σ_0 [MPa]	m
SiC-HP	26.9 ± 0.6	3.2 ± 0.2	422	387.61	5.66
SiC-AN1650	23.7 ± 0.2	3.6 ± 0.5	420	424.11	9.51
SiC-AN1850	25.8 ± 0.3	4.7 ± 0.3	410	142.59	2.06

The mechanical properties of prepared materials are summarized in Table 2. Vickers hardness did not show any difference between sintered and annealed samples. It can also be noticed that the measured hardness decreases with an increase in load, Fig.2. This is a well-known phenomenon of ceramic materials called indentation size effect (ISE) [18]. During annealing, the average grain size (G) increases in all systems, hence invoking Hall-Petch like H vs. $G^{-1/2}$ behaviour, one can expect a decrease in hardness (H) values with increasing average grain size. However, in poly-crystalline materials containing a glassy grain boundary and intergranular phases, after thermal treatment, reduction and crystallization of the secondary phases generally improve the hardness of the material

[19,20]. Hence, there seems to be a trade-off between glassy phase removal and grain coarsening effect.

The dynamic Young's modulus slightly decreased with temperature for all prepared samples, Fig.3. No variation of the Young's modulus due to the heat treatment has been observed. The Young's modulus varied from 400-420 GPa and is in agreement with other literature data reported for LPS-SiC ceramics [21,22].

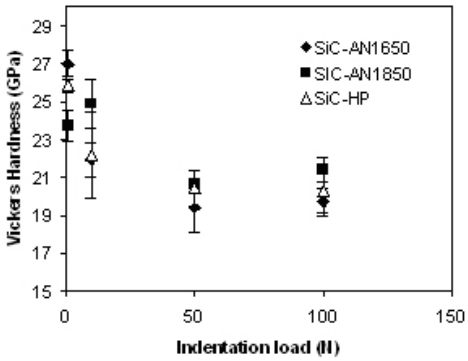

Fig.2. Dependence of Vickers hardness on applied indentation load.

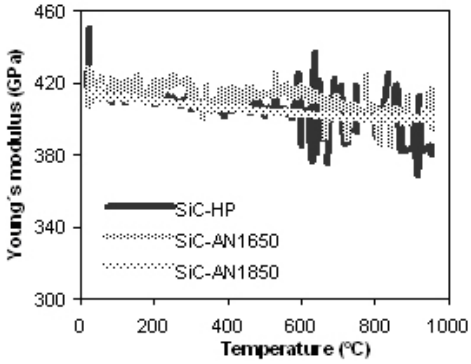

Fig.3. Dependence of dynamic Young's modulus on temperature.

In fine-grained globular microstructure of SiC-HP, the fracture toughness had a value of K_{IC}= 3.2 ± 0.2 MPa.m$^{1/2}$. By annealing at 1650°C the fracture toughness was 3.6 ± 0.5 MPa.m$^{1/2}$. In plateled microstructure (SiC-AN1850) a higher fracture toughness was obtained (4.7 ± 0.3 MPa.m$^{1/2}$). Microfractographic observations of the fracture surface and fracture profiles have shown that the crack propagation was controlled by mixed inter- and transgranular failure in all materials with a slightly higher intergranular portion in the system annealed at 1850°C/h. Crack deflection and crack bridging or crack branching were identified as the main toughening mechanisms in this material. Such toughening mechanisms are probably responsible for the higher fracture toughness. This is in agreement with the results of similar investigations [7,23].

The results of the statistical analysis of the bending strength using the Weibull statistics are shown in Fig.4. The characteristic strength and Weibull modulus were 387 MPa and 5.66 for SiC-HP, 424 MPa and 9.5 for SiC-AN1650 and 142 MPa and 2.1 for SiC-AN1850, respectively. The bending strength decreases with an increase of annealing temperature and aspect ratio of SiC grains. The highest strength (401 MPa) was observed for SiC-AN1650. The higher value of the Weibull modulus of the specimens in the case of low characteristic strength indicates that defects with a similar size, geometry and location are responsible for the strength degradation.

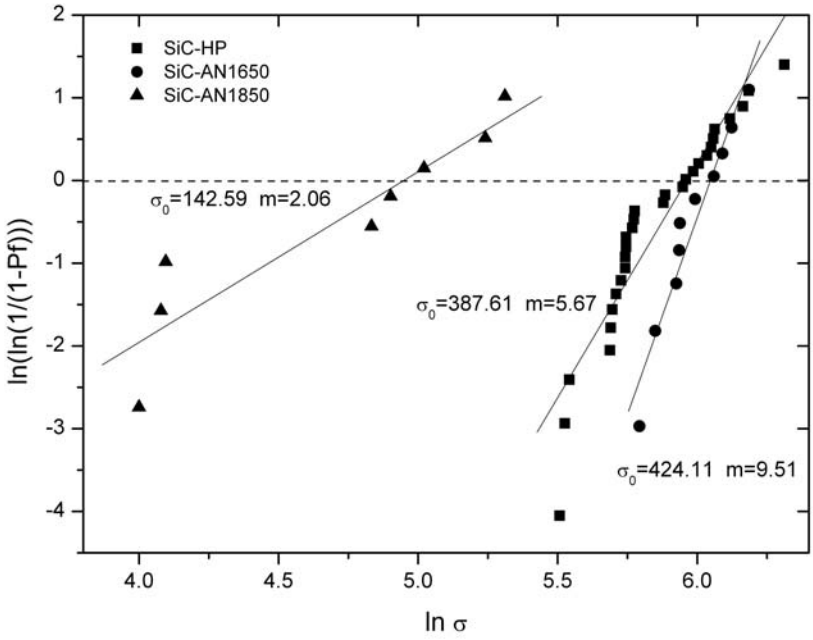

Fig.4. Weibull plot of hot pressed and annealed SiC.

Macrofractographic observations have shown that the fracture origins are often during processing defects seen mainly in the form of pores and clusters of pores (Fig.5). The fracture initiation sites are located predominantly in the volume of the specimens, sometimes out from the tensile surface. The size of fracture origins is resting in the interval from 5 μm to 500 μm. For the system SiC-AN1850, processing flaws as the fracture origin were found in almost all specimens. The presence of the flaws cause the low value of characteristic flexural strength.

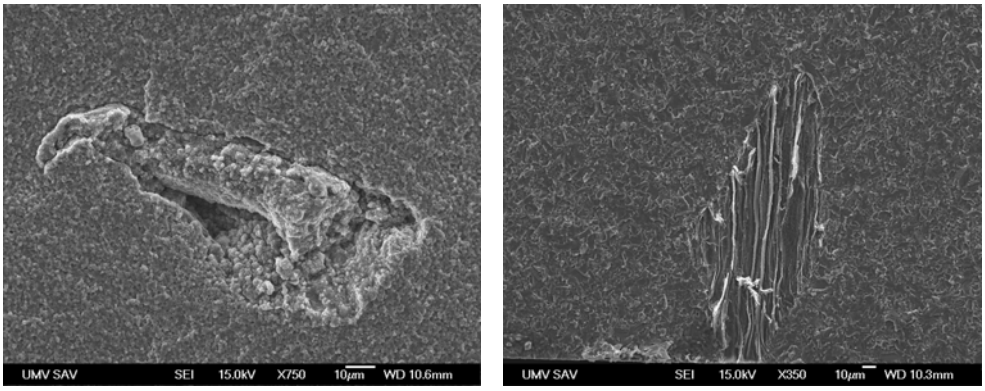

Fig.5. Characteristic fracture origins: pores and SiC agglomerates, SEM.

CONCLUSION

The influence of annealing on microstructure and mechanical properties (namely Young's modulus, Vickers hardness, fracture toughness) of liquid-phase-sintered SiC was investigated. The main results are the following:

- The microstructures of hot pressed SiC-HP and SiC-AN1650 material annealed at 1650°C consist of fine submicron-sized equiaxed SiC grains with a low aspect ratio (1.03). The microstructure of the material after the post-sintering high temperature treatment at 1850°C was significantly different. It has bimodal distribution and consisted of elongated SiC grains with a higher aspect ratio (4.41) and with smaller SiC grains. Annealing at higher temperature results in the β-α transformation, which is accompanied by α grain growth and a change of grain shape.
- The annealing at 1650°C and 1850°C has no influence on the Vickers hardness values and Young's modulus of the studied materials;
- The fracture toughness values were in the interval from 3.2 to 4.7 MPa.m$^{1/2}$, the highest value was identified for material annealed at 1850°C/5 h. The main toughening mechanisms of crack deflection, crack bridging and crack branching are responsible for the toughness improvement;
- The bending strength decreased with an increasing of annealing temperature from 1650°C to 1850°C. The strength values are degraded by processing flaws present in the investigated materials having different size from 5 μm to 500 μm. After eliminating these defects significant strength improvement can be expected.

Acknowledgement

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