Original Article

Silicon carbide hot pressing sintered by magnesium additive: microstructure and sintering mechanism

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A B S T R A C T

Silicon carbide was hot pressing sintered at 1300 °C/30 MPa by using magnesium additive. Microstructure and sintering mechanism are studied. Result shows that the hot pressing sintered sample composed of both α-SiC and β-SiC, indicating that no polypolytype transition has happened. Magnesium with stacking faults is located on the silicon carbide matrix as second phase particles. Dislocations and stacking defaults are initiated from grain boundaries and move toward the interior. Micropores locate on grain boundaries, substructure and triple grain junction, revealing a boundary diffusion mechanism. Long-range dislocations in grains and substructures in the lattice confirm a power-law creep mechanism.

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1. Introduction

Silicon carbide offers excellent ceramic properties such as creep resistance, chemical stability, higher modulus, hardness and strength even at high temperature owing to its extra-strong covalent bond [1,2]. So it is widely used in various industrial applications, including metallurgy, aerospace, environmental area, nuclear power plant and semiconductor industry [3]. However, due to the strong covalent binding energy between Si and C, silicon carbide is hard to be sintered, resulting in a high sintering temperature more than 1600 °C with conventional additives, such as B₄C and Al [2–5]. The high temperature not only increases energy consumption, but also brings potential safety hazards. Therefore, it is essential to develop high-quality sintered silicon carbide by more effective additives.

There is no doubt that liquid phase additives are more efficient than solid phase additives in lower temperature which act as a binder [6,7]. Aluminum is a most widely used liquid phase additive in silicon carbide sintering. However, compositions such as boron, carbon or boron carbide must be added, resulting in a large content of impurity [8]. According to the results reported by Huang et al. [9] and Easton et al. [10], reaction products between silicon carbide and magnesium/aluminum have a crystal structure closer to magnesium.
Industrial silicon carbide powder (purity >99%, average size of 3.31 μm measured by a laser particles analysis) was used as the raw material and magnesium alloy powder (average size of 86.4 μm) was used as sintering additive. XRD patterns, phase content and SEM observations are presented in Fig. 1.

Fig. 2 shows preparing process and heating schedule of the ceramic. The powders were mixed homogeneous followed by sintering at 1300 °C/30 MPa for 2 h, then cooled down to the ambient temperature in furnace. Bulk density of the hot pressing sintered sample was determined by the Archimedes method in water, and the relative density (RD) could be calculated as the quotient of bulk density to theoretical density (TD = 3.08 g/cm³). Microhardness (H_V) and elasticity modulus (E) were measured with a nano indenter (NanoIndenter XP). Flexural strength (σ_f) was measured on rectangular bars (3 mm × 4 mm × 30 mm) by using a three-point bend fixture with a span of 20 mm. The crosshead speed was 0.5 mm/min. Fracture toughness (K_{IC}) was measured on single-edge notched beam (SENB) bars (3 mm × 4 mm × 20 mm) by using a three-point bend fixture with a span of 16 mm. The notch was made with 1.5 mm in depth and 0.2 mm in width. The crosshead speed was 0.05 mm/min. Five measurement runs were carried out to determine the average value of every properties. XRD analyses were conducted at ambient temperature. The scanned angles were ranging between 30° and 70° with a step of 0.02°/s. Microstructural observations were carried out on a FEI Tecnai F30 G² TEM with a SAED attachment. Crack prolongation was observed using a LEO1450 SEM.

3. Results

3.1. Macroscopic appearance and properties of silicon carbide ceramic

Fig. 3 shows the macroscopic appearance and SEM image of the hot pressing sintered 2-in. sample. Clearly, pores can hardly be observed in the silicon carbide ceramic, indicating that the ceramic has already been dense. Relative density and mechanical properties of the hot pressing sintered sample were listed in Table 1. It shows that the relative density of the hot pressing sintered sample has reached 92.76 ± 1.24%. It is well known that the sintered ceramic could consider to be dense when its relative density RD > 90% [14]. Particularly, all open pores are closed when RD ranging from 92% to 95% [15]. Thus the specimen after hot pressing sintering is dense enough without open pores. As the response of high relative density, the microhardness (H_V) was 6.7 ± 1.3 GPa, elastic modulus (E) was 236.3 ± 24.5 GPa, bending strength (σ_f) was 172.3 ± 32.0 MPa and fracture toughness (K_{IC}) was 4.6 ± 0.3 MPa m^{1/2} for the hot pressing sintered sample. All the mechanical properties are comparable to the previous
works [16,17]. At a fundamental level, elastic modulus is a measure of the bond strength between atoms and microhardness is governed by bonding strength, cohesive energy and crystal structure of materials [18]. Therefore it can be concluded that the current study has realized atomic bonding, namely, the sample is successfully sintered.

### 3.2. Microstructure of silicon carbide ceramic

Fig. 4a shows that the hot pressing sintered sample composed of α-SiC, β-SiC, magnesium and a little MgO. The (1 2 1) diffraction peak of MgO is broadened obviously, indicating that the size of MgO particles is smaller [19]. The evaluation of polytype proportion has been carried out and is presented in Fig. 4b. It should be noted that the polytype content is close to that of raw material, indicating that none crystal transition happened. Since the β-SiC to α-SiC transformation appears around 2000 °C [2], a lower temperature in this work cannot provide the transition. Fig. 4c shows typical microstructure of the sintered sample. It composed of elongated α-SiC (defined as aspect ratio >2 in this work, particles 1–13), quasi-equiaxed β-SiC (particles 14–22) and some equiaxed second phase particles (particles 23–39). All particles are quasi-homogeneously distributed. The ratio of α-SiC to β-SiC grains shown in Fig. 4d is fit that of Fig. 4b. Particle size data of Fig. 4c are shown in Fig. 4e. As a result, the width of α-SiC grains is relatively equal to the equivalent diameter of β-SiC grain size, which is obviously larger than that of second phase particles. The aspect ratio of α-SiC is ranging from 2.4 to 8.4, with an average value of 4.8. Fig. 4f and g shows microstructures of α-SiC and β-SiC respectively. Dislocations exist in both kinds of grains and some of them have evolved into dislocation walls (Fig. 4f). The dislocation structures can be regarded as evidences of
plastic flow. Moreover, a large number of parallel striations can be observed in both $\alpha$-SiC and $\beta$-SiC grains, which is identified as plane defects in Ref. [20].

3.3. Characterization of second phase particle

In order to further understand microstructure of the hot pressing sintered sample, the second phase particles must be characterized firstly. Fig. 5a shows TEM micrograph of a typical second phase particle, indicating that the grain boundary between the second phase particle and silicon carbide grain is not as straight as that between silicon carbide grains. Fig. 5b shows Selected Area Electron Diffraction (SAED) result of the second phase particle. It is clear that the second phase in Fig. 5a is magnesium. Fig. 5c and d are high resolution transmission electron microscopy (HRTEM) images of the particle in Fig. 5a. Combining with the SAED pattern in the right-down corner, Fig. 5c indicates that a large number of stacking defaults existed in the magnesium grain. Meanwhile, dislocations are aggregate at grain boundary, resulting in an intense lattice distortion near the grain boundary. Moreover, some smaller particles with several nanometers can be observed in both Fig. 5c and d, which may have an effect on pinning dislocations. Fig. 5d shows structure of grain boundary.

Fig. 4 – Characterization of the sintered sample: (a) XRD patterns; (b) determination of the polytype content calculated by (a); (c) distribution of particles; (d) determination of the polytype content according to (c); (e) size of particles and aspect ratio of $\alpha$-SiC grains; (f) and (g) are TEM observations of $\alpha$-SiC and $\beta$-SiC grains respectively.
between magnesium and silicon carbide and further characterizations are shown in Fig. 6. Dislocations and stacking faults are observed in magnesium next to the grain boundary. SAED shows a feature of stacking fault and some diffraction spots marked by yellow arrows reveal that new phases formed on grain boundary (Fig. 6a). There are misorientations between (1), (2) and (3) regions in Fig. 5d, accompanied with a nano-sized disordered region (Fig. 6b). The disordered region can also be observed in region (4). The formation of such microstructure may be mainly attributed to the dissolution and precipitation reaction of magnesium [20]. Region (6) and particle (7) in Figs. 5d and 6d can be defined as Mg₂C₃ according to crystalline interplanar spacing. The irregularly curved grain boundaries in Fig. 5a indicate the pinning effect of smaller particles on matrix grains.

4. Discussion

4.1. Sintering mechanisms

Fig. 7 focuses on substructure of the sintered sample, including dislocations, stacking faults and micropores. According to Fig. 7b, stacking faults of the α-SiC grain are approximately along (10 – 10) plane. Micropores locate on not only grain boundaries but also boundaries of substructure (Fig. 7a). Fig. 8a shows a β-SiC grain with a micropore on its boundary and Fig. 8b is magnification map of Fig. 8a. The micropore locates on triangle grain is the apparent evidence for boundary motion during grain growth. The dislocations inside silicon carbide grain are initiated from grain boundaries and moved...
toward the interior of the grain. A network of dislocations inside silicon carbide is found in the sintered sample. It is related to sliding motion and propagation of dislocations under the high temperature and stress [21]. Microstria- tions are found on grain boundary where the dislocation nucleates, suggesting that plastic deformation has performed. An obvious dislocation loop is discovered near by the grain boundary.

Fig. 5a focuses on staking faults in a β-SiC grain. It was suggested that both isolated stacking faults and dislocation
Fig. 8 – TEM images of pores and dislocations: (a) bright field image; (b) magnification map of (a).

Fig. 9 – TEM images of stacking faults: (a) bright field image; (b)–(d) are magnification maps of (a) respectively.
loops formed at higher stress was ascribed to the precipitates sheared by \( a/2 <110> \) dislocations [22]. It can also be found that a large number of defects are concentrated at the corners of grains, which is supposed to play the role in adjusting the internal stress generated by plastic flow, thereby accommodating plastic flow and preventing the grains from intragranular deformation [23]. Fig. 9b–d shows details of region (1)–(3) in Fig. 9a respectively. Stacking faults are initiated from lattice distortion regions near grain boundary and expanded to interior of the grain. Fig. 9c shows the source of dislocation and stacking faults on a straight grain boundary. It appears that the density of stacking faults is much lower than that of corners as is shown in Fig. 9b. Fig. 9d focuses on a second phase particle with high density dislocations surrounded on the grain boundary of silicon carbide. It visually confirms the pinning effect of smaller second phase particles.

Seeing that opinions vary, mechanisms that commonly operate during liquid phase hot press sintering are diffusion (including volume, boundary and surface diffusion) [24], plastic deformation (by dislocation motion) [25] and particles rearrangement (by pore growth and grain-boundary sliding) [26]. For the sake of maintaining grain continuity, several mechanisms should be activated to accommodate plastic flow [27]. However, according to the result that little grain growth happened (Fig. 4e), the effects of grain-boundary migration and grain rotation seems very limited [25], thus particles rearrangement can be neglected.

Indeed, surface diffusion is suggested to be one of the main mass transport mechanisms in the intermediate stage of sintering. However, it may only work on continuous network pores. So the surface diffusion cannot play a key role in the destination process of sintered sample with closed pores (Figs. 7a and 8a). Both volume and boundary diffusion are belong to a pore driving mass transport mechanism. Since all the pores in Figs. 7a and 8a are located on grain or substructure boundaries, boundary diffusion may plays a key role in sintering. Shi et al. suggested that local boundary network would form in the initial and intermediate stage of sintering [26]. Thus, boundary diffusion will take place via the local boundary network. However, the densification process based on intrinsic diffusion mechanism is limited by the transport capabilities of boundaries [25].

It is no doubt that the dislocations intersecting with grain boundary would be fettered and impossible to move into the interior of grains [28,29]. Surprisingly, some long-range dislocations can be found in grains. It is logical to infer that the contribution of power-law creep mechanism is likely to be significant. On account of the results that there are both visible long-range dislocation and substructures in the lattice, the power-law creep mechanism can be confirmed [25,30].

4.2. Strengthening mechanisms

There is no doubt that dislocations, stacking faults and the second phase particles have strengthening effect on the sintered sample. Meanwhile, stacking faults may work as the induced nuclei of deformation twin and benefit the formation of twin in deformation process [20]. For the ceramic sample lacks of slip systems, plastic flow and grain boundary sliding can be realized by plastic yield [31]. It results in the formation of subboundaries under the presence of internal stress, which can refine grains and contribute to the improvement of the mechanical properties of the sintered sample [20]. Besides, the critical stress of dislocation loop is higher than that of stacking faults and Orowan strengthening mechanism is favored [32].

Defects can absorb partial crack propagation energy by self-deformation or pin cracks. They also have a passivated effect on crack tip, which results in a rise of the R-curve [33]. Furthermore, the complicated dislocation lines may be considered as second refinement on matrix grains. Therefore, the defects act as effective barriers for crack propagation. In this way, fracture toughness of the sintered sample is improved. Propagation of cracks introduced by hardness indentation is shown in Fig. 10. Owing to the defects above, the propagation behavior is prevented by deflecting, branching and bridging, which are common methods to prevent crack growth [34].

5. Conclusions

In the present paper, silicon carbide was hot pressing sintered at 1300 °C/30 MPa for 2 h with magnesium additive. XRD and TEM analyses indicated that there is no polypeptide transition and only a little \( \text{Mg}_2\text{Si}_3 \) formed. Silicon carbide grains and particles distribute homogeneously. A number of dislocations and stacking faults are found in both \( \alpha\)-SiC and \( \beta\)-SiC. Magnesium with high density stacking faults acts as the second phase particle. Dislocations entangle near the boundaries between magnesium and silicon carbon. Some tiny \( \text{Mg}_2\text{Si}_3 \) also observed on the boundaries. Substructures such as dislocation structures, stacking faults are found in the silicon carbide grains, dislocation loops are found on or near the grain boundaries. All of the substructures have a strengthening effect on the sintered sample. Micropores are observed on both grain boundaries and substructure boundaries, indicating a boundary diffusion mechanism. Long-range dislocations in grains and substructures in the lattice confirm a power-law creep mechanism.

Conflicts of interest

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