The effect of graphite type on the growth of dense SiC ceramics prepared by the HTPVT method

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Abstract. Dense silicon carbide (SiC) ceramics were prepared by the high-temperature physical vapor transport (HTPVT) method at 2300°C using three types of graphite materials, namely common graphite (CP), isostatic graphite (IG), and graphite paper (GP), as crucible lids. The results indicated that the nucleation of SiC on CG was much easier than that on GP at the initial stage, but the polycrystalline growth on GP was faster. Moreover, the polycrystalline SiC ceramics growing on CG and IG lids were smaller than that grown on GP lid because many pores appeared at the interfaces between the grown polycrystalline SiC and CG and IG lids. As a result, the strength of the grown dense SiC ceramics on GP lid was about 8%–20%, higher than the strength of ceramics grown on the CG and IG lids.

1. Introduction
Dense silicon carbide (SiC) ceramics are used in high-performance structural components, due to their lucrative high-temperature properties, such as high-temperature strength, corrosion resistance, good thermal conductivity, oxidation resistance, and a relatively low thermal expansion coefficient [1, 2]. However, due to the covalent nature of Si–C bonding and low self-diffusion coefficient, fabrication of dense SiC ceramics needs sintering aids, which prohibits their large-scale application in the industry [3-6].

Presently, methods used to fabricate high-density SiC ceramics, such as reaction sintering, hot-press sintering, and liquid-phase sintering, are realized at moderate temperatures. In spite of distinct advantages of low sintering temperature (1400–1600°C) and ease in scaling up the production, some sintering aids are still needed to promote the sintering of SiC powders [7-10]. Thus, sintering aids become a “weak” secondary phase in the fabrication of SiC ceramic products. In addition, the abundance of voids in sintered SiC ceramics would degrade the high-temperature performance of SiC ceramics seriously [11-16]. Therefore, further studies of ways to fabricate high-density SiC ceramics without additives is still needed. Although Dai et al. [17] reported that the high-temperature physical vapor transport (HTPVT) method could be used to fabricate high-density SiC ceramics without additives, their mechanical properties are poor due to their large grain size, and the effects of some processing parameters still need further investigation.

This study is aimed to study the effects of the materials of crucible lids, namely common graphite (CP), isostatic graphite (IG), and graphite paper (GP) on the growth characteristics and properties of dense SiC. The above three types of graphite were used to fabricate high-density SiC ceramics using a modified HTPVT method.
2. Experimental

2.1. Raw materials
Three types of graphite materials, namely CP, IG, and GP, were used as crucible lids. Commercial SiC powders (average size, 120 μm; purity, 99.9%; specific surface area, 0.018 m²g⁻¹; Zaozhuang Liyuan SiC Co., Ltd., Zaozhuang, China) were used as starting materials in the experiments. SiC ceramics were grown on the graphite lid in a medium-frequency vacuum induction furnace (3.5 kHz, Model ZGRS-160/2.55 Jinzhou Electric Furnace Co., Ltd., Jinzhou, China).

2.2. Fabrication process
Dense SiC ceramics were fabricated by the HTPVT method at 2300°C with three types of graphite materials as crucible lids. The growth process was comprised of the following steps. Firstly, a gas pressure of 10⁻² Pa and an elevated temperature between 800 and 1000°C were applied to reduce nitrogen contamination in the furnace. Subsequently, the temperature was gradually increased to the growth temperature in a high-purity argon atmosphere with a pressure of 5 × 10⁴ Pa. Thirdly, the temperature at the bottom of the crucible was maintained at 2350°C, and the system pressure of argon gas was gradually decreased to 4 × 10³ Pa to trigger the growth of SiC on the crucible lid. After a 2h growth, 8-mm thick polycrystalline SiC specimens of 10mm in diameter were obtained.

2.3. Characterization
The microstructures of graphite materials and SiC specimens were observed using the scanning electron microscope (SEM, JEOL JSM-6460, Japan). The graphitization degrees of the graphite materials and the phase formations of the specimens were characterized by x-ray diffraction (XRD, Bruker D8 ADVANCE, USA) using Cu Kα radiation. The resistance of the specimens was measured by the digital four-probe tester (DFPT, JG ST2253, China), and their densities were determined by the Archimedes method.

3. Results and discussion

3.1. Characterization of different types of graphite lids
Figure 1 shows the surface morphologies of three types of graphite. The surface of GP was the most homogenous, with only a few scratches (figure 1c). On the contrary, the surfaces of CG (figure 1a) and IG (figure 1b) had many macro-pores. Especially, on the surface of GP, the pores were 100–200 μm in diameter. As an important kinetic factor, these macro-defects could inevitably affect the nucleation and growth of polycrystalline SiC.

Figure 2 shows the XRD patterns of the three types of graphite. Only two diffraction peaks, (002) and (004), were seen on GP, both of which were sharper and stronger than those on CP and IP, indicating that GP had a higher graphitization degree and preferred orientation. Moreover, the preferred orientation was the [002] direction. On the XRD patterns of CP and IP, besides the (002) and (004) peaks, the prominent (101) and (100) peaks appeared, indicating that their crystallographic orientations were isotropic.
Figure 1. SEM images of the surface morphologies of the three types of graphite: (a) CP, (b) IG, and (c) GP.

Figure 2. XRD patterns of the three types of graphite materials: (a) CP, (b) IG, and (c) GP.

The graphitization degree \( G \) was estimated using the following formula:

\[
G = \left( \frac{0.334 - d_{002}}{0.0086} \right) \times 100\%
\]  

(1)

where \( G \) is the graphitization degree, and \( d_{002} \) is the crystal plane distance of graphite (002) planes obtained from the XRD results. The \( d_{002} \) and calculated \( G \) of the three types of graphite are listed in table 1. The graphitization degree of GP was shown to be higher than that of CG and IG.

| Sample | CG   | IG   | GP   |
|--------|------|------|------|
| \( d_{002} \) (nm) | 0.3339 | 0.3335 | 0.3325 |
| \( G \) (%)         | 0.7093  | 0.7558  | 0.8721  |

3.2. Effects of different types of graphite lids on the nucleation and growth of SiC
Figure 3 shows the SEM images of SiC growth for 2 min on different types of graphite lids. The nucleation density of SiC on the CG and IG lids was much larger than that on the GP lid, demonstrating that it was much easier for SiC to nucleate on CG and IG lids than on the GP lid. Because of the much smaller nucleation density of SiC on CP, more vapor SiC-containing species integrated into the lattice of the existing SiC nuclei, accelerating the growth of SiC nuclei, as demonstrated in figure 3c. This distinctive nucleation characteristic was attributed to the different characteristics of the three types of graphite lids.

![Figure 3](image.png)

**Figure 3.** SEM images at the beginning of SiC growth at 2300°C for 2 min on different types of graphite lids: (a) CG lid, (b) IG lid, and (c) GP lid.

The nucleation and growth of SiC by HTPVT are complicated physical and chemical processes, which mainly consist of the dissociative sublimation of the source materials (SiC powder), the mass transport of the Si and C containing vapor species, and the deposition of the vapor species [18-20]. In this study, the effect of different graphite lids on the deposition of the vapor species needed to be investigated because the graphite lid could not affect other processes. During the deposition of the vapor species, the solid SiC was formed mainly through the following reactions [21]:

\[
\text{SiC (gas)} \rightarrow \text{SiC (solid)} \tag{2}
\]
\[
\text{SiC}_2 \text{(gas)} + \text{Si (gas)} \rightarrow 2\text{SiC (solid)} \tag{3}
\]
\[
\text{C (solid)} + \text{Si (gas)} \rightarrow \text{SiC (solid)} \tag{4}
\]
\[
\text{C (solid)} + \text{Si}_2\text{C (gas)} \rightarrow 2\text{SiC (solid)} \tag{5}
\]

In reactions (2) and (3), SiC (gas), SiC₂, and Si (g) resulted from the dissociative sublimation of the SiC powder, indicating that the deposition of SiC was a heterogeneous nucleation process affected by the surface energy of the graphite lid. The lower the surface energy, the difficult the nucleation. However, in reactions (4) and (5), the component of solid C came from the graphite lid, indicating that the deposition of SiC was accompanied by the nucleation process, which was determined by the reactivity of the graphite lid. The lower the reactivity, the more difficult the nucleation.

As shown in Section 3.1, different types of graphite lids owned different surface morphologies and crystallographic orientations. CG and IG had macroscopic isotropy because of the random distribution of the graphite flakes. On the contrary, GP had high macroscopic anisotropy and a preferred orientation of [002], indicating that the graphite flakes were laminated parallel to the surface. Because
the surface energy of the (002) of graphite flake was the lowest and the specific surface area of GP was also the lowest among the three types of graphite lids, the number of active nucleation sites on the GP lid was far lesser than that on the CG and IG lids. Moreover, the reactivity of carbon atoms in GP was the lowest because the graphite degree of GP was the highest. It was much more difficult for carbon atoms in GP to react with the Si-containing vapor species to form the SiC molecules. As a result, the nucleation density of SiC on GP lid was the smallest. CG was much more beneficial for SiC nucleation because its specific surface area was larger, and the graphite degree was lower than those of IG. Therefore, the nucleation density of SiC on CG was higher than that on IG.

![SEM images of the surface morphology of SiC ceramics grown at 2300°C for 60 min on different types of graphite lids: (a) CG lid, (b) IG lid, and (c) GP lid.](image)

Figure 4 shows the SEM images of the surface morphology of SiC ceramic grown at 2300°C for 60 min on different types of graphite lids. Many protrusions and pores were observed on the surface of the SiC ceramics grown on the CG and IG lids, while almost no such defects were found on the SiC ceramics grown on the GP lid. These defects of protrusions and pores might prolong into the fabricated SiC ceramics, degrading the excellent properties of SiC ceramics. Therefore, the origin of these defects needed to be determined to fabricate high-performance SiC ceramics.

The fabricated SiC specimens on the three types of graphite lids were cut longitudinally to investigate the origin of the protrusions and pores. The interfaces between the fabricated SiC ceramics and different graphite lids show many pores of larger sizes in SiC/CG lid and SiC/IG lid interfaces, but less in the SiC/GP lid interface. The number and size of the pores were consistent with those in the graphite lid. In the CP lid, the number and size of the pores were the largest; therefore, the SiC polycrystals were the largest as well. The number and size of the pores were the smallest in the GP lid; therefore, those in the SiC fabricated on GP lid were also the smallest. This phenomenon could be attributed to the transport of Si-containing vapor species during the SiC growth. The dissociative sublimated Si-containing species were transported from the hot zone (SiC polycrystals) into a cooler zone (graphite lid) because of a large temperature gradient in the SiC polycrystals and graphite lid. This led to the formation of pores at the interface, which extended into SiC polycrystals [22]. As GP was produced by the lamination of imperforate graphite flakes, no pores existed in the graphite flake of the GP lid for the Si-containing species to transport. Therefore, almost no visible pore defects were found. As for CG and IG, a large number of pores in the lids favored the transport of Si-containing vapor species, leading to the formation of pores in the SiC ceramics. According to the edge effect, the
pore diffusion rate was proportional to the edge length of holes (or area). Therefore, the pores moved much faster in the CG and IG lids than in the GP lid, resulting in the appearance of many pore defects (figure 4a and 4b).

![Figure 5. SEM images of the interfaces between the fabricated SiC ceramics and different graphite lids: (a) CG, (b) IG, and (c) GP.](image)

3.3. Effects of different types of graphite lids on the property of the fabricated SiC ceramics

The densities, strengths, and resistances of the SiC specimens fabricated on the CG, IG, and GP lids are listed in Table 2. The density of SiC specimen fabricated on the GP lid was found to be the largest, while that on the CP lid was the smallest. This was consistent with the SEM results because the number of pores in the SiC specimen fabricated on the GP lid was the least while that on the CP lid was the largest, as illustrated in figures 4 and 5. Moreover, the strength of the fabricated SiC specimens had the same change trend with the density. The SiC specimen fabricated on the GP lid had the highest strength because of the least crystal defects (pores), which was about 8–20% higher than that fabricated on the CG and IG lids. The tested resistances demonstrated that the resistance of the SiC specimen fabricated on the CP lid was the least while that fabricated on the CP lid was the largest. The lesser the pores, the smaller the resistance because the resistance of materials was sensitive to the pores. Therefore, the obtained resistance value was rational.

| Sample | CG lid | IG lid | GP lid | Standard deviation |
|--------|--------|--------|--------|--------------------|
| Density (g/cm³) | 3.186 | 3.194 | 3.208 | ±0.02 |
| Strength (MPa) | 241 | 269 | 290 | ±17 |
| Resistance (×10⁹ Ωcm) | 17.5 | 16.8 | 14.7 | ±0.2 |

4. Conclusions

Three types of graphite materials (CP, IG, and GP) were used as crucible lids to fabricate dense SiC ceramics using the HTPVT method. The results demonstrated that the nucleation density of SiC on the CG lid was the largest and that on the GP lid was the smallest at the initial stage. Moreover, the densities of grown polycrystalline SiC ceramics on the CG and IG lids were smaller than the densities of ceramics grown on the GP lid because many pores appeared at the interfaces between the grown polycrystalline SiC, CG, and IG lids. As a result, the strength of the dense SiC ceramics grown on the GP lid was about 8–20% higher than those grown on CG and IG lids.
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