PAPER

Silicon carbide low temperature sintering: the particle size effect of raw materials and sintering additive

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Abstract

Aiming at dense sintering of silicon carbide ceramic, magnesium alloy powder was taken as additive, and silicon carbide powders with two different particle size were sintered by the same hot pressure sintering process. Result shows that ceramic sintered by the powder with larger particle size is denser. Magnesium and carbon segregation is observed in the sample prepared by powder with smaller particle size, in which silicon carbide particles cannot be uniformly dispersed by sintering additives. However, sintering additives distribute homogeneously among silicon carbide particles in the sample prepared by powder with larger particle size, which can effectively play a bonding role. In the selection of liquid phase sintering additives, particle size matching of raw material and sintering additives should be emphasized.

1. Introduction

As a ceramic with excellent mechanical and thermal properties [1], silicon carbide is widely used in a large number of fields, such as porous ceramics [2, 3], composite materials [4, 5], microscopy technology [6], quantum research [7], nano science and technology [8] and optical components [9, 10]. Sintering is the most common method in producing silicon carbide ceramic, including pressureless sintering [11, 12], hot pressure sintering [13], spark plasma sintering (SPS) [14, 15], hot isostatic pressing sintering (HIP) [16], reaction sintering [17] and so on. For any of the methods aforementioned, silicon carbide powders are necessary raw material. Therefore, researchers have done a lot of researches on preparation of raw silicon carbide powders [18–20].

Particle size of raw silicon carbide has a determinative influence on the properties of ceramic under certain technological conditions [21, 22]. In conventional view, the smaller particles are, the better properties of the ceramic there will be, prepared under the same process conditions [23]. Therefore, a lot of researches are focusing on particle refinement [13, 23–26]. However, almost all the refining processes are along with problems including long time, high noise and potential safety hazards, which makes the simple SiC powder sintering process seem more complicated.

In this research, silicon carbide were sintered by two different starting powders with different particle size. The influence of particle size on density, microstructure, component distribution and phase structure of the sintered samples were investigated and sintering mechanisms were discussed.

2. Materials and methods

2.1. Raw materials

Silicon carbide powders (purity >99%) with two different particle sizes were taken as raw materials and 8 wt% magnesium alloy powder as additive (Mg ≥ 94.0 wt%, Al≈2.5 wt%–3.5 wt%). Average particle sizes of silicon carbide are 0.09 μm and 3.31 μm respectively, and average particle size of magnesium alloy is 86.30 μm.
2.2. Sample preparation

Silicon carbide powder and magnesium alloy powder were weighted by electronic balance and mixed by a three-dimensional mixing machine for 2 h. Powder with 0.09 μm silicon carbide particles was marked as Powder 1 and powder with 3.31 μm silicon carbide particles was marked as Powder 2. After mixing, the powders were cold compacted into a cylindrical graphite mold of 90 mm in diameter and 30 mm in thickness. Sintering stage was carried out in a hot pressure sintering furnace. Schematic diagram of experimental procedures is shown in figure 1. The heating profile consisted of a heating rate 15 °C min$^{-1}$ from room temperature to 1000 °C. The samples were then heated to the maximum temperature at 10 °C min$^{-1}$. Sintering was performed at 1300 °C for 2 h with pressure of 30 MPa under pure flowing argon atmosphere and freely cooled down to room temperature. Ceramics sintered by Powder 1 and Powder 2 are marked as Ceramic 1 and Ceramic 2, respectively.

2.3. Characterizations

The powders were measured using an ESJ-220-4B electronic balance. The particle size distribution was characterized using a laser particles analysis. The phase condition was characterized using an Ultima-IV XRD analysis with Cu target between 30° and 80° at a 0.02° s$^{-1}$ step at 35 kV/40 mA. Microstructure and component of ceramics were characterized using a LEO1450 scanning electron microscope (SEM) with an energy dispersive spectrometer (EDS) attachment. Further microstructural observations were carried out on a FEI Tecnai F30 G2 transmission electron microscope (TEM) with a SAED attachment. The density was measured by Archimede’s method [13, 14, 25, 27, 28].

3. Results

3.1. Characterization of powders

Figure 2 shows x-ray diffraction pattern and particle size distribution of powders after mixing. As shown in figure 1(a), there is no new diffraction peak observed comparing with each powder, which indicates that the composition of both powders are mainly consisted of silicon carbide and magnesium. In addition, the peak of Powder 1 is wider than that of Powder 2, indicating that the grain size of Powder 2 is smaller [23]. Figure 1(b) shows particle size distributions from 0 to 100 μm (Enlarged view of 0–10 μm was shown in the corner). Average particle size of Powder 1 is 1.15 μm and average particle size of Powder 2 is 3.95 μm, which is consistent with the particle size of raw materials and sintering additives after homogeneous mixing. Since the tested powders are randomly sampled, we can draw a conclusion that both powder can mixed homogeneous.

3.2. Density of ceramics

Figure 3(a) shows macroscopic appearances of Ceramic 1 and Ceramic 2. It is shown in the picture that ceramic 2 is thinner than ceramic 1, which indicates that ceramic 2 is much denser. It is also noted that some black structures of different sizes were formed in ceramic 1. Figure 3(b) compares density of ceramics, where Ceramic 1 has a density of 48.45% and Ceramic 2 has a density of 92.53%, which is contrary to common sense.

3.3. Microstructure of ceramics

In order to investigate mechanisms of difference in density, microstructure and composition should be observed. Figure 4 shows x-ray diffraction pattern of ceramics. On the one hand, compared with raw material powder, the orientation of sintered ceramics is more concentrated, and some peaks have disappeared. This is...
because, according to the principle of minimum energy, the grain orientation during the sintering process is deflected toward the densest row [29]. On the other hand, the main component of sintered ceramics remains stable of silicon carbide and magnesium. However, diffraction peaks of silicon carbide in Ceramic 1 are more than that in Ceramics 2. In addition, the crystalline transformation (the diffraction peak of 15R-SiC) occurs, which proves that the sintering process of the two ceramics is different. Weak peaks of Si and C can be observed in the XRD pattern of Ceramic 1, which prove slight decomposition happened during sintering process [30].
Figure 5(a) shows SEM image of Ceramic 1. It can be seen that particle size of Ceramic 1 is still small. However, there are microcracks between particles. As BSE image shown in figure 4(b), Region 1 is the inner black zone; Region 2 is the edge of black zone; and Region 3 is the grey zone. Table 1 presents component of regions in figure 5(b). It shows that Region 1 and 2 are carbon-enriched regions, where the content of Si and Mg is lower.

From the micro-morphology and BSE diagram and the element surface distribution in figure 6, we can see that the sintered ceramics not only have no obvious defects such as voids and cracks. The magnesium alloys additive is distributed between SiC, so sintering densification process can be realized.

### 4. Discussion

Figure 7 shows morphology and element distribution of Powder 1. It obvious shows that the distribution of magnesium is concentrated, which is caused by the large particle size of magnesium alloy. Since particle size difference between magnesium alloy and silicon carbide is too large, it is difficult for silicon carbide and magnesium alloys particles contact effectively. With the decrease of SiC particle size, the number of surface atoms increases rapidly and the specific surface area increases. Atoms on the surface are subjected to the asymmetric valence bond force of the neighboring internal atoms and the remote van der Waals force of other atoms. The force is not uniform and the valence bond is unsaturated. It results in the lack of coordination of surface atoms. As a result, atoms on the surface of particles get high surface activity. It becomes a thermodynamically unstable system and produces van der Waals bonds and chemical bonds between particles, which leads to the segregation of particles.

On the other hand, diffusion behavior of Mg follows (1) according to one-step diffusion control mode, however, it follows (2) according to grain boundary diffusion mode [27, 31, 32]:

\[
\frac{d(L/L_0)}{dt} = n \left( \frac{5.34 \gamma_2 bD_V}{kT G^3} \right) t^{n-1} n = 0.49
\]
\[
\frac{d(\Delta l/l_0)}{dt} = n \left( \frac{2.14 \gamma \Omega b D_k}{kT G^4} \right) t^{n-1} \Rightarrow n = 0.33
\]

(2)

Where \(d(\Delta l/l_0)/dt\) represents diffusion rate; \(\gamma\) represents surface tension (hypothetical isotropy), \(\Omega\) represents atomic volume; \(D_k\) and \(D_b\) represent diffusion coefficient of grain volume and boundary respectively, \(k\) is Boltzmann constant, \(G\) represents grain size and \(b\) represents thickness of grain boundary. It can be seen from the formula that as the particle diameter decreases, the grain boundary diffusion rate decreases more than the...
Intragnanuar diffusion. Therefore, a large amount of surface in Powder 1 effectively hinders the diffusion from magnesium alloys to silicon carbide.

Figure 8(a) shows the high resolution transmission electron microscope (HRTEM) micrograph of Ceramic 1 and figures 8(b)–(d) show related selected area electron diffraction (SAED) patterns of figure 8(a). It can be clearly seen that Mg segregate in the ceramic. The interface between SiC and Mg is straight and clear, without intermediate compounds. Since the fraction of Mg is relatively higher, it could be observed easily in the XRD pattern shown in figure 4. Meanwhile, some amorphous particles (figure 8(d)) locate on the SiC matrix. This can be indicated as Si or C decomposed from SiC during sintering process. Since the fraction of Si and C is relatively lower, while some of them are amorphous particles, they can hardly be observed in the XRD pattern shown in figure 4. So the peaks of Si and C in Ceramic 1 are slight and weak. TEM observations of Ceramic 2 have been shown in our previous work [33]. The microstructure of Ceramic 2 is homogeneous without Si or C particles. However, some Mg segregations could also be found on the SiC matrix.

Figure 9 shows schematic diagram of microstructure evolution during hot press sintering process with different silicon carbide particle size. Silicon carbide and magnesium mixed homogeneous after mixing. During sintering process, atoms of silicon carbide diffuse continuously with increase of temperature and the Si atoms and C atoms in silicon carbide decompose partially due to different diffusion rates.

Some magnesium atoms are agglomerate in Ceramic 1. The mechanisms are complex. First, both difference in particle size and surfaces of small silicon carbide can prevent diffusion between silicon carbide and magnesium particles. Meanwhile, Si and C elements obtained by silicon carbide decomposition also accumulate separately due to the bonding effect without sintering additive, in which the C element plays the role of carbon inoculation treatment [34]. It forms the black zones where are carbon-rich in figure 3(a).

For Ceramic 2, particle sizes matched properly, and (111) crystal plane of silicon carbide matched well with (0001) crystal plane of magnesium. Silicon carbide can act as the nucleus of magnesium when solidified. Magnesium atoms can enter lattice of silicon carbide successfully. In the meanwhile, reaction process between magnesium and silicon carbide can be promoted by tracing Al element in magnesium alloy [35–38]. Therefore, during sintering process of silicon carbide, particle size of raw materials is not as small as possible, but needs to be reasonably matched with the size of sintering additives, so that the effective reaction of the sintering additives and silicon carbide can be achieved.
5. Conclusions

Hot pressure process of 2 h was taken in 1300 °C and 30 MPa, with silicon carbide powder of 0.09 and 3.31 μm as raw materials, magnesium alloy powder as additive. Two ceramic samples were sintered, and the following conclusions could be drawn:

(1) Density of silicon carbide ceramic sintered by powder with 3.31 μm average particle size is 92.53%, which is higher than that 48.45% of ceramic sintered by powder with 0.09 μm average particle size.

(2) Component of ceramics keep stable after sintering, but microstructure have changed. Ceramic sintered by powder with 0.09 μm average particle size formed segregation of elements of Si, C and Mg, among which segregation of C lead to black C-rich zones. However, ceramic sintered by powder with 3.31 μm is homogeneous without segregation.

(3) Particle size between silicon carbide and sintering additives should be matched to achieve sufficient diffusion of sintering additives in SiC lattice.

Declarations of interest

None.

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