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RESEARCH

Micron-sized silicon carbide particle production via rapid unloading of high-pressure liquid CO_2

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Abstract
We describe a novel methodology for micron-sized silicon carbide particle production via rapid unloading of high-pressure liquid CO_2. The method is based on the physical characteristics of liquid CO_2 such as low viscosity, high permeability, and a high dilation coefficient. A series of silicon carbide powdering experiments were performed. The overall process includes water saturation, water and silicon carbide filling, pressure initialization, CO_2 filling, high pressure initialization, and CO_2 gasification, which is a completely physical process. After high-pressure penetration and CO_2 gasification expansion, the silicon carbide will immediately be converted into micron-sized particles. Most importantly, this method is much more effective than the most popular method of SiC synthesis (Acheson method). Laser grain size analysis indicates that the grain size of the silicon carbide particles ranges between 30 and 50 μm, and the percent grain size less than 176.9 μm accounts for 90%. The rapid unloading of high-pressure liquid CO_2 method is much more environmentally friendly, efficient, energy saving, and effective.

Keywords Rapid unloading of liquid CO_2 · High pressure initialization · Silicon carbide · Micron-sized particle

Introduction

Silicon carbide is a compound of silicon and carbon with chemical formula SiC. Due to its excellent thermal, mechanical, and chemical stability as well as its high mechanical strength and hardness, chemical inertness, wide band gap, and unique optical properties, silicon carbide is a promising ceramic for various industrial applications including electronic devices, optic devices, composite reinforcement, catalyst support, etc.

Carbide compounds are very hard ceramics with outstanding chemical properties due to the strong bonds between carbon atoms and cations such as Si, B, Ti, etc. Of these compounds, silicon carbide is one of the non-oxide ceramics. It exists in nature as the extremely rare mineral moissanite, but synthetic silicon carbide powder has been mass-produced since 1893 [1]. Particles of silicon carbide can be bonded together by sintering to form very hard ceramics that are widely used in manufacturing industry such as car brakes, car clutches, and ceramic plates in bulletproof vests.

The conventional method for preparing silicon carbide is the Acheson process [2]. In this method, carbothermic reduction [3] of silica is the basic reaction for SiC formation. However, silicon carbide is a covalent material and is difficult to be sintered without additives [4, 5]. Micron-sized particles can be obtained by several advanced technologies such as rice hull conversion [6], CVD and laser-induced chemical vapor deposition (LICVD) processes [7], combustion synthesis technology, sol-gel processes [8, 9], and laser gas phase pyrolysis or laser evaporation processes [10].

The Acheson method is a long process that uses high temperatures (2273–3273 K). Recently, various processes have been proposed to improve the carbothermic reduction process [11, 12]. Due to the high reaction temperature and the long reaction time, the resulting silicon carbide powders are large. It is necessary to crush and mill coarse-grained products [13]. Therefore, simpler and more economical approaches for silicon carbide powder production are still needed.

To obtain a high-density silicon carbide body by a sintering process, the initial powders must have high purity, non-agglomeration, and fine particle size with narrow size distribution. Silicon carbide powders were prepared by chemical vapor deposition (CVD) using $(CH_3)_2SiCI_2$ and H_2 as source

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gases at temperatures of 1273 to 1673 K. Various silicon carbide powders such as amorphous powder, β-type single-phase powder, and composite powder were obtained [14]. The average particle sizes measured by TEM ranged from 46 to 114 nm [15].

Spherical and ideal nanometer-scale silicon carbide powders with high purity and low agglomeration were synthesized by the LICVD method with SiH_4 and C_2H_4 as the initial materials [16]. The results show that the powder of β-SiC crystallization has a purity above 98% silicon carbide with a diameter 20 nm. Silicon carbide powder is prepared from crystalline silicon cutting waste via vacuum carbonization [17]. Combustion synthesis (CS) [18] was proposed many years ago for producing ceramic powders. CS is still a very attractive modern method for large-scale production of high-quality ceramic powders. The powder of SiC by this method can be characterized as a highly fine powder because the nanoparticles (diameter < 400 nm) of the observed clusters had round shape and homogenous.

Liquid CO_2 plays an important role during silicon carbide powder production because it has unique features such as a liquid-like density and gas-like diffusivity, which ensures effective infiltration. CO_2 is non-toxic, non-corrosive, and non-abrasive. Furthermore, it is non-conducting and chemically inert. CO_2 is the most widely used supercritical fluid because it has a relatively low critical temperature and a moderate critical pressure (Tc = 31.0 °C, Pc = 7.38 MPa). The method is based on the physical characteristics of liquid CO_2 such as low viscosity, high permeability, and a high dilation coefficient.

Liquid CO_2 blasting is a physical blasting method developed in the early 1960s in the USA and other developed countries. The liquid CO_2 blasting technology is based on the large volume expansion characteristics of liquid CO_2. The core concept underlying this technology is the blasting system, which consists of an inlet control valve, seal cover, sealing ring, needle valve, and release holes following the order from top to bottom.

Conventional techniques used in the production of silicon carbide particle are mostly based on chemical methods. In this paper, we develop a new alternative method for the production of micron-sized particle of silicon carbide via rapid unloading of liquid CO_2, which is a purely physical separation process. The grain size of the silicon carbide particles is between 30 and 50 μm, and the percent of particles less than 176.9 μm accounts for 90%. The particle size distribution curve conforms to a normal distribution.

Methods

Powdering experiments include a high-pressure chamber, liquid CO_2 filling system, pressure gauge, water pump, and high-pressure pipeline. The entire powdering process is carried out in the high-pressure chamber. The high-pressure chamber consists of an inlet control valve, seal cover, sealing ring, and needle valve, double layer rupture disk, and release holes. The double-layer rupture disks are located at the end of the high-pressure chamber. This is called the low-pressure chamber, and the pressure here is about 30–50 MPa. The seal cover and sealing ring not only avoid liquid CO_2 leakage but also ensure installation of the rupture disk. The liquid CO_2 filling system is equipped with a temperature- and pressure-monitoring system. The water pump, pressure gauge, and high-pressure pipeline are used for high-pressure initialization.

Currently, the overall process for production of micron-sized silicon carbide particles includes water saturation, water and silicon carbide filling, pressure initialization, CO_2 filling, high-pressure initialization, unloading, and CO_2 gasification. This is a completely physical process. The impact of the process is the filling pressure and temperature [19], which determines whether CO_2 is liquid or gas. Its permeability will be greatly reduced if it is gaseous. The silicon carbide powdering is based on the physical characteristics of liquid CO_2 such as low viscosity, high permeability, and a high dilation coefficient.

First, to enhance the filling efficiency of liquid CO_2, silicon carbide should be saturated. There will be more liquid CO_2 infiltrating the silicon carbide after saturation. Second, we pour water into the high-pressure chamber; water occupies 50% of the volume. The saturated silicon carbide materials are then put into the high-pressure chamber. At this moment, the silicon carbides and water will fill the high-pressure chamber. The second process can effectively reduce the impact of silicon carbide on the high-pressure chamber and avoid gasification of liquid CO_2. Third, pressure initialization is responsible for liquid CO_2 filling. According to the physical characteristics of CO_2, CO_2 is always liquid when pressure is over

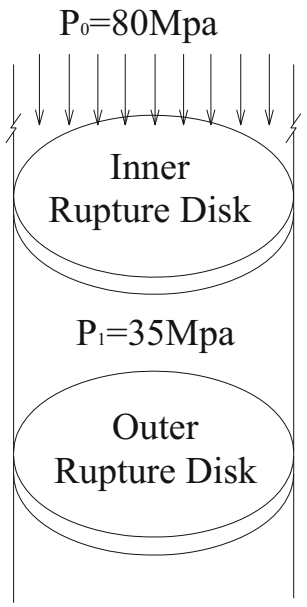

Fig. 1 Schematic diagram of the double-layer rupture disks

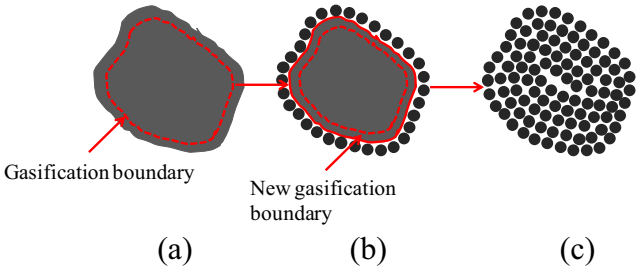

Fig. 2 Powdering process

8 MPa regardless of temperature. Forth, liquid CO_2 is poured into the high-pressure chamber. The injection temperature and pressure are controlled at − 10 °C and 10 MPa, respectively, to ensure that the injected CO_2 is liquid and energy consumption is minimal. After about 20–30 s, the saturated penetration time of liquid CO_2 under 10 MPa is accomplished. Fifth, high-pressure initialization significantly increases the total energy input, and the pressure of liquid CO_2 stored inside of the silicon carbide will increase greatly. The fifth process can substantially promote pressure gradient when the rupture disk bursts. Sixth, the liquid CO_2 is rapidly unloaded after the rupture disk bursts. Two rupture disks are loaded on the bottom of the high-pressure chamber. There are full of high-pressure water between the two rupture disks. We can promptly release the high-pressure water between the two ruptures to realize bursting. A schematic diagram of the two-rupture disks is shown in Fig. 1. When the double-layer rupture disks are adopted, the unloading pressure can be controlled more accurately than via a single-layer rupture disk.

The time of rupture disk bursting is about 5–8 ms, and the high pressure is reduced to zero during this time. During the unloading process of the liquid CO_2, the gasification boundary of liquid CO_2 is in a certain depth within the silicon carbide where the gasification pressure is maintained at 3 MPa as illustrated in Fig. 2a by red dotted lines. The silicon carbide body between the outer surface and gasification boundary is then converted into the micron-sized silicon carbide particles. Subsequently, the gasification boundary gradually moves inward as illustrated in Fig. 2b. Finally, the silicon carbide body is converted into powder layer-by-layer. Under the high-pressure gradient, micron-sized silicon carbide particles are obtained and are illustrated in Fig. 2c.

Results and discussion

Model test for production of micron-sized silicon carbide particles

The silicon carbide is saturated before being put into the high-pressure chamber. First, the double-layer rupture disks are installed and sealed. Water and the silicon carbide are poured into the high-pressure chamber followed by pressure initialization, CO_2 filling, and high-pressure initialization. The volume of the high-pressure chamber is 0.003 m^3, and the volume ratio of the silicon carbide and water is 1:1. The density of the silicon carbide is 3200 kg/m^3, and the quality is 4.8 kg. The initial pressure is maintained at 10 MPa after the silicon carbide and water are put into the high-pressure chamber. Second, the CO_2 filling pressure is 10.1 MPa, which is a slightly higher than the initial water pressure. This ensures that water can easily be substituted by the liquid CO_2. There is no freezing because CO_2 is liquid during the substitution process.

The quality of liquid CO_2 put into the high-pressure chamber is 2.6 kg, and the low-pressure chamber is filled with water. Pressure in the high-pressure chamber and low-pressure chamber

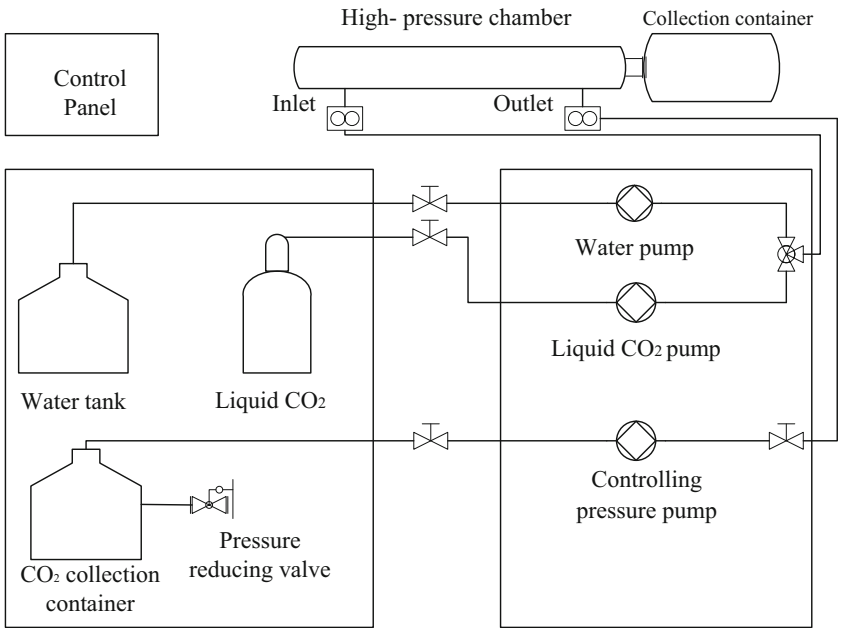

Fig. 3 Process flow diagram for silicon carbide powder production

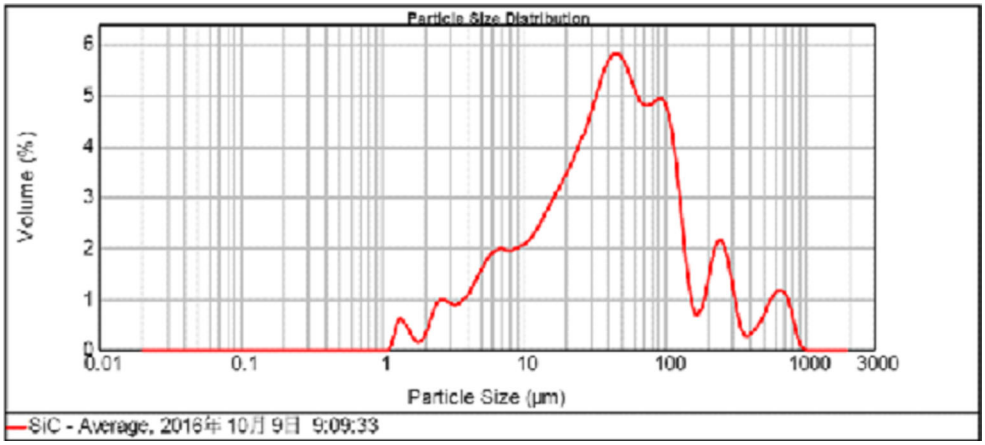

Fig. 4 Particle size distribution of silicon carbide particles

is 80 MPa and 35 MPa, respectively. Third, the high-pressure chamber is placed in the collection container to ensure effective collection of the mixture of silicon carbide powder and water. The process flow diagram is illustrated in Fig. 3. Eventually, water pressure between the two rupture disks is evacuated as soon as possible, and the upper and lower rupture disks will instantly break sequentially. Simultaneously, the silicon carbide powder and water spray into the collection container.

Grain size measurement and particle shape observation

Grain size is a key factor that determines the materials' performance. Because it is a purely physical separation process, the purity of silicon carbide particles is 100%. Laser grain size analysis indicates that the grain size of the silicon carbide particles ranges from 30 to 50 μm, and the percent grain size less than 176 μm accounts for 90%, as illustrated in Fig. 4 and Fig. 5. When observed by electron microscopy, the shape of the particles is mostly irregular, as illustrated in Fig. 6. This satisfies the requirements for sharp cutter production.

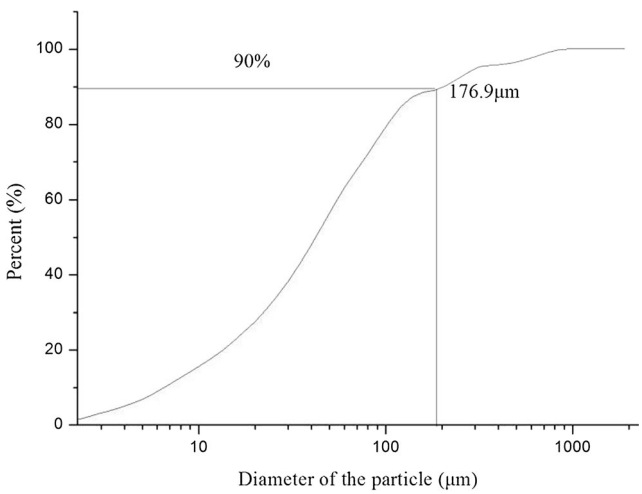

Fig. 5 Cumulative distribution of silicon carbide particles

Discussion

Rapid unloading of high-pressure liquid CO_2, as already demonstrated, can produce micron-sized particles of silicon carbide. This process is different from conventional methods because it does not require high-temperature conditions and catalyst. This case study shows that the production of micron-sized particles of silicon carbide is possible. We note that the method is a completely physical method, which is much more environmentally friendly, efficient, energy-saving, and effective.

Based on the micron-sized silicon carbide particle production experiments, there is now a general consensus that the grain size of the silicon carbide particles ranges between 30 and 50 μm via rapid unloading of high-pressure liquid CO_2. Compression-shear is the main failure mode during the conventional ball milling process. Silicon carbide particle production via rapid unloading of liquid CO_2 belongs to tensile failure. As the tensile strength of silicon carbide is approximately one-tenth of the compressive strength, so much energy could be saved. However, the grain size of the silicon carbide particles obtained by this new method is greatly larger than the traditional methods, so secondary powdering is necessary.

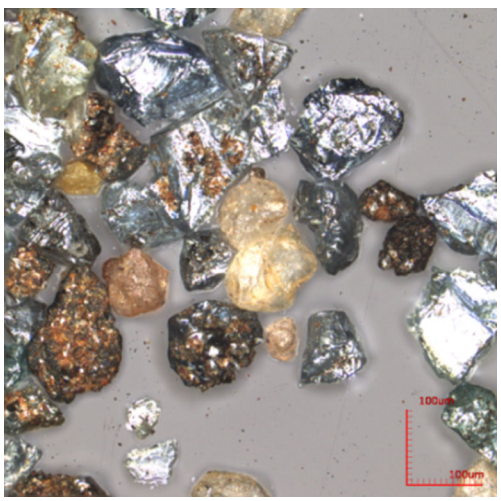

Fig. 6 Irregular shape of silicon carbide particles

The particle size distribution curve obtained by this new method conforms to a normal distribution, while the traditional method by CVD, LICVD, and CS conforms to an evenly distribution. So, optimization and integrant are necessary.

What has not been delineated is the effect of the initial filling pressure of liquid CO_2 on the powdering effect of silicon carbide. It is well accepted that the higher the initial filling pressure is, the more liquid CO_2 penetrates into the silicon carbide, and the better the gasification expansion effect is when the rupture disk bursts. Whether the diameter of silicon carbide powder is diminished along with the increasing of initial high water pressure? Among the questions that remain to be resolved is the process of silicon carbide powdering because the whole powdering process occurs inside an opaque high-pressure chamber. The physical model about gasification boundary moving inward is only a hypothesis and not a mechanism. Experiments on contrast in the extent of silicon carbide powdering in different positions of high-pressure chamber should be carried out. After that, the powdering mechanism of silicon carbide and the construction of high-pressure chamber will be clear. To further determine the mechanism of silicon carbide powdering, X-rays or a transparent chamber deployed with a high-speed camera should be adopted.

Conclusions

The results of the powder production experiments indicate that it is possible to produce micron-sized particle of silicon carbide via rapid unloading of high-pressure liquid CO_2. The production of silicon carbide particle via rapid unloading of high-pressure liquid CO_2 is a truly original approach that is based on the physical characteristics of liquid CO_2 such as low viscosity, high permeability, and a high dilation coefficient. This approach is different from the traditional methods that use high-temperature conditions and catalyst.

The overall process of production of micron-sized silicon carbide particle includes water saturation, water and silicon carbide filling, pressure initialization, CO_2 filling, high pressure initialization, unloading, and CO_2 gasification. The double-layer rupture disks are adopted, and the unloading pressure can be controlled more accurately than via a single-layer rupture disk. The gasification boundary of liquid CO_2 is imaginarily in a certain depth within the silicon carbide where the gasification pressure is maintained at 3 MPa, and the silicon carbide body is converted into powder layer-by-layer. Because it is a purely physical separation process, the purity of silicon carbide particles is 100%. As the tensile strength of silicon carbide is approximately one-tenth of the compressive strength, silicon carbide powdering via rapid unloading of liquid CO_2 belongs to tensile failure, so much energy could be saved. Laser grain size analysis indicates that the grain size of the silicon carbide particles ranges between 30 and 50 μm, and the grain size below 176.9 μm accounts for 90%. The shape of the particle is irregular and will satisfy the requirements of sharp cutter production. Of note, versus the most popular method of silicon carbide synthesis, the rapid unloading of high-pressure liquid CO_2 is much more environmentally friendly, efficient, energy saving, and effective.

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