Thermal plasma synthesis of Si/SiC nanoparticles from silicon and activated carbon powders

Chang-Hyun Lee, Prabhakar Rai, Se-Youn Moon, Yeon-Tae Yu

Abstract

In this study, Si/SiC nanocomposites were synthesized by non-transferred arc thermal plasma processing of micron-sized SiC powder. First, micron-sized SiC was synthesized by solid-state method where waste silicon (Si) and activated carbon (C) powder were used as precursor materials. The effect of Si/C mole ratio and solid-state synthesis temperature on structural and phase formation of SiC was investigated. Diffraction pattern confirmed the formation of SiC at 1300 °C. High C content was required for the synthesis of pure SiC as Si remained unreacted when Si/C mole ratio was below 1/1.5. Highly agglomerated micron-size (0.6–10 μm) SiC particles were formed after solid-state synthesis. Thermal plasma processing of solid-state synthesized micron-sized SiC resulted into the formation of uniformly dispersed (20–60 nm) Si/SiC nanoparticles. It was proposed that Si/SiC nanocomposites were formed due to partial decomposition of SiC during high temperature plasma processing. The formation of Si/SiC nanoparticles from micron-sized SiC was resulted from dissociation of grains from their grain boundary during plasma processing.

1. Introduction

In non-oxide ceramic material, silicon carbide (SiC) is highly desirable for many applications, such as turbine blades, diesel engine parts, and nuclear reactor materials. The growing applications of SiC are mainly attributed to its high mechanical strength, semiconducting properties, chemical inertness, high-temperature stability, and good thermal conductivity [1–4]. It is well known that nanomaterials exhibit different mechanical, physical, and chemical properties than those of bulk forms [5–7]. Therefore, nanomaterials are often more useful in many application as compared to bulk mainly due to their higher specific surface areas. For example, high density of nanosized SiC provides low-temperature sinterability in the consolidation processing and the improvement of mechanical properties [8]. However, low self-diffusion coefficient and covalent nature of Si-C bonding hinder the densification of SiC, and therefore additives are required for its densification [9,10]. Therefore, carbon, boron, aluminum, or their compounds are successfully used as sintering aids to fabricate SiC ceramics at high temperature (about 2000 °C) [11–13]. Meanwhile, these additives occasionally form a secondary phase in the final ceramic, which usually lower its mechanical properties at high temperature [14,15]. This unfavorable effect of additives suggests that the smallest fraction of additives is desirable for the fabrication of SiC ceramics. In addition, the effectiveness of the additives greatly depends on the homogeneity of their distribution [14]. On the other hand, reaction sintering has also been performed by adding free silicon and carbon into SiC ceramic to get high density SiC ceramics [15–17]. Therefore, silicon decorated SiC (Si/SiC) composite nanoparticles are highly desirable for preparing high density SiC ceramics, where free Si acts as a sintering aid. Si/SiC nanocomposite can also reduce the adding amount because it has ‘reaction effect’ as well as ‘nano-size effect’ in sintering process. Furthermore, Si/SiC nanocomposites have variety of functional properties for potential applications such as photocatalyst, catalysis support materials, light emission materials, thermoelectric, Li-ion battery, electronic device etc. [18–24].

There are many methods to synthesize SiC, however thermal plasma processing is considered as one of the most promising methods for industrial applications. This is mainly because thermal plasma produces nanosized powders due to its high processing temperature to vaporize all reactants and a high quenching rate [25–27]. Furthermore, plasma processing yields high-purity...
products due to clean reaction atmosphere. Recently, our research group have developed a thermal plasma processing technique for nanosized SiC synthesis [28,29]. In the present work, non-transferred arc thermal plasma system is used for the preparation of nanosized Si/SiC powder. Here, solid-state synthesized micro-sized SiC is used as a source material for the preparation of silicon coated Si/SiC composite nanoparticle using thermal plasma processing. The effect of Si/C mole ratio, calcination temperature and plasma processing on structural and morphological properties have been investigated.

2. Experimental

2.1. Solid-state synthesis of SiC powder

The SiC was synthesized by solid-state method using waste Si powder produced by Neoplant Co Ltd. Company (98.5–99%) and activated carbon (Sigma-Aldrich). In a typical procedure, different mole ratio of Si and C (1/1, 1/1/C\textsubscript{25}, 1/1/C\textsubscript{5}) were mixed together using ball mill (10 h). The Si and C mixture was calcined in an electric furnace at 1200–1400 °C for 2 h with 10 °C min\textsuperscript{-1} heating rate. The calcination process was carried out in inert atmosphere using Ar gas (1 L min\textsuperscript{-1}). Solid-state synthesized SiC powder was grounded in agate mortar for further characterization and plasma synthesis.

2.2. Plasma processing of solid-state synthesized SiC powder

Si/SiC nanocomposites were synthesized from solid-state synthesized SiC using non-transferred arc thermal plasma reactor (Plasnix Co. Ltd.) as shown in Fig. 1.

This system was equipped with a DC plasma generator (1) with a downward plasma torch (2), cylindrical reactor (3), collector (4), vibration type powder feeder (5), vacuum pump (6), controller for pressure and gas flow rate (7), cooling system (8) and a bag filter (9).

The thermal efficiency of the non-transferred arc plasma was about 60%. The solid-state synthesized SiC was milled into fine powder, which was fed into the plasma torch using a specially designed powder feeder. The powder feeding system was equipped of an entrained-flow powder feeder, a vibrator, a carrier gas line, a sample container, and an internal feeding line. The diameter of internal feeding line was 2 mm through which the precursor was fed into the internal feeding port of plasma torch. Powder was fed by vibrating feeder at 70 V with 1 g min\textsuperscript{-1} feeding rate.

The plasma processing was carried out at 300 Torr and 300 A DC current, where Ar gas flow rates was 30 L min\textsuperscript{-1}, H\textsubscript{2} gas flow rates was 3 L min\textsuperscript{-1}. After plasma ignition, material was supplied by feeder. The synthesized nanopowder were collected from the side wall and bottom of the plasma reactor. The yield of plasma synthesized Si/SiC was about 80–85%.

2.3. Sample characterization

The crystallographic structures of the powder samples were determined by X-ray diffractometer (XRD; D/Max 2005 Rigaku) equipped with graphite monochromatized high-intensity Cu-Kα radiation (λ = 1.5405 Å). The XRD patterns were recorded from 20° to 80° (2θ) with a scanning speed of 0.04° s\textsuperscript{-1}. Morphology was investigated by scanning electron microscopy (SEM; JSM-5900, JEOL) and transmission electron microscope (TEM; JEM-2010, JEOL).

3. Results and discussion

SEM images of silicon and activated carbon, used for the synthesis of SiC, are shown in Fig. 2. It shows the presence of 1–60 um particles in both samples. However, the BET surface area of activated carbon (1082 m\textsuperscript{2} g\textsuperscript{-1}) was much higher as compared to silicon powder (0.35 m\textsuperscript{2} g\textsuperscript{-1}). These silicon and activated carbons were mixed by ball mill to get uniform distribution of elements prior to solid-state synthesis. The SEM image and elemental mapping of ball milled mixture of silicon and activated carbon are shown in Fig. S1. Elemental mapping confirms the uniform distribution of both elements (Si and C) in the mixture sample after ball milling.

The effect of Si/C mole ratio on phase formation was investigated and corresponding XRD results are shown in Fig. 3. XRD analysis confirmed the formation of β-SiC in all three specimens. A very weak diffraction pattern for α-SiC is also found in the XRD profile of all the three specimens, which suggest that small amount of α-SiC is also present in these specimens. However, free

![Fig. 1. Photograph of non-transferred arc thermal plasma reactor for Si/SiC synthesis.](image)

![Fig. 2. SEM images of (a) silicon and (b) activated carbon powder.](image)
Si peaks are found when Si/C mole ratio was either 1/1 or 1/1.25 (Fig. 3(a) and (b)), which suggest that these free Si remained un-reacted during synthesis. This result suggest that high Si/C mole ratio (1/1.5) is required to synthesize pure SiC and avoid the presence of free Si (Fig. 3(c)).

The effect of solid-state synthesis temperature on phase formation was also investigated, where Si/C mole ratio was fixed to 1/1.5. It has been found that free Si peaks appear below 1300 °C (Fig. 4(a)). Further increase in temperature resulted in the formation of pure SiC without any impurity phases, such as free Si (Fig. 4(b) and (d)).

SEM images of solid-state synthesized SiC show the formation of non-uniform particles at every temperature as shown in Fig. 5. These particles are large in size and their shape and size is not defined. The size of these particles varies from 0.5 to 10 μm. These particles are highly agglomerated which suggest that large particles are formed due to agglomeration of smaller particles. The particle size was relatively larger below 1300 °C due to the presence of non-reacted silicon as shown in Fig. 5(a). Elemental mapping and line scaling of solid-state synthesized SiC confirmed the uniform distribution of Si and C as shown in Fig. S2.

Plasma processing of solid-state synthesized SiC microstructures with 1/1 and 1/1.5 mol ratio of Si/C is carried out and results are shown in Fig. 6. SEM images show the formation of well dispersed, 20–60 nm spherical particles in both specimens (Fig. 6 (a) and (b)). The surface area of plasma processed SiC (∼68 m² g⁻¹) was very high as compared to solid-state synthesized SiC. These results show that Si/C mole ratio of solid-state synthesized SiC has no significant effect on surface area, particle size and shape of plasma processed SiC. TEM images also show the formation of well dispersed, 20–60 nm SiC nanoparticles (Fig. 6 (c) and (d)). However, HRTEM image of SiC confirms the formation of Si/SiC nanocomposite as clear lattice fringes of both materials.
are present (Fig. 6(e)). XRD results also confirm the formation of Si/SiC nanocomposites. The presence of free Si peaks after plasma processing of solid-state synthesized SiC having 1/1.5 Si/C mole ratio is interesting and need to be explain. The formation of free Si after plasma processing is possibly related to partial decomposition of SiC at very high plasma processing temperature. Therefore, plasma processing of solid-state synthesized SiC microstructures resulted in the formation of Si/SiC nanocomposite. Furthermore, the formation of nanosize particles after plasma processing suggests that high temperature of plasma arc has weakened the bonding of grains present at the grain boundaries, which resulted into the formation of ultrafine particles. It is clear from these results that thermal plasma is a useful technique for the preparation of uniform nanosized Si/SiC nanoparticles.

4. Conclusions

Nano-sized Si/SiC composites were synthesized by non-transferred arc thermal plasma processing of solid-state synthesized SiC powder. Pure micron-sized (0.6–3 μm) SiC powder was synthesized at 1300 °C using solid-state method when Si/C mole ratio was 1/1.5. Solid-state synthesis of SiC required higher mole ratio of activated carbon as compared to silicon to synthesize pure SiC. The size of plasma processed Si/SiC nanocomposites was 20–60 nm, where metallic silicon (15 nm) was present on the surface of SiC. It was found that nano-sized Si/SiC composites were formed due to partial decomposition of SiC and dissociation of grains from their grain boundaries. These nano-sized Si/SiC composites can be used as sintering additive for the preparation of pure and high density SiC ceramic.
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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ceramint.2016.06.137.

References