Synthesis of SiC coating from SiO by a chemical vapor deposition (CVD) process

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A new chemical vapor deposition process for coating SiC is proposed in which gaseous SiO and toluene vapor are reacted to generate SiC in the presence of iron oxide as a catalytic component. At a temperature of 1450°C, SiC can be formed substantially from gaseous SiO and toluene vapor only at positions of iron oxide deposition. When iron oxide is deposited as a coating on a substrate, SiC can also be formed as a coating on the substrate by calcinating at 1450°C while supplying gaseous SiO and toluene vapor. In this process, SiC coating of several tens μm in thickness is formed on the substrate, and fibrous material is also formed on the SiC coating. The fibrous material is composed of fibrous SiC as well as an Fe-containing spherical substance and can be easily removed mechanically from the SiC coating. This process for coating SiC is based on a vapor–liquid–solid mechanism.

Key-words : SiC, Coating, SiO, CVD

1. Introduction

SiC (silicon carbide) has excellent properties such as oxidation resistance, abrasion resistance and high-temperature strength and SiC coating is thus expected to improve the properties of various materials such as carbon material, heat-resistant metal and ceramic materials.1) Heretofore, chemical vapor deposition (CVD) processes known to form SiC coating involved reacting a silane compound and a hydrocarbon with an excessive amount of hydrogen gas at about 1600°C under an argon atmosphere.2)–7) In the CVD processes, however, a large volume of hydrogen gas is necessary and the coating yield is low because of SiC deposition at other than the intended positions. Halide CVD processes require especially high expenditures for scrubbing halogen-containing waste gas.

In addition, synthesis of SiC from silica and carbon can be promoted in the presence of an iron catalyst.8),9) We have found that SiC coating can be formed from raw materials of silicon monoxide (SiO) and hydrocarbon at intended positions where iron oxide has been deposited. This will be introduced in this paper as a new CVD process for SiC. In the new CVD process, hydrogen gas is unnecessary, and the coating yield may be high due to limiting of SiC deposition to only intended positions. Furthermore, iron oxide can be easily deposited on surfaces with complex shapes by dipping, spraying, etc.; the new CVD process can therefore be adapted to form SiC coating on intended surfaces with complex shapes. Furthermore, since the new CVD process does not employ halide compounds as halide CVD processes do, costly scrubbing of halogen-containing waste gas is unnecessary.

2. Experimental procedures

2.1 Formation of SiC coating

One side of an alumina plate measuring 10 × 10 mm and 0.2 mm thick employed as a substrate was wetted with an iron(III) nitrate aqueous solution, and the alumina plate was then dried and heated to 800°C in air atmosphere, thereby depositing a layer of iron oxide as a catalytic component measuring about 5 μm thick on one side of the alumina plate.

Next, 300 mg of granular SiO available as a reagent was poured into an alumina crucible with an inner volume of 15 ml, an alumina support plate measuring 15 × 15 mm and 1 mm thick was placed on the granular SiO, and the above-mentioned 10 × 10 mm alumina plate with deposited iron oxide was then placed on the support plate, as shown in Fig. 1.

The alumina crucible was disposed in this state into an electric furnace and the air in the furnace was exchanged with argon. The alumina crucible was then heated to a predetermined temperature for a set time while toluene vapor was fed continuously into the crucible. Consequently, various SiC coatings accompanied by fibrous materials were formed at the positions on the alumina plates where iron oxide had been deposited.

2.2 Evaluation

SiC coatings and fibrous materials, formed on the alumina plates by means of the above-noted procedures, were observed using a scanning electron microscope (SEM) and analyzed by energy dispersive X-ray spectroscopy (EDX) for elemental content.
3. Results

As shown in Fig. 2, a layered substance was observed on the alumina plate after calcinating at 1450°C for 2 h, in which the layered substance was composed of a SiC coating on the alumina plate and a layer of fibrous material on the SiC coating.

Figure 3(a) is an SEM image in which the fibrous material is observed in the direction from the upper side of Fig. 2; and Fig. 3(b) is an element map of Fe using SEM-EDX at the same position as in the SEM image. Figures 3(a) and 3(b) demonstrate that the fibrous material is composed of straight or tortuous rods with a spherical substance at the tips of the rods and that the spherical substance at the tips of the rods contains the Fe element exclusively. The straight or tortuous rods were substantially composed of Si and C atoms from SEM-EDX images (not shown).

Figure 4 is an SEM image of the SiC coating after removal of the fibrous material shown in Fig. 2; here, the fibrous material could be removed easily by slightly hand-rubbing the surface of the layered substance on the alumina with a polishing paper. That is, the layered substance shown in Fig. 2 consists of two materials: one is the fibrous material composed of straight or tortuous rods and a spherical substance, and another is the SiC coating.
applied to the alumina plate.

The SiC coating shown in Fig. 4 was observed and analyzed using SEM-EDX; the results showed that the SiC coating was composed substantially of non-porous polycrystalline SiC, and each rate of Fe and O atoms amounted to no more than 1 atomic % of the SiC coating.

Figure 5 is a graph of calcination periods at 1450°C and the atomic ratio Si/Fe observed from above the layered substance and determined by SEM-EDX. The results shown in Fig. 5 demonstrate that a calcination period of 2 h results in almost the maximum atomic ratio Si/Fe.

Figure 6 shows an X-ray diffraction pattern of the SiC coating shown in Fig. 4, in which X-rays were irradiated from above to the upper side of the SiC coating on the alumina plate. The peaks of the X-ray diffraction pattern correspond substantially to those of the β-type SiC or corundum alumina on the alumina plate.

In the above-noted experiments in calcinating at 1450°C after depositing iron oxide on the alumina plates, generation of SiC was observed only at the positions where iron oxide had been deposited. Figure 7 shows such a position-selective deposition of SiC; i.e. Fig. 7(a) shows a state in which iron oxide has been deposited on an alumina plate, and Fig. 7(b) shows a state in which SiC has been generated only at the position where iron oxide had been deposited.

4. Discussion

As described above, SiC could be generated substantially only at positions where iron oxide had been deposited on alumina plates. The Si in SiC is considered to derive from gaseous SiO which had been poured into the crucible as granular SiO and would be vaporized at high temperatures, and the C of SiC is considered to derive from pyrolyzed toluene vapor. Accordingly, this process for forming SiC can be defined as one of the CVD processes.

The reason why SiC is formed at the positions of iron oxide (expressed as “FeO”) for convenience sake) deposition is considered to be as follows:

FeO is reduced to Fe by C, H, etc. in the pyrolyzed toluene vapor, and this reaction cycle occurs repeatedly to produce SiC. The oxygen in SiO will finally turn to CO, H2O, etc.

Figures 2 and 3 are considered to reflect the reaction mechanism defined as the so-called VLS (vapor, liquid and solid) mechanism, i.e. gaseous SiO and gaseous carbon components correspond to “vapor”; the iron-containing spherical substance in Figs. 2 and 3, which will have been droplets when forming SiC, corresponds to “liquid”; and the straight or tortuous rods of SiC extending from the iron-containing spherical substance correspond to “solid”.

5. Summary

In many papers in which SiO is discussed in relation to SiC synthesis, the SiO is no more than an idea or concept as an intermediate compound for synthesizing SiC. In this study, commercially available SiO itself was used, and a new CVD process for coating SiC can be consequently proposed in which SiO acts as a gaseous source of SiC for forming SiC at sites where iron oxide has been deposited. This new CVD process may provide specific advantages; in particular, SiC coating can be formed on surfaces of complex shapes, since SiC coating can be formed in intended positions.

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