Synthesis of nano-composite powder composed of silica and carbon and characteristic behavior at a high temperature thereof

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A nano-composite powder composed of silica and carbon with a unique property could be prepared from a mixture of a silicate compound and an epoxy compound, in which the silica within the nano-composite powder has a BET surface area of as high as greater than 800 m²/g although the nano-composite powder has a BET surface area of less than 10 m²/g. It was estimated that the silica and the carbon are in a very finely and uniformly mixed state within the nano-composite powder and that the silica and the carbon form particles having a diameter of several tens nm and a number of silica particles having a diameter of several nm exist within the every particle of the nano-composite powder. It was demonstrated that the nano-composite powder exhibits characteristic behaviors under calcination at a temperature of 1450°C such that an amorphous state of the nano-composite powder is maintained, a large amount of gaseous reactant generates from the nano-composite powder, and a reaction product of SiC is synthesized in the presence of another ingredient.

Key-words : Nano-composite powder, Silica, Silicate, Epoxy, Carbon, SiC

1. Introduction

SiC has been conventionally used for abrasives, shelf boards, heaters, etc. and highly pure SiC is used for tools in manufacturing semiconductors. SiC has therefore many applications from conventional materials to high grade materials.1,2) SiC of these conventional and high grade materials is mainly manufactured by mixing silica and carbon and heating the mixture at 2100°C or higher using an Acheson furnace; alternatively, a mixture of silica and carbon is heated to about 1800°C to produce relatively pure β-SiC.3,4)

For the purpose of enhancing the reactivity between silica and carbon, it is believed that silica and carbon are to be mixed as finely and uniformly as possible. However, we recognize that finely and uniformly mixing two or more kinds of powders is very difficult; specifically, mechanical mixing of silica sand and coke inevitably results in a mixture of coarse particles of silica sand and coke, and it has also been experienced that even when fine particles such as fumed silica and carbon black are mechanically mixed under a heavily-loaded condition, the resulting mixed state is no more than a mixture of secondary agglomeration of fumed silica particles and secondary agglomeration of carbon black particles and the reactivity of the mixture is not significantly improved.

In regards to previous investigations of such a fine and uniform mixture of silica and carbon for producing SiC powder, for example, a mixture composed of silica and carbon was prepared by spraying silicon tetrachloride and heavy oil into air-propane flame;5) by mixing and carbonizing a mixture of silica sol and a hydrocarbon,6) by polymerizing and carbonizing a mixture of a silicate compound and a phenol-formaldehyde resin,7,8) by curing and carbonizing a mixture of silica and a phenolic resin,9) or the like.

In this work, the nano-composite powder composed of silica and carbon was prepared starting from a silicate compound and an epoxy compound. The silicate compound and the epoxy compound were selected such that these compounds are compatible each other. It was therefore expected that siloxane units in the silicate compound and epoxy units in the epoxy compound are uniformly mixed in a molecular level within the mixture solution and thus the mixed state thereof will result in a fine and uniform mixed state of silica and carbon in a level that could not be achieved heretofore.

2. Experiment

2.1 Preparation of nano-composite powder

The procedures to prepare the nano-composite powder were as follows: 50 parts by mass of a silicate compound [polytetra-methoxysilane SiOx(OCH3)4–x (OCH3)x, by Tama Chemicals Co., Ltd.] and 100 parts by mass of a base compound (alkyldiphenol type, by DIC Corporation) of an epoxy compound were mixed to form a transparent solution of the two compounds, to which then 50 parts by mass of a hardener (modified amine, by DIC Corporation) of the epoxy compound was mixed to form a transparent solution of the three compounds, which to then 50 parts by mass of a hardener (modified amine, by DIC Corporation) of the epoxy compound was mixed to form a transparent solution of the three compounds, followed by allowing to stand the transparent solution composed of the three compounds at room temperature overnight, thereby obtaining a transparent hardened body.

Then the resulting hardened body was heated in an alumina crucible with a lid having an inner volume of 100 cm³ at 800°C for 2 h under nitrogen atmosphere.

The resulting calcined body was crushed to pass through a 1-mm screen, thereby obtaining the nano-composite powder shown in Table 1.

2.2 Preparation of mechanical mixture

For comparison, commercially available fumed silica particles having a BET value of 295 m²/g and carbon particles having a BET value of 120 m²/g were mechanically mixed using a mortar
and a pestle to prepare a mechanical mixture shown in Table 1. The BET value of the mechanical mixture was measured to be 228 m²/g.

The carbon particles were prepared by the same manner as the nano-composite powder described above except that the silicate compound was not used, i.e. the carbon particles were prepared only from the epoxy compound through hardening and calcination.

Furthermore, since the silica particles are very fluffy and the bulk density thereof is excessively low for introducing the mixture of the silica particles and the carbon particles into a crucible in the amount the same as that of the nano-composite powder, initially the silica particles and the carbon particles were mixed using the mortar and pestle for 10 min, then the mixture was heated at 1000°C for 2 h under nitrogen atmosphere to induce shrinkage of the mixture.

After this pretreatment, the densified mixture was crushed and mixed again using the mortar and pestle for 10 min, then the resulting mixture was used as a comparative material of the nano-composite powder.

2.3 Repeated calcination of nano-composite powder and mechanical mixture

The nano-composite powder of 3.0 grams was calcined in an alumina crucible with a lid having an inner volume of 10 cm³ under a condition of 1450°C for 2 h using an annular electric furnace equipped with an alumina tube of 1 meter long and 50 mm inside diameter; the time to raise the temperature from room temperature to 1450°C was 2.5 h. The inside space of the alumina tube was initially flushed with nitrogen gas and then constantly supplied with a small amount of nitrogen gas.

The calcination of 3.0 grams of the nano-composite powder in this manner was repeated 10 times together with 3.0 grams of the mechanical mixture, which was poured into another crucible with a lid substantially identical to the crucible described above, by heating the two crucibles at the same time.

Once each calcination was finished, the two alumina crucibles were taken out from the electric furnace, and the alumina crucibles were weighed and the contents in the alumina crucibles were observed.

2.4 Calcination in the presence of another ingredient

The nano-composite powder of 3.0 grams and an additive of 0.3 gram of nickel chloride hexahydrate NiCl₂·6H₂O were gently mixed and poured into an alumina crucible having an inner volume of 10 cm³, and a lid was placed on the crucible, then which was calcined under a condition of 1450°C for 2 h using an annular electric furnace similarly as described above. At the same time, the nano-composite powder of 3.0 grams with no additive was also calcined.

For comparison, the calcination in the presence of the additive of NiCl₂·6H₂O was carried out in the same manner as described above except that 3.0 grams of the mechanical mixture was used in place of 3.0 grams of the nano-composite powder. At the same time, the mechanical mixture of 3.0 grams with no additive was also calcined.

3. Result

3.1 Property of nano-composite powder and mechanical mixture

Figure 1(a) shows a TEM image of particles of the nano-composite powder and Fig. 1(b) shows a TEM image of particles of silica which has remained after combusting to remove carbon in the nano-composite powder. Hereinafter the silica remained after removing the carbon by heating the nano-composite powder in air at 630°C for 2 h is referred to as “carbon-removed silica”. The appearance of this carbon-removed silica was stark white, and by means of elemental analysis using SEM-EDX, carbon was not detected from the carbon-removed silica and thus the content of carbon in the carbon-removed silica was determined to be no greater than 0.1 wt%.

From observation of Figs. 1(a) and 1(b), it is apparent that the particle size of the carbon-removed silica is considerably smaller than the particle size of the nano-composite powder and is in a range of several nm; therefore, it is believed that the silica is embedded, at a size as small as several nm, within the nano-composite powder.

Table 1 shows BET surface area and mole ratio of C/SiO₂ in the nano-composite powder and the mechanical mixture. Provided that the particles of the carbon-removed silica, having a BET value of 851 m²/g, are of the same spherical shape, the particle diameter is calculated to be 3.2 nm. In view of Fig. 1 and Table 1, it is believed that the nano-composite power composed of silica and carbon produced from the silicate and the epoxy resin described above can be truly referred to as “nano-composite power”.

Figure 2 shows X-ray diffraction patterns of the mechanical mixture of silica and carbon, the silica particles, and the carbon particles in Table 1, together with X-ray diffraction patterns of the nano-composite powder and the carbon-removed silica described above, which indicating that all of these powders are in an amorphous state before calcination and representing references for after calcination of Fig. 6 explained below.

3.2 Repeated calcination of nano-composite powder and mechanical mixture

Figure 3 shows the change of weight of the nano-composite powder and mechanical mixture as a function of calcination times until 10 times. There is a remarkable difference between

<table>
<thead>
<tr>
<th></th>
<th>C/SiO₂ (mole ratio)</th>
<th>BET surface area (g m⁻²)</th>
<th>BET surface area of silica (g m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano-composite powder</td>
<td>3.1</td>
<td>9.8</td>
<td>851</td>
</tr>
<tr>
<td>Mechanical mixture</td>
<td>3.1</td>
<td>228</td>
<td>295</td>
</tr>
</tbody>
</table>
the weight loss in the nano-composite powder and the weight loss in the mechanical mixture.

Figure 4(a) shows the state of the nano-composite powder within the alumina crucible after 10 times of the calcination. Figure 4(b) shows the state of the mechanical mixture within the alumina crucible after 10 times of the calcination. There is a remarkable difference between the appearance in the nano-composite powder and the appearance in the mechanical mixture such that a relatively large volume of cotton-like substance has deposited in the space above the nano-composite powder as shown in Fig. 4(a); on the other hand, a relatively small amount of agglomerated granules has deposited on the mechanical mixture as shown in Fig. 4(b).

3.3 Observation of deposit resulting from repeated calcination

Figure 5(a) shows a SEM image of the deposition which has generated from the nano-composite powder after 10 times of the calcination at 1450°C for 2h, which represents that the deposition is fibrous; and Fig. 5(b) shows a SEM image of the deposition which has generated from the mechanical mixture after 10 times of the calcination at 1450°C for 2h, which represents that the deposition is massive and non-fibrous.

3.4 Products under calcination

Figure 6 shows X-ray diffraction patterns of the nano-composite powder and the mechanical mixture respectively after calcination.
the calcination at 1450°C for 2 h with or without the additive of NiCl₂·6H₂O.

It is understood from Fig. 6 that very definite peaks corresponding to cristobalite SiO₂ clearly appear in the mechanical mixture without additive (d), whereas no definite peak appears in the nano-composite powder without additive (b); definite peaks corresponding to cristobalite SiO₂ clearly appear in the mechanical mixture added with NiCl₂·6H₂O (c), whereas definite peaks corresponding to 3C-SiC appear in the nano-composite powder added with NiCl₂·6H₂O (a).

Here, it is noted that the shift of peaks has generated in the diffraction pattern of the nano-composite powder added with NiCl₂·6H₂O (a) by about 0.5° to right side from the peaks of 3C-SiC and also in the diffraction pattern of the mechanical added with NiCl₂·6H₂O (c) by about 1° to right side from the peaks of cristobalite SiO₂. These shifts are supposed to be an influence of Ni.

4. Consideration

The nano-composite powder has exhibited characteristic behaviors at a temperature of 1450°C in comparison to the mechanical mixture as follows:

(i) the weight loss under repeated calcination is larger; the reason is considered that silica and carbon contact in the nano-composite powder much more closely than the mechanical mixture, therefore, the reactivity between silica and carbon is enhanced and the reaction below proceeds much more promptly;

\[ \text{SiO}_2(s) + C(s) \rightarrow \text{SiO}(g) + \text{CO(g)} \]

(ii) the amount of deposition after the repeated calcination is larger; the reason is considered that much more amount of SiO(g) is generated in the nano-composite powder and gaseous SiO(g) transforms into the deposition SiO(s) when cooled;

(iii) the shape of deposition is fibrous; the reason is considered that the deposition is generated from gas phase in the nano-composite powder, on the other hand, the fine particles of silica agglomerate themselves under a solid or liquid state in the mechanical mixture;

(iv) the amorphous state is maintained up to 1450°C in the nano-composite powder and not maintained in the mechanical mixture; the reason is considered that the finely and uniformly mixed carbon inherently prevents the contact of silica particles each other in the nano-composite powder; on the other hand, fine particles of silica easily agglomerate each other in the mechanical mixture; and

(v) SiC is synthesized from the nano-composite powder in the presence of nickel chloride; the reason is considered that metal such as Ni catalysts a reaction to synthesize SiC by reaction: \( \text{SiO} + 3\text{CO} \rightarrow \text{SiC} + 2\text{CO}_2 \), for example, from the viewpoint that SiC was not generated from the mechanical mixture which exhibited very lower weight loss under repeated calcination although consisting of silica and carbon in substantially the same contents as those of the nano-composite powder. In addition, SiC synthesis with a Ni catalyst is described in prior papers, however, our results are different from the previous papers in that Si source of SiC is SiO₂ rather than polycarbosilane or silicon tetrachloride, or the like.

5. Conclusion

The nano-composite powder, which represents the finely mixed state of silica and carbon in nano-order, could be prepared from the silicate compound and the epoxy compound which are compatible each other. It has been found that the nano-composite powder has a high reactivity between silica and carbon compared to the mechanical mixture such that a gaseous reactant effectively generates from the nano-composite powder and also SiC is synthesized when NiCl₂·6H₂O is added even at a temperature as low as 1450°C, which is believed to be due to finely and uniformly mixed state and thus close and tight contact between silica and carbon.

References