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# Nanocomposite powders from coating with heterogeneous nucleation processing

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**Abstract**

A nanocomposite SiC powder was prepared by coating nano-SiC particles with $Y(OH)_3$ and/or $Al(OH)_3$ via heterogeneous nucleation processing using a buffered pH solution as the precipitation reagent. TEM micrographs showed the coating materials nucleated and grew on the surface of nano-SiC and did not form sol particles in solution. The isoelectric point (IEP) of coated SiC was different from that of as-received SiC. The IEP of $Al(OH)_3$-coated SiC occurred at pH 7.3, which is close to that of alumina. When $Al(OH)_3$-coated SiC particles were coated with $Y(OH)_3$,the IEP of nanocomposite powder shifted from pH 7.3 to pH 8.6, which is close to that of yttria. In addition, the dispersability of $Al(OH)_3$-coated SiC was greatly improved when it was coated using heterogeneous nucleation processing. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

*Keywords:* A. Powders: chemical preparation; B. Surfaces; C. Chemical properties; Heterogeneous nucleation processing

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## 1. Introduction

The increased interest in using ceramics in severe environments leads to greater emphasis on the production of reproducible, high-quality ceramics. Current research in ceramics emphasizes the control of powder properties and the development of robust economic processing techniques to achieve denser, more uniform microstructure [1]. Composite particles, having a structure where a core particle is coated with a second phase, have attracted attention from various sources. Coatings are applied to improve the dispersability of powders [2], provide a well-dispersed minor phase [3–9], control interfacial properties [10], and/or modify the colloidal behavior of powders [11–15].

There are several promising techniques for coating particles. Many of them are chemical processes similar to those used to make ceramic powders. The adaptation of homogeneous precipitation techniques for the coating of particles and whiskers was reported by Mitchell [7] and Hu [9], who coated SiC particles and whiskers with alumina precursor. Luther et al. [12] and Wang [16,17] succeeded in coating $Si_3N_4$ using aluminium alkoxide, and Shih et al. [15] coated the same material using boehmite by a sol–gel technique. Liden and his colleagues [3] coated SiC particles with yttria and alumina by surface interaction. However, these results showed that, in most cases, these techniques need further development before full advantage can be taken of them. One problem is that they often result in a non-uniform coating owing to the growth of isolated nuclei. These nonadsorbed sol particles may migrate during the forming stage, and it may lead to an inhomogeneous microstructure [3]. In addition, by these techniques, it is difficult to control the amount of coating layer on the particle surfaces, and this limited their application.

It is well known that the metal hydroxide can be precipitated from solution by heterogeneous nucleation or homogeneous nucleation. Normally, the preparation of powders with controlled characteristics by chemical method relies on homogeneous nucleation and growth [18]. In the preparation of coated powders, homogeneous nucleation and growth would lead to free precipitation, which is undesirable [9]. The ideal processing requires the precipitation of coating materials being predominantly heterogeneous rather than homogeneous. In aqueous solution the solubility of metal hydroxide $M(OH)_n$ can be expressed by the following equation: $\mathrm{K}sp = \left[\mathrm{M}^{n+}\right]\cdot[\mathrm{OH}^-]^n(\left[\mathrm{M}^{n+}\right], [\mathrm{OH}^-]$, $n$ represents the

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concentrations of $M^{n+}$ and $OH^-$ in water and valence, respectively). It is seen from the above equation that, it changes with the pH, that is, it will reach the highest when the pH is low and lower down as the pH goes up. When the concentration of metal hydroxide exceeds the solubility limit, precipitation will occur [18]. It indicates that precipitation of coating materials can be controlled via controlling the pH of solution.

To form a coating using heterogeneous nucleation, the pH of suspension of the particles to be coated is controlled at a certain regime with a buffered pH solution to control precipitation of the coating materials on the surface of coated particles by heterogeneous nucleation. Fig. 1 shows a schematic of the nucleation and growth behavior of a precipitate from solution with increasing solution pH. As the pH of suspension rises, the solution becomes more saturated. The ideal path would edge over the heterogeneous nucleation limit without touching the homogeneous nucleation regime, the coating materials will precipitate by heterogeneous nucleation and not by homogeneous nucleation. Moreover, the thickness of coating layer can be controlled by controlling the amount of coating materials.

In this study, heterogeneous nucleation processing was used to coat nanosized silicon carbide particles with aluminum and/or yttrium hydroxide, and the dispersability of nanocomposite powder in water was investigated.

## 2. Experimental procedure

Nanometer β-SiC powder (Institute of Chemical Metallurgy, Beijing, China) with a mean particle size of 80 nm were used in the present work. The SiC powder were etched with pure HF to eliminate the effect of the oxide surface on coating (there was no discernible effect). Then, it was cleaned with distilled water until the pH value of supernatant solution was about 6.0. After cleaning, 1.5 g of nano-SiC was thoroughly dispersed in 300 ml of distilled water with an ultrasonic vibrator for several minutes to remove any agglomerates. The pH value of dispersed nano SiC suspension was controlled at 4.5 with the buffered pH solution composed of NaAc and HAc. Corresponding solution containing 0.05 M aluminum nitric was added dropwise to the SiC suspension with vigorous stirring. Finally, the pH of SiC suspension was adjusted to about 7.0 with ammonia water. $Al(OH)_3$-coated SiC were obtained from the above suspension, at centrifuged 10,000 rpm. A procedure for coating $Y(OH)_3$ was similar to that for coating $Al(OH)_3$. $Al(OH)_3$-coated powder were dispersed with the method as mentioned above. The pH value of $Al(OH)_3$-coated SiC suspension was controlled at 7.5 with the buffered pH solution composed of $NH_4C1$ and $NH_4OH$. Corresponding solution containing 0.05 M yttrium chloride was added dropwise to the suspension of $Al(OH)_3$-coated SiC with vigorous stirring. After the pH of the suspension was adjusted to about 9.0 with ammonia water, $Al(OH)_3$ and $Y(OH)_3$-coated SiC powder were obtained from the above suspension, centrifuged at 10,000 rpm. For comparison, the $Al(OH)_3$ formed from the aluminum nitric solution without nano-SiC, then it was added to nano-SiC suspension. All chemicals were reagent grade.

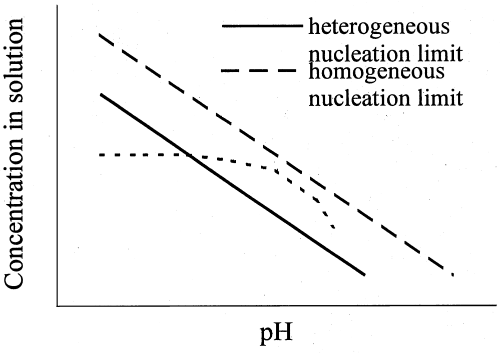

Fig. 1. Schematic of the nucleation and growth behavior of a precipitate from solution with increasing solution pH.

The uncoated and coated nano-SiC particles were subjected to Zeta-potential measurement (Brookhave Zetapuls) to evaluate the surface potential of the powders, and the pH was adjusted with dilute HCl and NaOH. The layer of coated powders was also studied by transmission electron microscopy (TEM). The particles size distribution of uncoated and coated powders in optimal condition was measured with a BI-XDC particles size analyzer.

## 3. Results and discussion

Examination by TEM verified that a uniform coating layer formed on the surface of nano-SiC particles, which was not the case that sol particles packed on the surface and reserved in the solution (see Fig. 2). It indicated that $Al(OH)_3$ and $Y(OH)_3$ nucleated and grew on the surface of nano-SiC particles and did not form small sol particles. TEM micrographs of $Al(OH)_3$-coated SiC before and after $Y(OH)_3$ was coated can be found in Fig. 2 respectively. It can be found that the coating layer of $Al(OH)_3$ and $Y(OH)_3$-coated was thicker than that of only $Al(OH)_3$-coated, but there was not an interface between two kinds of coating layer.

Fig. 3 shows the Zeta potential versus pH of as-received SiC with isoelectric point (IEP) of pH 3.4. Also shown are the behaviors of SiC particles for different processes. $Al(OH)_3$-coated SiC shows IEP between 7.0 and 7.5, nearly identical to that of alumina in literature [19]. In contrast, the IEP of $Al(OH)_3$ sol-added SiC lies

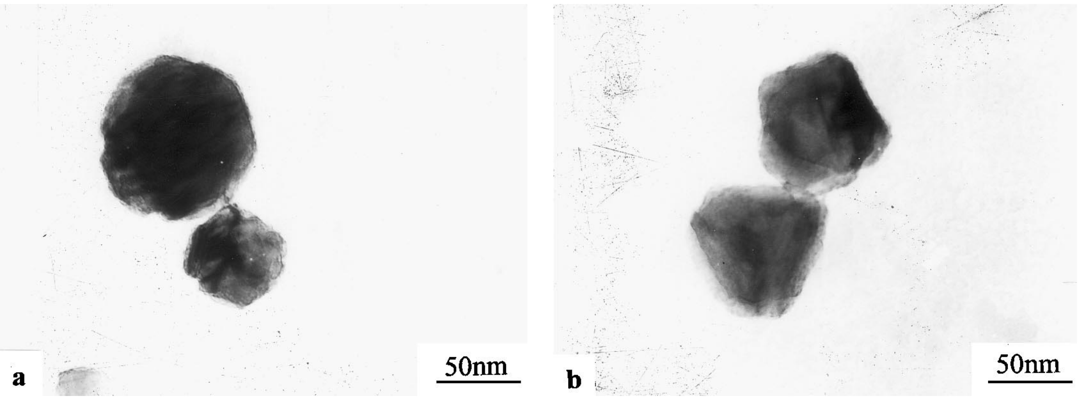

Fig. 2. TEM micrographs of SiC coated with (a) 15 wt.% $Al(OH)_3$ and (b)15 wt.% $Al(OH)_3$, and 20 wt.%$Y(OH)_3$.

between 3.4 and 4.0, similar to that of as-received SiC. When $Al(OH)_3$-coated SiC particles were coated with $Y(OH)_3$, the IEP of coated SiC shifted from pH 7.3 to pH 8.6, similar to that of $Y_2O_3$ [20]. It testified that nanosized particles can be coated by heterogeneous nucleation processing.

The suspension properties of oxide powders are dominated by the particle surface charge that is generated by surface hydroxylation reaction [14]. After nano-SiC coated with $Al(OH)_3$, the surface of coated SiC was terminated with neutral surface sites (–Al–OH) which react with either $H^+$ or $OH^-$ in acidic or basic solution to produce dominant positive [–Al–$(OH_2)^+$] or negative (–Al–$O^-$) surface sites below and above the IEP, respectively [12]. So the IEP of coated SiC was similar to that of alumina. However, the surface of $Al(OH)_3$ and $Y(OH)_3$-coated particles was terminated neutral surface sites (–Y–OH). For $Al(OH)_3$ sol-added SiC suspension, a part of sol particles adsorbed on the surface of nano-SiC particles by an electrostatic adsorption. The other part reserved in the solution in the form of nonadsorbed sol particles [3]. Nano-SiC can not be coated by $Al(OH)_3$ sol because both are nanometer level in diameter. So by adding $Al(OH)_3$ sol, the colloidal behavior of nano-SiC can be affected, but not changed.

The particles size distribution of as-received and $Al(OH)_3$-coated SiC in the optimal condition [as-received at pH 9.5, $Al(OH)_3$-coated at pH5.0] was measured by particle size analyzer (see Fig. 4). The dispersability of nano-SiC was improved by coating: the average particle diameter decreased from 145 to 136 nm, the amount of agglomerate particles whose size was more than 0.7 μm decreased from 15% to less than 1.0%. Large agglomerate particles in SiC powder were alleviated by coating with heterogeneous nucleation processing. This improves the dispersability of the nano-SiC, probably due to a change in surface properties. The surface of $Al(OH)_3$-coated SiC particles is more acidic and as such possesses a higher positive charge in the water-base system (see Fig. 3). This helps stabilize the particles in suspension [2].

The coating materials can be completely coated on the surface of nano-SiC particles with heterogeneous nucleation processing. So the amount of coating layer equals that of the coating materials. The thickness of coating layer $d$ can be calculated with a simple equation:

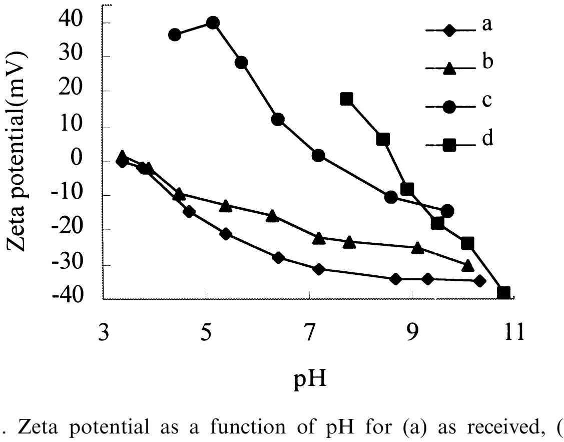

Fig. 3. Zeta potential as a function of pH for (a) as received, (b) $Al(OH)_3$-added, (c) $Al(OH)_3$-coated, and (d) $Al(OH)_3$ and $Y(OH)_3$-coated SiC.

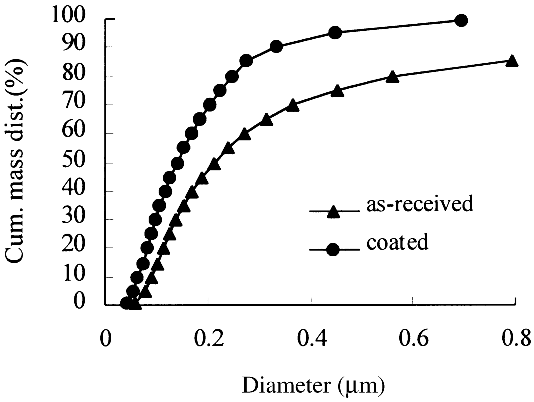

Fig. 4. Particles size distribution of as-received and $Al(OH)_3$-coated SiC.

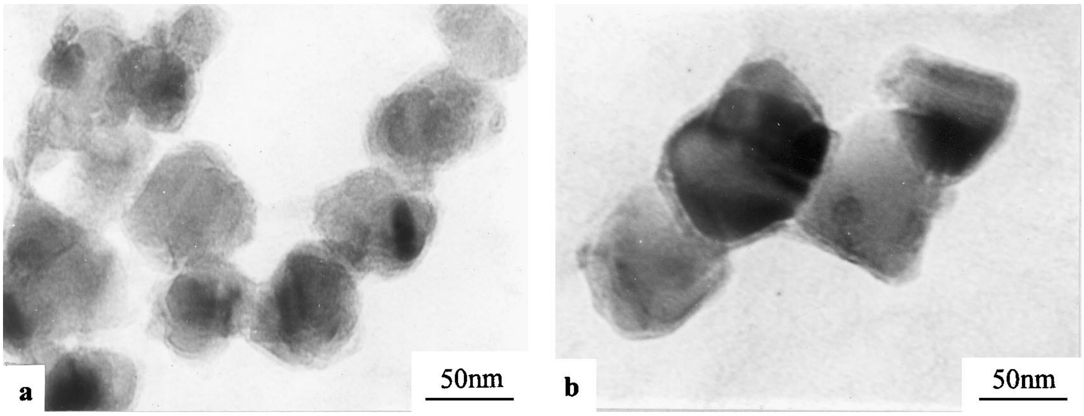

Fig. 5. TEM micrographs of nano-SiC coated with (a) 39 wt.% and (b) 58 wt.%.$Al(OH)_3$.

$$m_A = m_S \bullet BET \bullet d \bullet \rho \tag{1}$$

where $m_A$ is the weight of the coating materials, $\rho$ the density of coating layer materials, $BET$ the specific surface area of coated powders, $m_s$ the weight of coated particles.

$$d = \frac{m_A}{m_S \bullet BET \bullet \rho} \tag{2}$$

For given coated powders, $BET$ and $\rho$ were fixed values. The thickness of coating layer can be controlled by controlling the amount of coating materials. Fig. 5 shows TEM micrographs of nano−SiC coated with differing the amount of aluminum hydroxide. It can be found that the thickness of the coating layer was increased by increasing the amount of aluminum hydroxide. This result indicated that the thickness of coating layer can be easily controlled to different values as required in the course of coating with heterogeneous nucleation processing.

## 4. Conclusions

A nanocomposite powder, which is a nanometer powder coated with another phase, has been achieved with heterogeneous nucleation processing. TEM micrographs showed that the coating materials nucleated and grew on the surface of nano-SiC and did not form sol particles in solution using a buffered pH solution as the precipitation reagent. Thus, the thickness of the coating layer was easy to control by controlling the amount of coating materials. The results indicated that the nanosized particles can be coated with two different kinds of material by heterogeneous nucleation processing. In addition, the dispersability of nanocomposite powder was also greatly improved. It seems that heterogeneous nucleation processing is a promising method for coating nanometer powders.

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