

## Ni-coated $\text{Al}_2\text{O}_3$ powders

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### Abstract

A heterogeneous precipitation method was employed to prepare Ni-coated- $\text{Al}_2\text{O}_3$  powders using  $\text{Al}_2\text{O}_3$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_4\text{HCO}_3$  as the starting materials. The coated powders were characterized by TEM, AES,  $\zeta$ -pH. Results showed that a continuous amorphous  $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  film uniformly coated the  $\text{Al}_2\text{O}_3$  particles surface. After calcining at 400 °C for 2 h in air and reducing at 700 °C for 4 h in hydrogen atmosphere,  $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  was converted to Ni with size of about 20 nm, meanwhile, the continuous amorphous film become discontinuous. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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### 1. Introduction

The fracture toughness of brittle  $\text{Al}_2\text{O}_3$  ceramics can be increased through the incorporation of a ductile metal [1–4]. Reinforcement models show the importance of the homogeneity and fine size of the metallic inclusion [5]. In general, the control of the microstructure of  $\text{Al}_2\text{O}_3$ /metal composites is very difficult to achieve by traditional techniques involving mechanical mixing of  $\text{Al}_2\text{O}_3$  and metallic powders followed by hot-pressing. Although a small-scale homogeneity can be obtained using the sol-gel route [6–8], the relatively high cost of some reactants and the difficulty to control the gel drying step are drawbacks of the method.

In recent years, coating of processing aids on ceramic particles has been investigated for producing homogeneous ceramics. It not only improves the green density and sintering activity [9], but also enhances phase uniformity and mechanical properties of sintered body [10]. Various methods were used to prepare coated powders, such as co-precipitation [11], sol-gel [12], electroless plating [13] etc., among them, the co-precipitation seems very promising [14,15]. In the present work, Ni-coated  $\text{Al}_2\text{O}_3$  powders were prepared by the heterogeneous precipitation method.

### 2. Experimental procedure

Ni-coated  $\text{Al}_2\text{O}_3$  powders ( $\text{Al}_2\text{O}_3$ –10 vol% Ni) were prepared using a  $\text{Al}_2\text{O}_3$  powder with the average diameter of 0.35  $\mu\text{m}$  (Shanghai Songjiang Fertilizer, Co. China) and analytically pure  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_4\text{HCO}_3$ . The flow diagram of the coating process is shown in Fig. 1.  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  were first mixed in distilled water by ball milling for 24 h. Next,  $\text{NH}_4\text{HCO}_3$  solution of 1.0 M was added dropwise to the homogeneous slurry obtained above under vigorous stirring. To ensure complete reaction, excess  $\text{NH}_4\text{HCO}_3$  was used and the pH of the mixed solution was held between 8 and 9 during precipitation. The resulting precipitates were filtered and thoroughly washed with distilled water three times. Finally, the precipitates were washed with ethyl alcohol and dried at room temperature for 24 h. The as-dried precipitates were calcined in air at 400 °C for 2 h, and then the as-calcined samples were reduced at 700 °C for 4 h in hydrogen atmosphere [16].

Particle size, shape and thickness of the coated powders studied by transmission electron microscopy (TEM) (Model JEM-200CX, JEOL, Tokyo, Japan). Auger energy spectra (AES) (Microlab 310F, VG Scientific LTD., USA) have been used to investigate the composition of the coating on the surface of  $\text{Al}_2\text{O}_3$  particles. The zeta potential ( $\zeta$ ) of the powders as a function of pH was estimated from electrophoretic mobility and ionic conductivity (i.e. ionic strength) data.

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### 3. Results and discussion

Fig. 2 shows TEM images of the uncoated and coated  $\text{Al}_2\text{O}_3$  powders. It is observed that the uncoated  $\text{Al}_2\text{O}_3$  particles have a considerably smooth and dense surface without other particles adhering on it. A TEM image of the as-precipitated powders (Fig. 2b) shows the continuous amorphous  $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  coating layer formed on the surface of the as-received  $\text{Al}_2\text{O}_3$  [17]. So the  $\text{Al}_2\text{O}_3$  surface acts as a heterogeneous nucleation site. The preparation process of coated powders can be interpreted by the LaMer diagram as shown

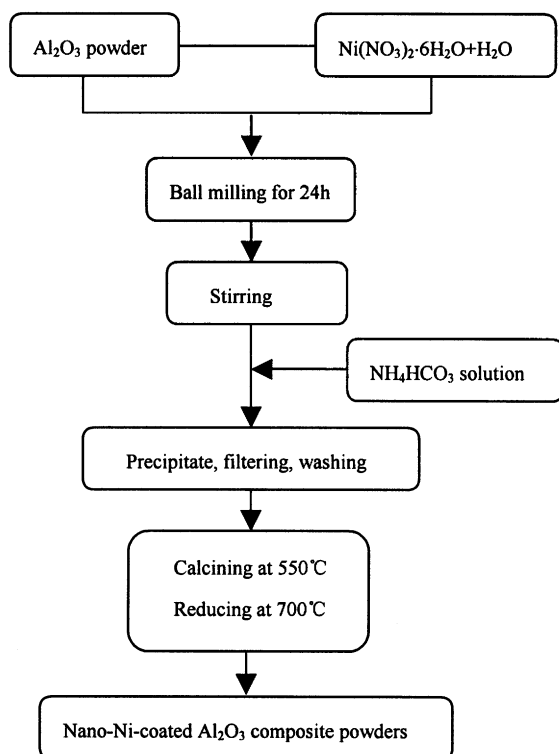


Fig. 1. Flow diagram for synthesizing Ni-coated  $\text{Al}_2\text{O}_3$  powder by the heterogeneous precipitation method.

in Fig. 3 [18]. In order to ensure heterogeneous precipitation occurs, the concentration ( $C$ ) of the produced  $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  must meet  $C_s < C < C_{\text{homo}}$  [ $C_s$  and  $C_{\text{homo}}$  are the solubility and the critical nucleation concentration of  $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  in water solution, respectively]. By the above model, the  $\text{NH}_4\text{HCO}_3$  solution added dropwise can ensure  $C$  to increase slowly. When  $C$  is higher than  $C_s$ ,  $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  begins to precipitate on  $\text{Al}_2\text{O}_3$  surface.

Fig. 4 shows TEM images of as-calcined and as-reduced coated powders. The amorphous coating layers of the coated  $\text{Al}_2\text{O}_3$  powders were crystallized to NiO particles after calcining at  $400^\circ\text{C}$  for 2 h in air [17]. Nanocrystalline NiO was completely reduced to Ni after as-calcined powders were treated at  $700^\circ\text{C}$  for 4 h in hydrogen atmosphere [16]. Fig. 4b shows that Ni in the coating layers is spherical and weakly agglomerated, and its particle size is about 20 nm. It is evident that the coating layers become discontinuous during heat treatment.

To further investigate the evolution of the structure of the coating layers during heat treatment, AES analysis was conducted on as-precipitated powders and those calcined at  $400^\circ\text{C}$  for 2 h in air and reduced at  $700^\circ\text{C}$  for 4 h in hydrogen atmosphere. A blank experiment was carried out on as-received  $\text{Al}_2\text{O}_3$  powder, which was

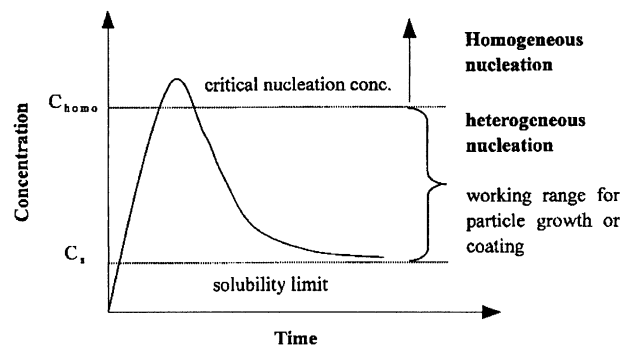


Fig. 3. LaMer diagram for the preparation of the coated powder.

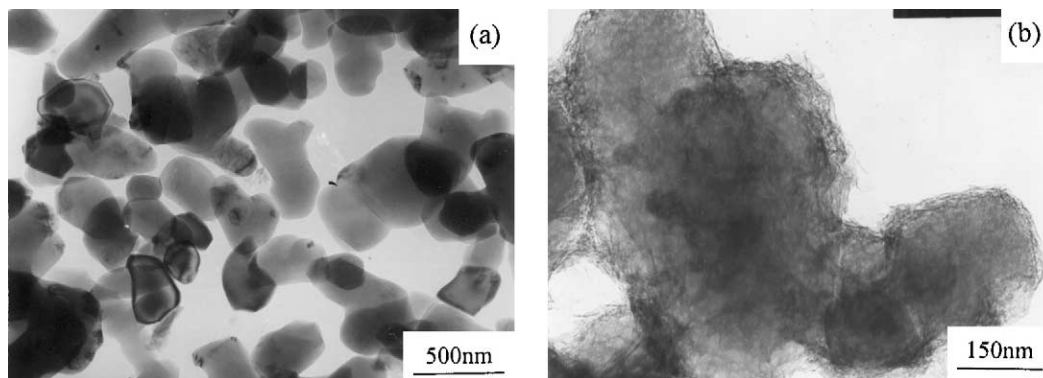


Fig. 2. TEM images of (a) the uncoated and (b) coated  $\text{Al}_2\text{O}_3$  powders.

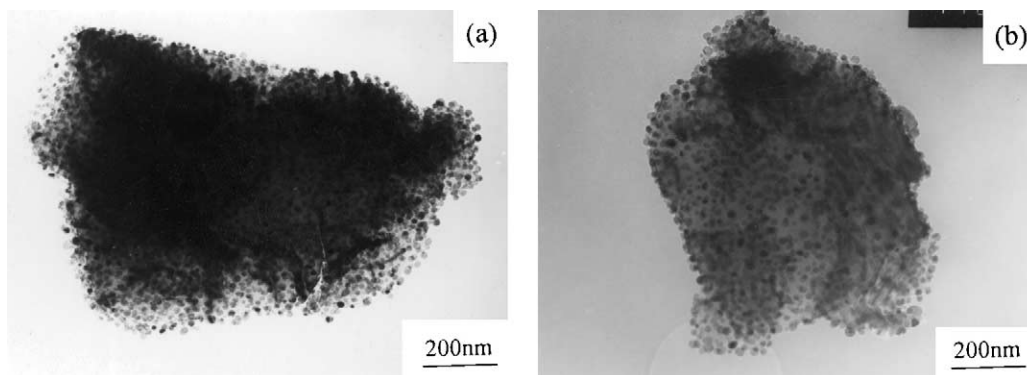


Fig. 4. TEM images of (a) as-calcined and (b) as-reduced coated powders.

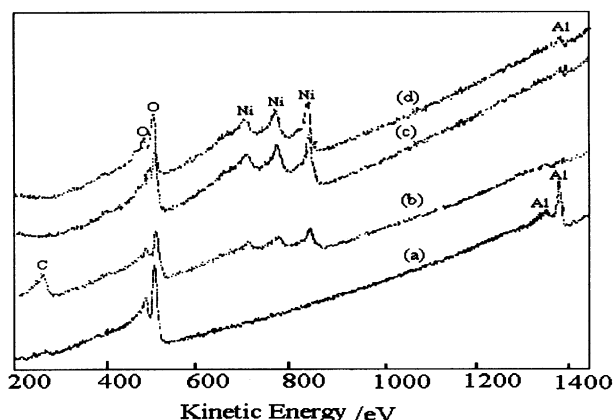


Fig. 5. AES spectra of (a) the uncoated (=as-received)  $\text{Al}_2\text{O}_3$  powders (b) the coated  $\text{Al}_2\text{O}_3$  powders (c) as-calcined powders at  $400^\circ\text{C}$  for 2 h in air (d) as-reduced powders at  $700^\circ\text{C}$  for 4 h in hydrogen atmosphere (after being calcined at  $400^\circ\text{C}$  for 2 h in air).

used for contrast. Their AES spectra are shown in Fig. 5. In the blank sample, only two kinds of elements were detected by the AES (Fig. 5a), i.e. O and Al, whereas as-precipitated powders (Fig. 5b) showed C, O, Ni and without Al. Both element C and Ni contribute to the  $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  precipitates. The above results show the amorphous  $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  uniformly precipitated on the  $\text{Al}_2\text{O}_3$  particles surface to be a continuous layer. From the spectrum of as-calcined powders at  $400^\circ\text{C}$  for 2 h in air (Fig. 5c), it is observed that Al peaks (at 1376 eV) appear again besides O and Ni, and the C peak disappears for the conversion of  $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  to NiO. The presence of the Al peak shows the coating layers to become discontinuous during calcination. The AES spectrum (Fig. 5d) of as-reduced powders shows that O Auger peaks are still strong, which probably contributes to the oxidization of nanocrystalline Ni surface and  $\text{Al}_2\text{O}_3$ .

As shown in Fig. 6, the isoelectric point of the NiO-coated  $\text{Al}_2\text{O}_3$  particles calcined at  $400^\circ\text{C}$  is higher than that of as-received  $\text{Al}_2\text{O}_3$  particles, and that the isoelectric point of the Ni-coated  $\text{Al}_2\text{O}_3$  particles reduced

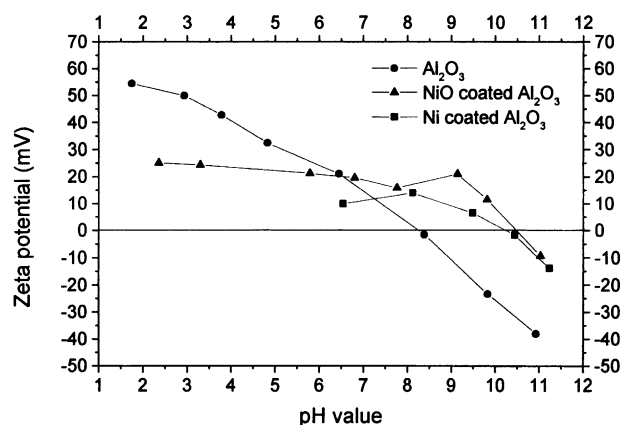


Fig. 6. Variations in the zeta potentials of as-received  $\text{Al}_2\text{O}_3$ , NiO-coated  $\text{Al}_2\text{O}_3$  at  $400^\circ\text{C}$  for 2 h in air, and Ni-coated  $\text{Al}_2\text{O}_3$  at  $700^\circ\text{C}$  for 4 h in hydrogen.

in hydrogen atmosphere at  $700^\circ\text{C}$  for 4 h approaches that of as-calcined NiO-coated  $\text{Al}_2\text{O}_3$  particles. It was observed that the solution became blue under pH of 6 during the measuring process because of Ni in the coating layers being dissolved. A reasonable explanation is that Ni particles are preferentially precipitated on the surface of  $\text{Al}_2\text{O}_3$  particles.

#### 4. Conclusions

Ni-coated  $\text{Al}_2\text{O}_3$  powders were successfully prepared by heterogeneous precipitation using  $\text{Al}_2\text{O}_3$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_4\text{HCO}_3$  as the starting materials. In the presence of  $\text{Al}_2\text{O}_3$  powder, when  $C$  met  $C_s < C < C_{\text{homo}}$ , the nuclei of the amorphous  $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  grown on the  $\text{Al}_2\text{O}_3$  surface acted as heterogeneous nucleation sites. After being calcined and reduced,  $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  was converted to Ni with a size of about 20 nm. The amorphous coating layers changed from continuous to discontinuous during heat treatment.

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