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Characterization of Al_2O_3–Al nano-composite powder prepared by a wet chemical method

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Abstract

A wet chemical method was used to prepare Al_2O_3-coated Al nano-size-composite powders using Al, aluminum nitrate and ammonia as the starting materials. TEM, SEM, TG/DSC, zeta potential, XPS, X-ray were used to characterize the composite powders. Results showed that a uniform thin $Al(OH)_3$ layer can formed on the surface of Al particles. After calcined at 1000 °C for 2 h, the thin $Al(OH)_3$ layer transforms to α-Al_2O_3 with mean size about 20 nm resulting in well dispersed Al_2O_3–Al composite powder.

Keywords: B. Nano-composite; D. Alumina; Wet chemical method; Coating; Aluminium

1. Introduction

Since Niihara and co-workers [1–3] began to report the beneficial effects of nanometer-sized Al_2O_3 particles in 1990s, many studies showed that the incorporation of nanometer-size metallic second phases in Al_2O_3 can significantly enhance its mechanical and thermal properties [4]. Metal phase has a better thermal conductivity and a greater thermal shock resistance than the monolithic Al_2O_3 ceramics. The metal phase can also enhance ceramic toughness since metal particles deform plastically and baffle cracks evolution [5].

In earlier works on alumina-metal nano-composites, various nano-size metals have been incorporated into alumina, such as Cr [6,7], Ni [8,9], Cu [10], Fe [11], W [12] and TiC [13], and the toughness can increase 2–3 times. Traditionally, the second phase was added by mechanical mixing of alumina and metallic powders and then followed by hot-press sintering in graphite dies. The main problem of the mechanical mixing method is how to obtain a fine dispersion of the second phase and a desirable thermal expansion mismatch between alumina and metal. If this problem is not solved properly it will limit wide applications of metal-ceramic nano-composites technique.

In recent years, a new route, the wet chemical coating process for preparing metal-ceramic nano-composites has been developed [14]. The wet chemical coating process has several advantages over mechanical mixing method and appears to be a suitable method for preparing metal-ceramic nano-composite powders. The phase of such obtained powder is more uniform, the surface bonding between metal and ceramic was enhanced, and the green density is improved greatly [15]. Therefore, research along this new route has potential applications in preparing metal-ceramic composites.

In present work, we use the wet chemical coating method to prepare α-Al_2O_3 coating Al nano-composites powders. α-Al_2O_3-coated Al particles were synthesized by calcining $Al(OH)_3$ gel coating on nano-size Al particles. As other metals, Al can serve as a second phase to toughen Al_2O_3 ceramics. In addition, it can improve ductility and thermal conductivity of Al_2O_3 ceramics. Furthermore, nano-size Al shows high yield strength and a high breaking strength, which are 5–6 times higher than that of coarse-grain [16]. And also, a thin oxidation film can be formed on the Al

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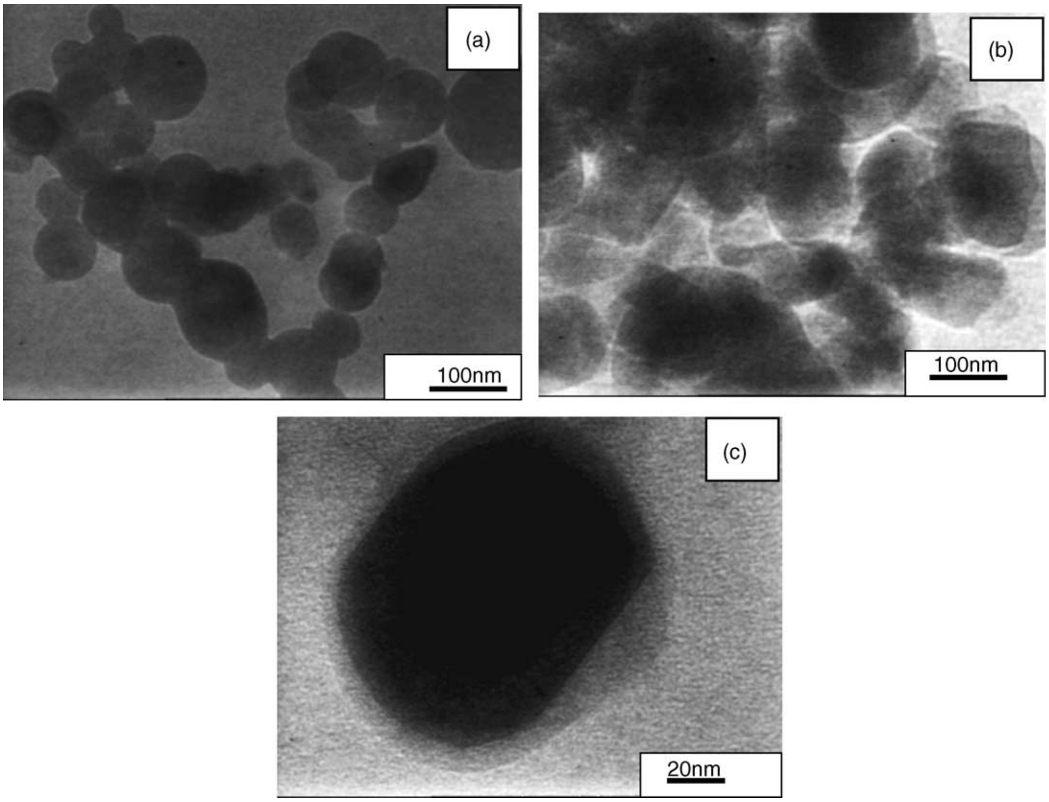

Fig. 1. TEM images of the uncoated Al (a) and coated Al powders (b, c).

particle surface. In this way, a fine intermediate layer can be formed between Al and Al_2O_3, which may improve the bonding between Al and Al_2O_3. Our result shows that composites studied have no obvious agglomeration. The composite particles have a spherical shape with a mean particle size about 130 nm and the coating α-Al_2O_3 powder has a size of about 20 nm.

2. Experimental

Al_2O_3 coated Al nano-composite powders were prepared by using commercial nanometer Al powders (particle size 80–100 nm, purity 99%), aluminum nitrate (purity of 99%) and ammonia. Aluminum nitrate was first dissolved in distilled water. Appropriate nano-size Al powder was

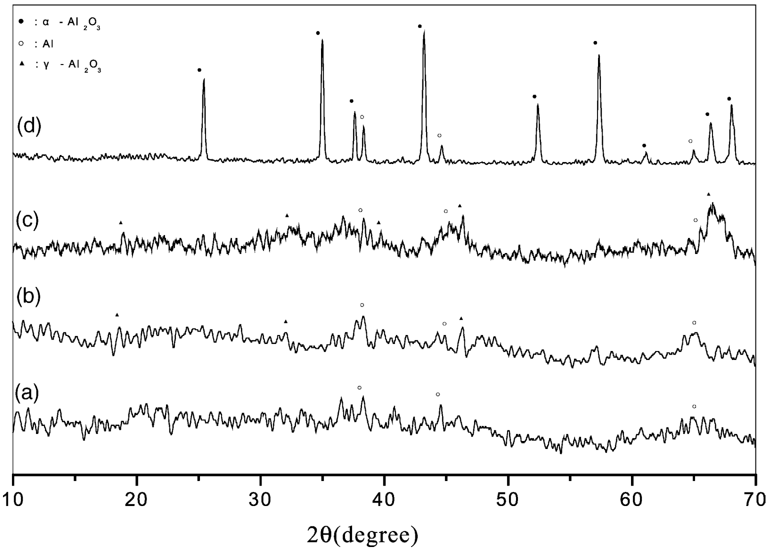

Fig. 2. XRD results for (a) the precursors before calcined, (b) composite powders calcined at 280 °C, (c) composite powders calcined at 450 °C, (d) composite powders calcined at 1000 °C.

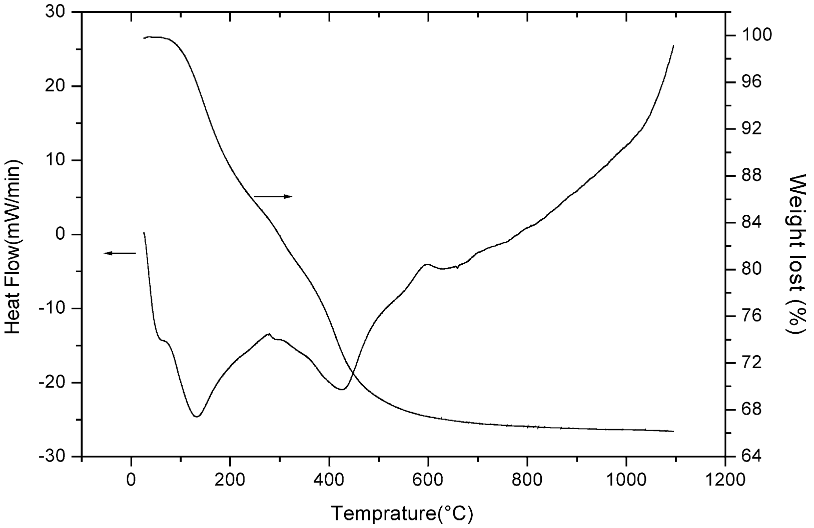

Fig. 3. TG/DSC results for the Al_2O_3-coated Al composite powders.

weighted according to a mol ratio Al:10Al_2O_3. The weighed Al powder was added into $Al(NO_3)_3$ solution under vigorous stirring in order to obtain a completely dispersing. Ammonia (diluted to 5 vol.% with distilled water) was then dripped into the mixture at a speed of 100 drips per minute. The reaction can be expressed as:

$$Al(NO_3)_3 + 3NH_4OH \rightarrow Al(OH)_3 \downarrow + 3NH_3NO_3,$$

and $Al(OH)_3$ can be formed on the surface of Al powders. To ensure a complete reaction, excess ammonia was used and the pH value of the solution was maintained at 7–8 during the reaction. Appropriate diluted hydrochloric acid was added in order to prevent aggregation. The composite deposits were vacuum filtered and washed by distilled water or ethanol for several times. The obtained precipitation was dried at 70 °C for 24 h, and then the obtained precursor was calcined at different temperature in argon atmosphere separately. The composite powders were milled in agate mortar for 2 h, pressed into pellets under 15 MPa, and then pressureless sintered at 1450 °C for 2 h.

Phases of the precursor before and after calcined were examined by X-ray diffraction (XRD) (Model D/MAX-3B, RIGAKU, Japan). X-ray photoelectron spectroscopy (XPS) (Model AXISULTRA, UK) was used to analyze the surface components of the powders. Particle size and shape of the coated powders were observed by transmission electron microscopy (TEM) (Model JEM-2010, JEOL, Japan). The microstructure of the sintered composite was determined by scanning electron microscopy (SEM)(Model JSM-5610LV, JEOL, Japan). Differential scanning calorimetry (DSC) and thermogravimetry (TG) (Labsys, Setaram, France) was used to analyze precursor crystallization and weight change with temperature. The surface potential of the powders was estimated with zeta potential (ζ) equipment (Model Zetasizer 3000HS, Malvern Instruments Ltd., Malvern, UK).

3. Results and discussion

Fig. 1 shows TEM images of the uncoated and coated Al powders. It can be seen that uncoated Al powders had a ball appearance with a smooth and clean surface (Fig. 1a). TEM image of the precipitated powders (Fig. 1b and c) verified that a uniform $Al(OH)_3$ layer was formed on the surface of

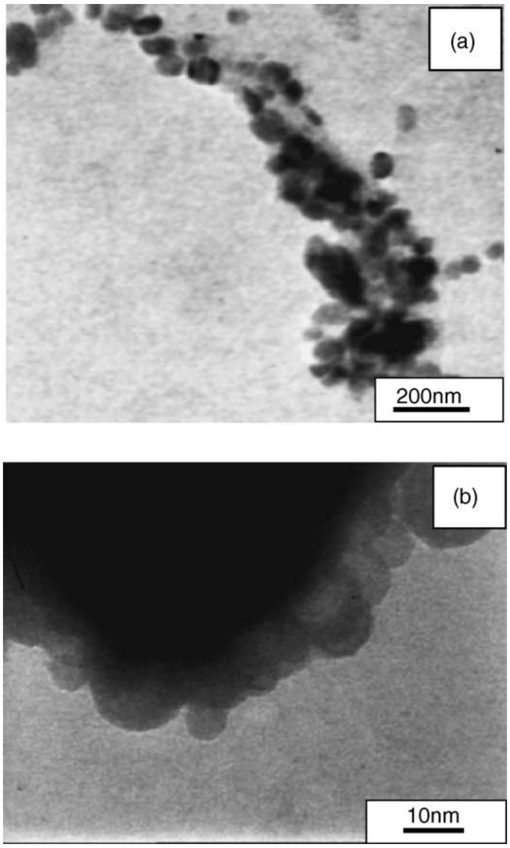

Fig. 4. TEM images of composite powders calcined at 1000 °C for 2 h.

nano-Al particles and the layer thickness was about 10–20 nm. Fig. 2 shows the XRD patterns of the coated powders before and after heat treatment at 280 °C, 450 °C, and 1000 °C, respectively. From these XRD patterns, it is clear that $Al(OH)_3$ in the precursor is in amorphous form before calcine since there are no significant peaks appearing. After heat treatment at 450 °C, peaks corresponding to the γ-Al_2O_3 appear. It means that a considerable phase change, from $Al(OH)_3$ to γ-Al_2O_3, occurs. When heated at 1000 °C for 2 h, peaks of α-Al_2O_3 become remarkable. Traditionally, it is reported that the $Al(OH)_3 \rightarrow \gamma$-$Al_2O_3$ and γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ transformation temperatures are about 500 °C and 1200 °C, respectively. In our experiment, these temperatures were reduced to 450 °C and 1000 °C, much lower than the normal transformation temperature. This reduction of transformation temperature may be caused by the high activity of nano-scale powders. Moreover, residual NH_4NO_3 in the precursor can release energy that is also beneficial to decrease transformation temperature [17]. Fig. 3 shows the DSC/TG data of the composite precursor powders. Endothermic peaks present at about 160 °C showing the loss of OH and 450 °C the formation of γ-Al_2O_3. TEM micrographs of as-calcined Al_2O_3-coated Al powders are showed in Fig. 4. After calcined at 1000 °C for 2 h, the thin layer of $Al(OH)_3$ surround Al particle was converted to α-Al_2O_3 particles with size about 20 nm. While, the Al nucleus still remained without obvious grain growth and oxidation. It is well known that pure Al will melt at about 660 °C and grain size become large obviously at about 180 °C. However, in our experiment, there wasn't obviously grain

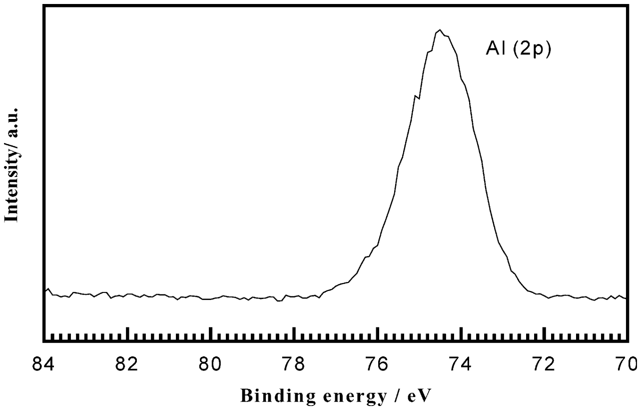

Fig. 5. Al(2p) spectra for alumina-coated Al after calcined at 1000 °C.

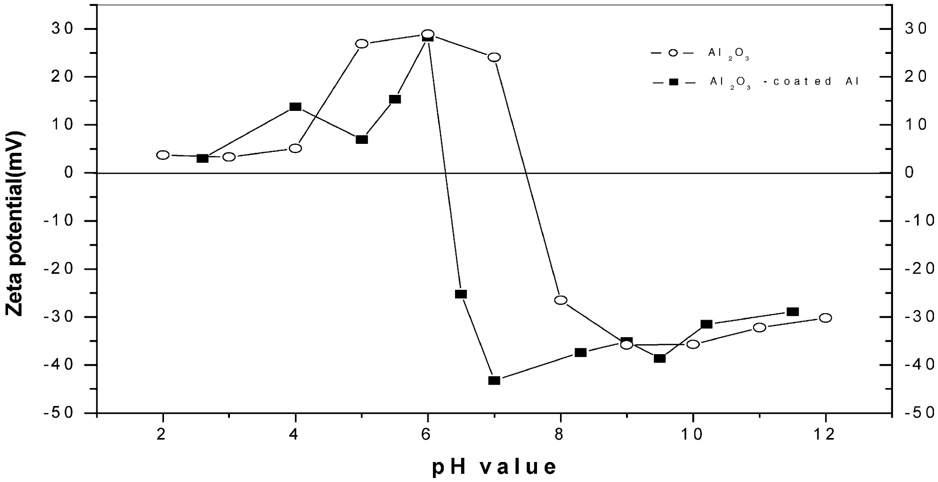

Fig. 6. Zeta potential as a function of pH for Al_2O_3 and Al_2O_3-coated Al.

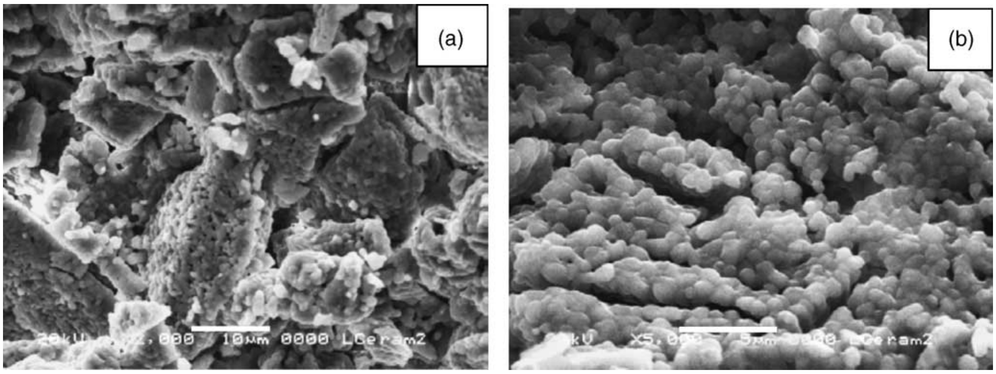

Fig. 7. SEM images of Al_2O_3-coated Al ceramics calcined at 1450 °C/2 h.

growth of Al. This may be due to that the Al particles surface are closely coated by Al_2O_3 powders layers which preventing strong oxidation and grain growth of Al.

Fig. 5 shows Al(2p) spectra for surface layer of Al_2O_3-coated Al composite powders measured by XPS. The peak appears at a binding energy of 74.7 eV, confirmed that the surface of the obtained powder is Al_2O_3 and Al particles are closely enclosed by Al_2O_3. Fig. 6 shows the zeta potential versus pH of monolithic Al_2O_3 and as-received composite powders with isoelectric point (IEP) pH7.5 and pH6.5. Obviously, the curve behavior of Al_2O_3-coated Al powders was similar to that of Al_2O_3. This also indicates that the surface of Al powders is coated with Al_2O_3. As seen from Fig. 6, the surface of Al_2O_3-coated Al particles possessed a higher negative charge at pH 7–8, which was away from the IEP. Under this condition, particles can be dispersed very well without agglomerates.

Fig. 7 shows the microstructure of the Al_2O_3-coated Al nano-composites ceramics sintered at 1450 °C. When sintering temperature becomes higher the coated Al_2O_3 particles grow up with a size about 500 nm. These Al_2O_3 particles surround Al nucleus uniformly as Fig. 8(a) indicated.

4. Conclusions

Al_2O_3-coated Al nano-composites powders were successfully prepared by heterogeneous precipitation using alumiun nitrate, ammonia and nano-size Al powder as starting materials. A uniform thin $Al(OH)_3$ layer can be formed on the surface of Al particle. After calcined at 1000 °C for 2 h, the $Al(OH)_3$ layers change to α-Al_2O_3 nano-particles with mean particle size of 10–20 nm and result in a well dispersed alumina-coated Al composite powder with spherical shape. The advantage of the Al_2O_3-caoting Al powder is that a fine transition layer may be formed between Al and Al_2O_3, which can be improved the bonding between Al and Al_2O_3. In addition, due to the close coating of Al_2O_3 on the Al surface that separate Al particles, there is no obvious grain growth of Al particles during the heat treatment. This is desirable for preparing Al_2O_3–Al composite ceramics.

Acknowledgement

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