

Preparation of zirconia coated graphite powders

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Abstracts

ZrO₂ coated flake graphite powders were prepared by the controlled hydrolysis of zirconium oxichloride. The stirring process plays an important role in the coating process. There are two types of coated ZrO₂ particles : (a)primary particles with few nm size were obtained by the direct formation of the shell by precipitation on the surface of the graphites and (b)Secondary particles of ZrO₂ with ~0.1 μ m size were obtained by the independent formation of primary particles of the ZrO₂ and subsequent heterocoagulation at the graphites surface.

1. Introduction

Graphite is widely used for engineering materials.[1,2] The graphite, however, have essential disadvantages in properties such as high porosity, low mechanical strength and a low degree of oxidation resistance at high temperatures.[1] Graphite-ceramic composites have been expected to be able to improve on these disadvantages of graphites.[3,4] However, the graphite-ceramic composites have not yet received practical applications. One reason of this is the weak sinterability of graphite and most refractory ceramic powders.

Coating of fine particles of given chemical composition with a layer of another kind can be used to modify the surface characteristics of core material.[3~6] Zirconia powders can be synthesized by hydrolysis of zirconium salt solutions or zirconium hydroxide suspensions with crystalline powders and low synthesis temperatures.[7~10] Characteristics of synthesized powders, such as crystallite size, crystalline phase, surface area, particle size distribution and degree of aggregation are dependent on the synthesis conditions such as solution chemistry(i.e. pH, concentration and anionic species) and temperature.

2. Experiments

Zirconium oxichloride(98%pure, Junsei Chem.) was dissolved in distilled water at

0.2M for all experiments. The solutions were highly acidic as prepared and they were hydrolyzed under acidic conditions. Few grams of flake graphite powders were dispersed and stirred for 24 hours in 0.2M $ZrOCl_2 \cdot 8H_2O$ aqueous solution, then the Zr ion concentrations of the supernatant were analysed by ICP analysis. The adsorption quantity of Zr ion was calculated from Zr ion concentrations of supernatant. A 125ml Teflon beaker was used in all experiments to minimize contamination from vessel. The beaker was set in a heating mantle on a magnetic stirrer to avoid settling of graphite powders during the process. The solution temperature was 100°C for all experiments, and the heating time was 48 hours. After the completion of each experiments, the powder was collected by filtering and washed in DI water repeatedly until the supernatant showed neutral pH. The graphite powders were dried at 120°C for 24 hours prior to characterization. Coated graphite powders were characterized by thermal analysis and TEM. A selected sample was analyzed by thermal gravimetry(TG) in air to measure the unreacted ionic species(OH^- , Cl^- etc.) content and weight loss of graphite by oxidation. The heating rate was 20°C/min up to 1000°C in TG analysis. The surface of coated graphite powder was studied by an TEM.

3. ICP analysis

Flake graphite was settled down after the coating process, no zirconium hydroxide precipitation could be observed and the solution was clear when the stirring process was carried out prior to the hydrolysis process. But, the solution was cloudy white in the case of no stirring process. Almost all of the Zr ions were precipitated after the 48hr reaction time in both case. The result of ICP analysis for the supernatant from the 24hr stirring process was shows that about 50% Zr ions were adsorbed at the graphite surface. It seems that the stirring process plays an important role in the coating process.

4. TG Analysis

Fig. 1 shows TGA results of raw and coated flake graphite. The slope of TGA curve of coated flake graphite was slightly decreased and also total weight loss was decreased. The weight loss beginning at about 350°C was caused by decomposition of OH^- and Cl^- ions in the coated flake graphite, because no calcination process was carried out after the coating process. The weight loss of low temperature range was about 3%. The total weight loss of raw and coated flake graphite powders at the temperature up to 1000°C in air was about 55% and 32%. Oxidation resistance of

graphite was increased by the ZrO_2 coating.

5. TEM Observation

Fig.2 shows bright and dark field image of transmission electron micrographs of zirconia coated flake graphite powders. Two types of ZrO_2 particles, secondary and primary ZrO_2 particle, was observed on the graphite surface. Fig. 2(a) shows that the secondary particles of ZrO_2 with $\sim 0.1\mu m$ size were distributed discretely on the graphite surface. Fig. 2(b) and (c) are dark field image and SADP of primary ZrO_2 particles with few nm size which coating the graphite surface more continuously than secondary particle.

In principle, zirconia coating by the hydrolysis of Zr-salt may be obtained by two different mechanism : (a)direct formation of the shell by precipitation on the surface of the graphites, or (b)independent formation of tiny particles of the ZrO_2 and subsequent heterocoagulation at the graphites surface to produce a shell. In our system either of the two processes may be operating.

6. Conclusions

We have prepared the ZrO_2 coated flake graphite powders by the controlled hydrolysis of zirconium oxichloride. The stirring process plays an important role in the coating process. There are two types of coated ZrO_2 particles and each of these may be obtained by two different mechanism[6]: (a)primary particles with few nm size were obtained by the direct formation of the shell by precipitation on the surface of the graphites and (b)Secondary particles of ZrO_2 with $\sim 0.1\mu m$ size were obtained by the independent formation of primary particles of the ZrO_2 and subsequent heterocoagulation at the graphites surface.

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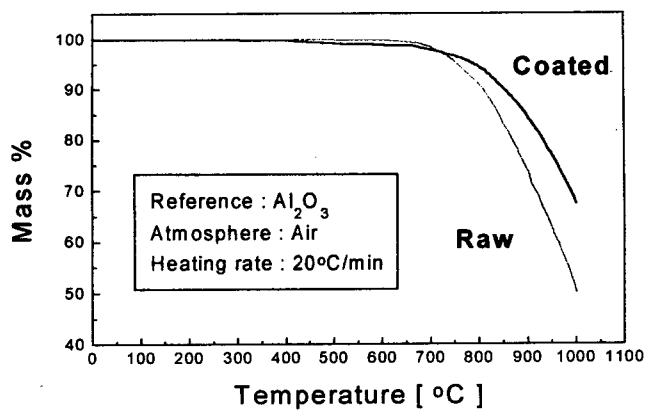


Fig. 1 TGA results for raw flake graphite and ZrO_2 coated flake graphite powder.

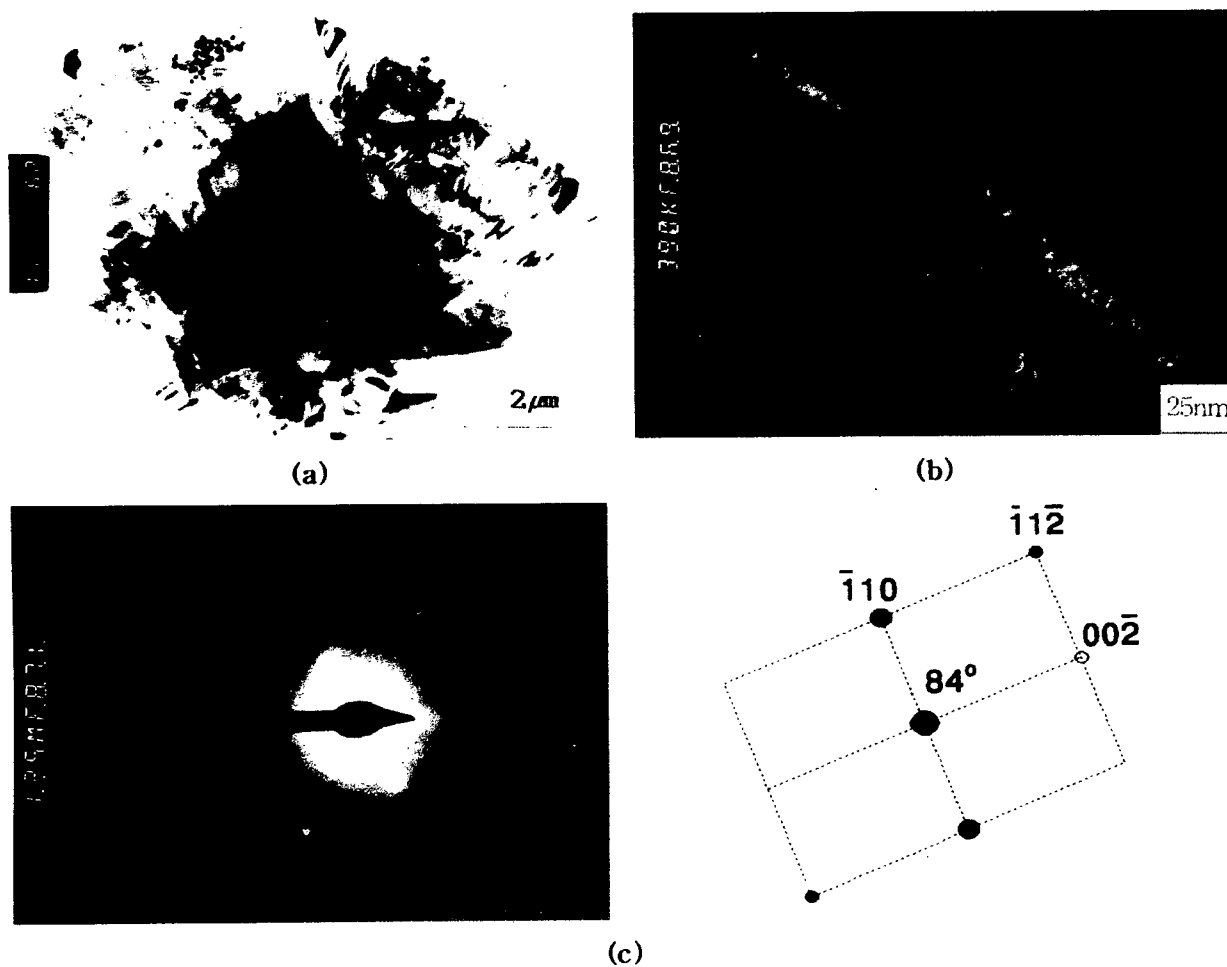


Fig. 2 TEM micrographs of ZrO_2 coated flake graphite powders.

- (a) Bright field image of secondary particles of ZrO_2 with $\sim 0.1\mu m$ size
- (b) Dark field image of primary particles of ZrO_2 with few nm size
- (c) SADP of primary particles of ZrO_2 with few nm size