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Preparation of ZrO_2 coated graphite powders

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Graphite powders were coated with ZrO_2 by the controlled hydrolysis of a zirconium oxychloride aqueous solution. The hydrolysis process was carried out with temperature control because of the low wettability of ZrO_2 to the surface of the graphite. PVA was added to the solution for the enhancement of Zr ion adsorption. The surface of the graphite particles coated with ZrO_2 was observed by TEM. There are two types of ZrO_2 particles; (a) primary particles a few nm in size and (b) secondary particles with $\sim$0.1 μm size were obtained. The data of oxidation weight loss and surface potential show that the graphite surface was successfully modified by the forced hydrolysis of the zirconium chloride aqueous solution. © *2000 Kluwer Academic Publishers*

1. Introduction

Graphite is widely used for engineering materials [1–3]. However, graphite has essential disadvantages in properties such as high porosity, low mechanical strength and a low degree of oxidation resistance at high temperatures [1–3]. Coating of fine particles with a layer of another kind of material can be used to modify the surface characteristics of core material [4–9]. In principle, particle coatings may be obtained by two different mechanisms; (a) surface precipitation and (b) heterocoagulation. Heterogeneous interfaces in colloidal dispersion can enhance the concentration of ionic species which is necessary for the selective formation of precursor precipitate at the particle/solution interface and also act as heterogeneous nucleation sites of the precipitates [4, 5, 8]. Solutions of metal salts can be treated in a variety of ways to precipitate amorphous metal hydroxide complex [8–11]. The driving force of the nucleation can be provided by the control of pH or temperature.

In this study, graphite powders were coated with ZrO_2 by the controlled hydrolysis of a zirconium oxychloride aqueous solution, for the purpose of enhancing the oxidation resistance of graphite. The surface of the coated graphite powders was observed by transmission electron microscopy (TEM). Oxidation weight loss and Zeta potentials were measured to estimate the effect of surface modification of the graphite powders coated with ZrO_2.

2. Experimental procedure

Zirconium oxychloride (98% pure, Junsei Chem.) was dissolved in distilled water at 0.2 M for all experiments. In some experiments, 1000 ppm of polyvinyl alcohol (PVA, M.W. 2000, Showa Chem.) was added to the solution. A few grams of flake graphite powder were dispersed and stirred for 0–24 hours in 0.2 M $ZrOCl_2.8H_2O$ aqueous solution, then the Zr ion concentrations of the supernatant were analyzed by induction coupled plasma (ICP) analysis. A 125 ml Teflon beaker was used in all experiments to minimize contamination from the vessel. The beaker was set in a heating mantle on a magnetic stirrer to avoid settling of the graphite powders during the process. The solution temperature was 100 °C for all experiments, and the heating time was up to 48 hours. After the completion of each experiment, the powder was collected by filtering and washed with hot distilled 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 TEM. To estimate the oxidation resistance of raw graphite and ZrO_2 coated graphite, weight loss after the oxidation of the graphite was measured. 0.5 g of graphite was introduced to a box furnace preheated to oxidation temperatures. Oxidation was carried out for 30 min at temperatures of 800, 900 and 1000 °C. The zeta potentials of the powders as a function of dispersion pH were estimated from the electrophoretic mobility data.

3. Results and discussion

3.1. ICP analysis

Results of the ICP analysis for the supernatant of graphite dispersion after stirring for 24 hrs, show that

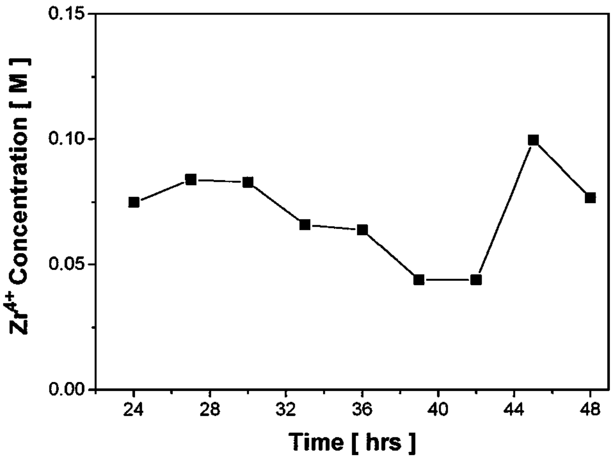


Figure 1 Concentrations of Zr^{4+} ion in supernatant of graphite suspension with various stirring times at 50°C. (0.2 M $ZrOCl_2 \cdot 8H_2O$ aqueous solution).

most of the originally added Zr^{4+} ions remain freely and such a result is expected because there are only a few adsorption sites for Zr ionic species on the graphite surface. After the forced hydrolysis reaction, graphite and ZrO_2 particles were distributed separately, and the solutions show a cloudy white color due to the ZrO_2 particles. This problem was resolved by the addition of a polymeric compound, PVA. PVA molecules can be easily adsorbed into the graphite surface and provide adsorption sites for Zr ionic species. Fig. 1 is the Zr concentration of the supernatants with various stirring times measured by ICP analysis. After stirring for 24 hrs, Zr concentrations of the supernatants were below 0.1 M, i.e. more than half of the added Zr ions in the original solution were adsorbed to the graphite surface.

3.2. TEM observations

Fig. 2 is a TEM micrograph of graphite particles coated with ZrO_2 precursors which had been stirred for 24 h without a hydrolysis reaction. Graphite surfaces were coated with fluffy layers of zirconia precursors which were a few linked tetramers [10] at the earlier stage of the hydrolysis of zirconium chloride.

Figure 2 TEM micrograph of the graphite particles coated with zirconia precursor.

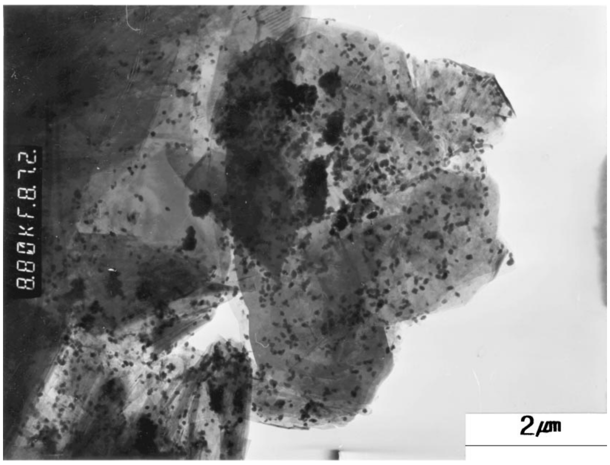


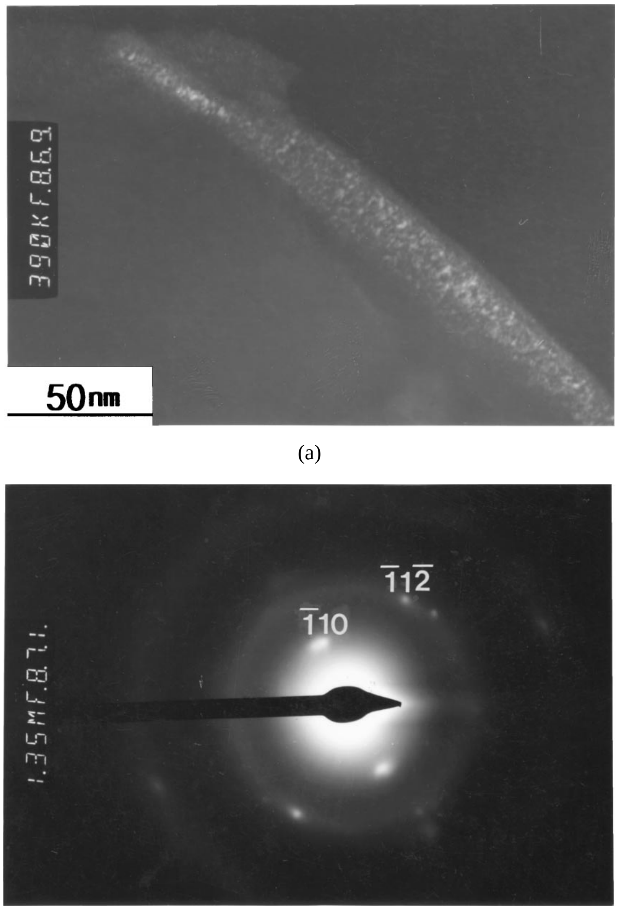
Figure 3 TEM micrograph of the graphite particles coated with secondary zirconia particles.

Fig. 3 shows the TEM image of the ZrO_2 particles which have an average size of ~0.1 μm. During the heating of the solution at 100 °C, hydrolytic polymerization happened to form an ordered array of tetramers. The uniformly coated amorphous zirconium hydroxide layer transformed into discrete particles of ZrO_2 through the hydrolysis reaction. Some of them could have been formed by heterocoagulation. Another type of ZrO_2 particles is represented in Fig. 4a. Fig. 4a is a dark field image using a $(\bar{1}10)$ reflection of monoclinic ZrO_2. The bright spots in Fig. 4a are primary particles of ZrO_2 of a few nm in size. These primary particles of ZrO_2 seem to have been formed by the heterogeneous nucleation process.

We can postulate the following coating mechanism from the results of the ICP and TEM analysis: 1) PVA molecules are adsorbed into graphite surfaces. PVA molecules at the graphite surfaces enhance adsorption of Zr ions into the graphite surfaces, and uniform zirconium hydroxide layers are formed. 2) The uniform zirconium hydroxide layers transform into discrete zirconia particles through a hydrolysis reaction. Zirconia particles are composed of primary and secondary particles of a few nm and 0.1 μm in size, respectively.

3.3. Oxidation resistance and zeta potential

The relative weight losses of the coated graphite with stirring and reaction times are represented in Fig. 5. Weight loss of the graphite stirred for 24 hrs without a hydrolysis process was smaller than the other samples. By the results of the TEM analysis, graphite without hydrolysis process had relatively uniform zirconium hydroxide layer which transforms to discrete zirconium oxide layer during the hydrolysis process. The mechanism of the improvement for oxidation resistance is not clear yet, but we consider the decrease of the accessible area as a major factor in the increase of oxidation resistance. Oxidation of graphite at the temperature below 1000 °C occurred by two mechanisms: a) surface reaction controlled at low temperature b) diffusion controlled at high temperature [3]. ZrO_2 coated graphite have a reduced accessible area on the graphite surface, so oxidation resistance was large at the low temperature



(a)

(b)

Figure 4 TEM micrographs of graphite particle coated with primary zirconia particles. (a) D.F. image using ($\bar{1}10$) reflection of m-ZrO_2 (b) SADP.

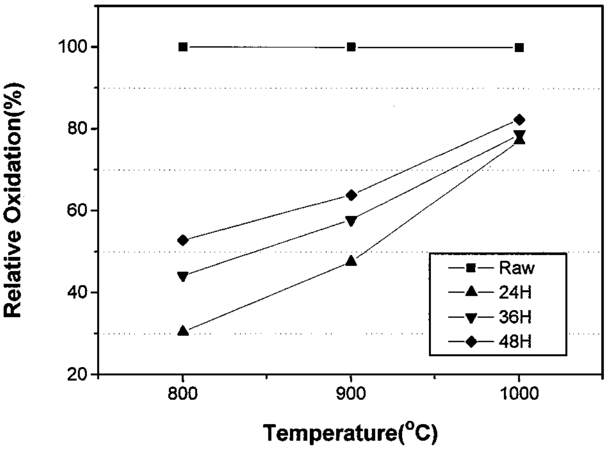


Figure 5 Relative weight losses of graphite powders coated with zirconia. (Rel. wt. loss [%] = (wt. loss of coated graphite)/(wt. loss of raw graphite) × 100).

region than at the high temperature region as shown in Fig. 5.

Fig. 6 shows zeta potentials of aqueous ZrO_2, graphite and coated graphite suspensions as a function of pH without adding any electrolyte to control the ionic strength. Raw and coated graphite were too large particles to estimate Zeta potential correctly by electrophretic method and they had s very small values of Zeta potential as shown in Fig. 6. The Zeta potential of raw graphite had the small positive value in the entire pH range under investigation (pH 2–13). Point of zero charge (pzc) of coated graphite was at pH 7.8 and the surface characteristics of graphite powder were modified by the ZrO_2 coating. Zeta potential was determined by electrophoretic mobility measurement in our experiments. Electrophoretic mobility is affected by particle shape and size. We used natural flake graphite which have large particle size, so Zeta potentials of graphite particles could be underestimated than its real value.

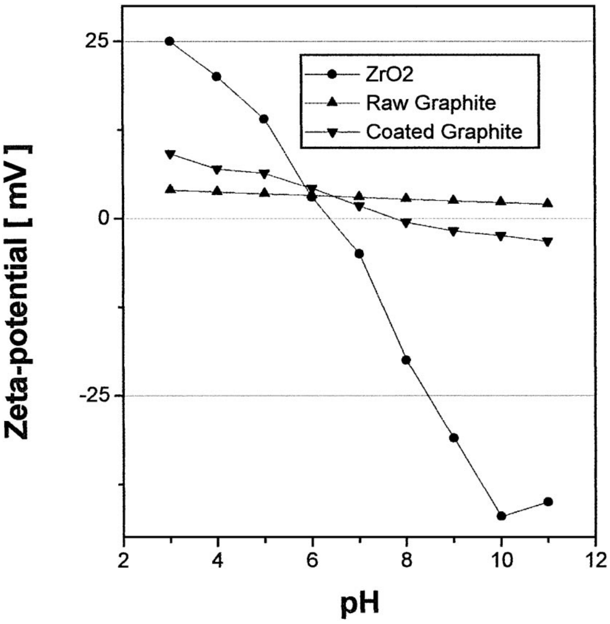


Figure 6 Zeta potential of ZrO_2, raw graphite and coated graphite powders as a function of pH.

4. Conclusions

We have prepared ZrO_2 coated flake graphite powders by the controlled hydrolysis of zirconium oxychloride. Uniform ZrO_2 precursor layers can be formed by the addition of PVA and a stirring process. During the forced hydrolysis process, uniform precursor layers transform into discrete ZrO_2 particles; (a) primary particles of a few nm in size and (b) secondary particles of ZrO_2 of $\sim 0.1\ \mu$m in size. The data of oxidation weight loss and surface potential shows that graphite surface characteristics are successfully modified by the forced hydrolysis of the aqueous zirconium chloride solution.

Acknowledgement

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