Enhancement of Dispersion and Fluidity of Aqueous Carbon Slurry by Addition of Various Dispersants

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The dispersion and fluidity of aqueous carbon slurries were studied to elucidate the optimum preparation conditions to obtain well-dispersed and fluidized aqueous carbon slurries. The mean particle diameter of the carbon powder used was 13 nm. Styrene/maleic copolymer (SM), poly(styrenesulfonic acid (HPSS), and naphthalene sulfonic acid formalin condensate ammonium salts (DEMOL–AS) were selected as dispersants. The rheological behavior of aqueous carbon slurries with various dispersants was examined and evaluated. The electrorheological behavior of the carbon particles in the presence of DEMOL–AS, SM, or HPSS indicated that the surface properties of the carbon particles changed from hydrophobic to hydrophilic by adsorption of dispersants. The fluidity of aqueous carbon slurries was effectively enhanced by the addition of DEMOL–AS, as compared with the addition of SM or HPSS. DEMOL–AS containing a naphthalene nucleus was an effective dispersant to improve the surface of carbon particles. The dispersion and fluidity of the carbon slurries were dependent on electrorheological and steric interactions. The carbon slurries with DEMOL–AS were well dispersed and fluidized over a wide range of pH. These observations indicated that DEMOL–AS is an effective dispersant for preparing aqueous carbon slurries.

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1. Introduction

Silicon carbide materials are prime candidates for structural ceramic parts, such as gas turbine engines, heat exchangers, wear-resistant seals, and diffusion furnace parts for semiconductor manufacture.1–5) The forming process for the materials as well as the preceding SiC powder preparation process is very important in the fabrication of ceramic parts as defects introduced in this process will normally remain in the product even after a successful sintering process. The slip casting of SiC is usually performed using non-aqueous media. However, slip casting in aqueous media6–9) is especially important in terms of ecology, safety, and cost. In slip casting, enhancement of the dispersion and fluidity of the SiC slurry is a key technique for fabricating structural silicon carbide parts.

We have reported previously that a SiC body of high sintered density can be obtained through the slip casting process, using aqueous slurries containing an anionic polymer dispersant and tetramethyl ammonium hydroxide (TMAOH) at a pH of ∼10–11.6,7) When boron carbide and carbon powders were added as sintering aids, boron carbide had no effect on the fluidity of the SiC slurries. However, enhancement of the dispersion and fluidity of carbon particles as a sintering aid are key concerns in slip casting of aqueous slurries, because of the hydrophobic surface and high specific surface area of carbon particles.

Systems for the dispersion of carbon are used in many industrial fields, including printing ink, organic polymer processing, and cable coating. Carbon slurries used in these industries are normally composed of carbon powder and non-aqueous media. The dispersion and fluidity of aqueous carbon slurries were investigated in coal water mixture (CWM), which is expected to provide an alternative to fuel oil as an energy source.8–10) As CWM is combusted directly in the furnace, it is necessary for CWM to have high solid loading, good storage characteristics, transportability, and a high degree of atomization. The rheological behavior in CWM is one of the most important factors. There have been many reports concerning CWM with respect to the effects of polymer dispersants, such as anionic surfactants8,9) and non-ionic surfactants,10) to obtain a well-dispersed and fluidized highly loaded CWM. However, the characteristics of carbon powders as a sintering aid in SiC had many differences from coal in CWM in terms of purity, particle size, and surface conditions. Fine and pure powders, such as carbon black, were desirable for carbon powders as sintering aids in SiC, because the purity of powder and dispersion of carbon in the SiC body influence fired density of SiC.

The present study was performed to elucidate the optimum preparation conditions to obtain a dispersed, fluidized, and thickened aqueous carbon slurry with fine carbon powder and to characterize the role of polyelectrolytes in the slurry.

2. Experimental

2.1 Materials

Carbon powder ( #2650, Mitsubishi Chemical Co., Tokyo, Japan) was used to prepare the slurries. The mean particle diameter and specific surface area of the powder supplied by the manufacturer were 13 nm and 320 m²/g, respectively. The density of the carbon powder was 1.9 g/cm³, as measured using a helium pycnometer (Micromeritics Gas Pycnometer, Accupyc 1300, Shimadzu, Kyoto, Japan) after drying in the oven at 150°C for 24 h. Three kinds of dispersants were used in this study: aqueous styrene/maleic copolymer (SM) (average M. W. = 1,900, Acros Organics, Geel, Belgium) solution with tetramethyl ammonium hydroxide (TMAOH) (Aldrich Chemical Co., Milwaukee, WI), sodium polystyrene sulfonate (PS–1900, average M. W. = 14,000, Lion Corp. Tokyo, Japan), and β-naphthalene sulfonic acid formalin condensate ammonium salts (DEMOL–AS, average M. W. = 7,000, Kao Corporation, Tokyo, Japan). Polystyrenesulfonic acid (HPSS) was prepared from sodium polystyrene sulfonate by the ion exchange method. Figure 1 shows the molecular structures of various polyelectrolytes used as dispersants.
2.2 Slurry preparation
Slurries containing ion exchanged water, dispersant, and carbon powder, which were added to the slurries in a fixed amount on a dry-weight basis (dwb) of carbon powder, were prepared by ball milling, with SiC balls in polypropylene pots for 24 h at room temperature. The pH of the slurries was adjusted with TMAOH and HNO₃ (Wako Pure Chemical Industries, Ltd., Osaka, Japan).

2.3 Measurements
Sediment volume were measured after pouring 100 ml of each carbon slurry into a graduated cylinder, which was then sealed and left to stand for 24 h prior to measurement. The apparent viscosities of the slurries were measured at 100 s⁻¹ using a controlled-stress rheometer (R590, Haake, Karlsruhe, Germany) at 25°C. The electrokinetic behavior was determined for slurries containing 2 vol% carbon powder and 10⁻² M KCl as a supporting electrolyte using an acoustophoretic spectrometer (DT-1200, Dispersion Technology Inc., Mt. Kisco, NY) at 25°C.

3. Results and discussion
3.1 Characteristic of aqueous carbon slurries
Figure 2 shows the sediment volume of 1 vol% (about 2 mass%) aqueous carbon slurries without dispersant as a function of pH. The sediment volumes of the carbon slurries at pH 2-11 showed similar values. Loose sediment formed in the slurries left for 24 h. The supernatants of the slurries were transparent from pH 2 to pH 4. Zeta potential values of the carbon particles in aqueous media showed very low absolute values at pH 2-12. These results indicated that the surfaces of carbon particles used in this study were almost completely covered by hydrophobic groups. In the carbon aqueous slurries, a flocculated structure was formed due to very weak electrostatic repulsive potentials of the particles based on the hydrophobic surface of the carbon particles. In addition, these observations indicated that it was necessary to improve the surfaces of the carbon particles by altering hydrophobic to hydrophilic to prepare a well-dispersed and fluidized aqueous carbon slurry.

3.2 Effect of various dispersants
Figure 3 shows the electrokinetic behavior of carbon particles as a function of the amounts of various dispersants. The electrokinetic behaviors of the carbon particles in the presence of various amounts of DEMOL-AS, HPSS, or SM showed similar trends. The zeta potential of carbon particles without dispersant had a low positive value. With the addition of dispersants, the zeta potential of carbon particles changed from a positive to a negative value, which decreased with increasing amount of dispersant added up to 10 mass% dispersant, and then exhibited high absolute surface charges above 10 mass% dispersant. Dispersion of carbon particles was enhanced by the addition of dispersants, because the electrostatic repulsive potential overcame the van der Waals attractive potential. This increase in electrostatic repulsive potential was explained as a switch in the surface properties of the carbon particles from hydrophobic to hydrophilic due to the adsorption of dispersant on the surface with increasing amount of dispersant. As a result, SM, HPSS, and DEMOL-AS were effective as dispersing agents for the carbon slurries.

Figure 4 shows the effects of the concentration of various dispersants on the apparent viscosity of 25 mass% carbon slurries. The apparent viscosity value of the carbon slurries with SM decreased abruptly up to 9.5 mass%, and had a minimum value with the addition of 9.5 mass% SM, and then increased gradually with increasing amount of SM. In the carbon slurry with HPSS, the apparent viscosity of the slurry decreased gradually up to 17 mass% HPSS, and then increased slightly with more than 17 mass% HPSS. The appar-
ent viscosity of the carbon slurries exhibited lower values with the addition of 17–40 mass% DEMOL−AS. The optimum amounts of SM, HPSS, and DEMOL−AS, required for the enhancement of fluidity of the carbon slurries, were around 9.5 mass%, 17 mass%, and 17–20 mass% of dry-weight base (dwb) of the carbon powders, respectively. Especially, the apparent viscosity of the slurries containing DEMOL−AS was effectively enhanced over a wide range of added amount, as compared with carbon slurries containing SM or HPSS. Although the zeta potential values of carbon particles with SM, HPSS, or DEMOL−AS showed no differences in the low apparent viscosity region of slurries containing various dispersants, the fluidity of the carbon slurry was effectively enhanced by the addition of DEMOL−AS. The enhancement of the fluidity of the slurry was suspected to influence not only electrokinetic but steric interactions, based on the types of hydrophilic groups and differences in molecular weight of the dispersants. The apparent viscosity values of slurries prepared with DEMOL−AS were much lower than the minimum apparent viscosity of those prepared with HPSS, which had the same hydrophilic group. The neutral chains of DEMOL−AS and HPSS are composed of a naphthalene nucleus and a benzene nucleus, respectively. The difference in fluidity of the carbon slurries prepared with HPSS or DEMOL−AS was based on their molecular structures. It was reported previously that the fluidity of CWM was enhanced by the selective adsorption of hydrophobic groups in polymer dispersants composed of a functional group (benzene nucleus etc.) on the hydrophobic surface of coal particles. The naphthalene nucleus in DEMOL−AS was considered an effective adsorption site for the carbon surface as compared with the benzene nuclei in HPSS and SM, because the surface of carbon black particles was more hydrophobic than that of coal particles as determined from the contact angle of water. These results indicated that the addition of DEMOL−AS strongly enhanced the fluidity of aqueous carbon slurries.

3.3 Effects of pH on fluidity in the presence of various dispersants

Figure 5 shows the effects of pH on the electrokinetic behavior of 2 vol% carbon slurries containing various dispersants. The amounts of DEMOL−AS, HPSS, or SM added to the carbon slurries were selected from the data shown in Fig. 4. With the addition of SM to the carbon slurry, the zeta potential value of the carbon particles gradually decreased up to pH 8, eventually reaching a constant low value. The electrostatic interaction of the carbon particles with SM was mainly dependent on the hydrophilic carboxyl group of SM. This carboxyl group was not dissociated in the acidic region, but existed as −COO− in the basic region. Due to this behavior, the flocculated structure was formed in the acidic to neutral regions due to weak electrostatic repulsive potential of the particles with a small negative surface charge, and these structures collapsed in the basic region. Therefore, the zeta potential values of carbon particles with SM gradually increased with increasing pH. The electrokinetic behaviors of the particles with HPSS and DEMOL−AS were not dependent on pH, and the zeta potential values for slurries containing HPSS and DEMOL−AS were similar at pH 2–11. As the sulfonic acid group in HPSS or DEMOL−AS exhibited stable hydrophilicity at all pH values, the carbon slurries with HPSS or DEMOL−AS were well dispersed by strong electrostatic repulsive potential of carbon particles with a high negative surface charge over a wide range of pH. The flow behavior of carbon slurries containing DEMOL−AS reflected this electrokinetic behavior as shown in Fig. 6. In the acidic to basic region, the fluidities of the carbon slurries showed little changes, with constant apparent viscosity up to pH 11. The apparent viscosity of carbon slurries prepared with HPSS was not as low as that of the slurry prepared with DEMOL−AS, but the flow be-
havior of the former as a function of pH was similar to that of the latter. These results indicated that DEMOL–AS was a very attractive dispersant for slip casting of SiC, because the fluidity of SiC slurries was enhanced by adjusting to the basic region. In fact, green bodies were obtained through slip casting from SiC slurries with carbon and B₄C containing the optimum concentration of DEMOL–AS of dwb of carbon powders, and then the sintered bodies with SiC powders exhibited higher densities of about 98% Th. D.²⁷ Taken together, these observations indicated that DEMOL–AS was an effective dispersant for the preparation of aqueous carbon slurries.

4. Conclusions

Dispersion of aqueous carbon slurries in the presence of DEMOL–AS, SM, or HPSS was enhanced by improvement of the surface properties on the particles from hydrophobic to hydrophilic, because of the adsorption of dispersants on the surface. The fluidity of aqueous carbon slurries was effectively enhanced by the addition of DEMOL–AS. This result indicated that DEMOL–AS, which has a naphthalene nucleus, was an effective dispersant, as compared with HPSS or SM, which contain benzene nuclei. The enhancement of the fluidity of the slurries was dependent on electrokinetic and steric interactions. The carbon slurries prepared with DEMOL–AS were well dispersed and fluidized over a wide range of pH. DEMOL–AS was an effective dispersant for preparation of aqueous carbon slurries.

References