Evaluation and control of the interaction between inorganic particle surfaces: application to environmental functional materials

Toshihiro ISOBET

Department of Metallurgy & Ceramics Science, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-S7-8 Ookayama, Meguro-ku, Tokyo 152–8550, Japan

The interaction between solid surfaces was evaluated by scanning probe microscopy using a colloidal probe. The dispersant provided a repulsive force between the solid surfaces at less than 30 nm. On the other hand, the binder provided a bridging force between the solid surfaces for retraction at less than 500 nm. Because of the complicated nature of the forces acting between the surfaces, the separation distance between ceramic particles (SDP) was calculated. Moreover, the relation between the agglomeration/dispersion of Al₂O₃ particles and the calculated SDP were discussed. As an extension of these results, Al₂O₃ pastes were prepared for tape casting from a viewpoint of the SDP. The tape casting of nanoparticles, which is generally difficult, was successful. On the basis of these fundamental studies applied to environmental functional materials, porous ceramics having oriented pores were prepared by an extrusion method. The obtained porous ceramics demonstrate high capillary action and are used for the relaxation of an urban heat island. Porous ceramics having nano-sized pores were prepared by a slip casting method.

1. Introduction

Inorganic particles are used for paints, cosmetics, ceramic products, industrial products including cement, and so on. In the last few decades, inorganic particles have also been applied to innovative colloidal processes, e.g., self-assembly processes, solid free-form fabrication, and solar cells. The control of particle dispersibility is closely related to the properties of the final products, as is well known. Essentially, the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory explains particle behavior in an aqueous solvent. However, there are interaction forces that are not predicted by this classical theory (non-DLVO forces). Because these forces are an important subject of research toward understanding the dispersion of particles, many studies have been conducted. Classical DLVO and non-DLVO forces are experimentally measured by the surface forces apparatus (SFA) developed by Israelachivili, et al. and the scanning probe microscopy (SPM). Table 1 lists the experimentally observed DLVO and non-DLVO forces. Thus far, many types of very complicated mechanisms have been reported. Therefore, working with non-DLVO forces in ceramic processing is still considered to be a matter of ceramic processing know-how, and thus it can be suggested that the evaluation of non-DLVO forces can be useful for the evaluation of ceramic processing know-how. In this study, the latest non-DLVO forces are introduced, and the preparation and properties of the resulting environmental functional materials as an example of the inflexion method of the non-DLVO forces are discussed.

2. Non-DLVO forces related to organic additives in ceramic processing

Polymer additives have generally been categorized as binders, plasticizers, and dispersants. The effects associated with these different types of additives have been primarily demonstrated using rheological tests. These results have greatly enhanced the understanding of slurries and pastes as a continuum and have significantly contributed to chemical engineering and powder technology. However, little research has been conducted on the effects in relation to surface science. Evaluations of polymer behavior on colloids in a solvent are expected to considerably improve colloidal processes because polymer behavior can exert control over dispersion and agglomeration.

First, poly(ammonium acrylate) (PAA), a typical dispersant, was evaluated by the colloidal probe method. The obtained force curves are presented in Fig. 1(a). The approach force curve (red diamonds) shows no interaction at separation distances of more than 30 nm and demonstrates only a repulsive interaction at separation distances of less than 30 nm. The retraction force curve (blue circles) was in good agreement with the approach force curve. Thus, PAA lends a repulsive force to the solid surface.

Poly(vinyl alcohol) serves as a binder for ceramic processing, and this material was also evaluated by the same method as PAA [Fig. 1(b)]. The average degree of polymerization of PVA was about 2000. The approach force curve also shows a repulsive interaction at separation distances of less than 30 nm. In contrast, the retraction force curve (blue circle) shows a different behavior. At distances greater than 200 nm, a smooth line was observed at approximately 0 mN/m. However, extensions were obtained at approximately 150 nm and 200 nm. It is considered that these extensions originate from the bridging of PVA between the
Table 1. Non-DLVO forces measured by SPM

| Solvent     | Solid surface | Interaction force | Ref. |
|-------------|---------------|-------------------|------|
| NaCl aq.    | Silica        | DLVO force        | 14   |
| KCl aq.     | Alumina       | Hydration force   | 15   |
| LiCl aq.    | Silicon       | Hydration force   | 16   |
| NaCl aq.    | Alumina       | Hydration force   | 17   |
| KCl aq.     | Alumina       | Hydration force   | 18   |
| PLL-g-PEG   | Niobium oxide | Steric repulsive  | 19   |
| AAE-EO      | Magnesia      | Steric repulsive  | 20   |
| PEIs        | Alumina       | Steric repulsive  | 21   |
| Asphaltene  | Silica        | Steric repulsive  | 22   |
| PS-dextrin  | Talc          | Steric repulsive  | 23   |
| SO-dextrin  | Clinochlore   | Steric repulsive  | 24   |
| NaCl aq.    | OTS           | Bridging force    | 25   |
| PAA         | Zirconia      | Steric repulsive  | 26   |
| Aluminum    | Alumina       | Steric repulsive  | 27   |
| PVA         | Glass         | Steric repulsive  | 28   |
| PDMS        | Silica        | Steric repulsive  | 29   |
| PEI         | Silica        | Steric repulsive  | 30   |
| PS          | Gold          | Steric repulsive  | 31   |
| PVA         | Glass         | Steric repulsive  | 32   |
| PS          | Gold          | Steric repulsive  | 33   |

PLL-g-PEG: Poly(L-lysine)-graft-poly(ethylene glycol)
AAE-EO: Anionic acrylic ester-ethylene oxide
PEIs: Polyethyleneimines
Asphaltene: n-heptane/n-heptane/butane = 40:1
PS-dextrin: Phenyl succinate regular maize dextrin
SO-dextrin: Styrene oxide regular maize dextrin
OTS: Octadecyltrichlorosilane
PAA: Ammonium polyacrylic acid
Aluminon: Aurintricarboxylic acid ammonium salt
PVA: Poly(vinyl alcohol)
PDMS: Poly(dimethyl siloxane)
PEO: Poly(ethylene oxide)
PEI: Polyethyleneimines
MEMA: Methylethermethacrylate
PS: Polystyrene
PVAc: Poly(vinyl acetate)

that estimate the mean separation distance between particles (SDP) in a slurry.35-38) Woodcock35) described the SDP, \( h \), as follows:

\[
h = D \left( \frac{1}{3 \pi \phi} + \frac{5}{6} \right)^{1/2} - 1,
\]

where \( D \) and \( \phi \) are the median particle size and the solid loading in the slurries, respectively.

Figure 2. A schematic model of PVA molecules between the colloidal probe and the substrate.34)

Figure 3. (a) Average particle sizes measured using the electro-acoustic method and (b) the SDP calculated from Eq. (1) as a function of powder content.39)
with increasing Al₂O₃ particle loading at less than 15, 30, and 45 vol.% for suspensions A, B, and C, respectively. The results demonstrate that the particles were well dispersed in these suspensions. The SDP was around 10 nm and the particles were agglomerated to maintain a constant SDP at more solid loading. The results suggest that the dispersion/agglomerate state of Al₂O₃ particles depends on the SDP. These basic findings were applied to ceramic processing. As an example, tape casting of nano-sized Al₂O₃ particles was carried out.⁴⁰ Figure 4 shows a schematic illustration of the Al₂O₃ pastes used for tape casting and designed as a basis for the application of the SDP. The illustration shown in Fig. 4(a) indicates the conditions where the immersion of PVA between particles in the paste is difficult. It may be regarded that the immersion of PVA into agglomerated particles is also difficult because PVA was added to an already agglomerated Al₂O₃ slurry used in this tape casting trial. Under these conditions, PVA was expected to bind flocculated particles heterogeneously, which leads to uneven capillary forces between particles during drying. As a result, cracks were formed in the sheets prepared from this paste, as shown in Fig. 5(a). On the other hand, the paste shown in Fig. 4(b) indicates the conditions where the immersion of PVA between particles is easy. The SDP of the paste used in this tape casting trial was calculated to be 16.2 nm, and this allowed PVA to be immersed between particles. Thus, the existence of more homogeneous capillary forces within the sheet resulted in crack-free drying, as shown in Fig. 5(b).

However, not only the dispersion/agglomerate state of the particles affects the cracking of the ceramic sheets prepared by tape casting but also the polymer state between ceramic particles is extremely important for their quality.

4. Application to environmental functional materials

Ceramic products were prepared from the pastes designed as a base for the SDP studies discussed in Section 3, and their design was equivalent to that already discussed. The reparation and properties of the environmental functional materials are introduced in this section.

4.1 Porous ceramics for heat islands

Porous ceramic having unidirectionally aligned pores are favorable for the relaxation of urban heat islands.⁴¹,⁴² This type of porous ceramics was prepared by the extrusion method⁴³⁴⁷ and is termed as “Lotus ceramics”. Extrusion is a widely used process in the ceramics industry. If the particles incorporated in an extrusion paste have a high aspect ratio, they tend to orient in such a way that the flow resistance reduces. Such anisotropy in green products is generally unsuitable because it causes inhomogeneous shrinkage in the drying and sintering processes. However, this method can be used intentionally to fabricate unidirectionally porous ceramics using flammable fibers as pore formers, as illustrated in Fig. 6. The most typical Lotus ceramic microstructures are shown in Fig. 7. In this case, carbon fibers were used as pore formers. Lotus ceramic microstructure indicates cylindrical pores unidirectionally aligned parallel to the extruded direction. This type of porous ceramic was also prepared using other flammable fibers, such as nylon 6-6,⁴⁵⁴⁷ rayon⁴⁹ and polyactic acid.⁴⁹ Moreover, the effect of the paste composition on pore orientation was investigated.⁴⁵⁴⁷ After these examinations, flammable fibers were shown to have better dispersion and agglomeration was suppressed by the addition of a lubricant that allows extrusion under higher pressures. The fiber orientation also improves with addition of the lubricant. In this way, porous ceramics having characteristic microstructure were prepared by an appropriate paste preparation. The relation between the properties of Lotus ceramics and their ability to raise water owing to capillary action has recently been discussed.⁴⁹-⁵²

4.2 Gas separation filters

Porous ceramic filters are suitable for gas separation because of their high heat resistance and chemical stability. Use of porous ceramics enables low-cost and maintenance-free continuous processing of gas separation filters. Therefore, it is expected that application of these filters to energy and environmental engineering, e.g., carbon dioxide capture and storage (CCS),⁵³ integrated
The theoretical gas selectivity calculated by Knudsen diffusion and above, as shown in Fig. 8(c). In porous ceramic was determined to be 1.36 at 0.01 MPa and about 1.25 at 0.1 MPa selectivity calculated from these results was almost constant and but diminished at lower pressures, as shown in Fig. 8(b). Gas coefficients before surface modification (c) N2/CO2 gas selectivity before surface modification; (d) N2 and (e) CO2 gas permeability coefficients after surface modification; (f) N2/CO2 gas selectivity after surface modification.58

Theoretical gas selectivity can effectively inform our design and preparation of higher-performance ceramic materials.57) Based on these results, Al2O3 developed on the basis of dispersion data.55),56) Furthermore, intensify. Instruments designed for particle dispersion have been obtained.58) The N2 gas permeability coefficient was nearly constant, being coated by AlOOH was lower than that before being coated with AlOOH, as shown in Fig. 8(d). However, the CO2 gas permeability coefficient of the sample after hydrothermal treatment declined notably at low pressures [Fig. 8(e)]. Consequently, the gas selectivity at was observed to raise more low pressures, up to a maximum of about 1.47 [Fig. 8(f)].

5. Summary

In this study, non-DLVO forces were measured by scanning probe microscopy using a colloidal probe and ceramic processing was evaluated using non-DLVO forces. DLVO theory is a superior theory for describing the interaction between solid surfaces in liquids. Interactions that do not match this theory function are in the realm of ceramic processing know-how and involve various factors without pursuing a detailed cause. However, non-DLVO theory can effectively inform our design and preparation of slurries and pastes if we definitely understand the characteristics. The investigations introduced in this study are only a few cases. We have also studied slurries and pastes including polymer/ceramics containing negative thermal expansion hybrid films.59) porous magnetic filters for O2 gas concentration,60) and so on. It is hoped that this research will lead to scientific elucidation of present ceramic processing know-how and result in the development of higher-performance ceramic materials.

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Toshihiro Isobe received a Master of Engineering from Nagoya Institute of Technology in 2003 and Doctor of Engineering from Tokyo Institute of Technology in 2006. He was a Postdoctoral Fellow in the National Institute of Advanced Industrial Science and Technology (AIST) from 2006 to 2008. He has been working as an assistant professor at Tokyo Institute of Technology since 2008. His current research interests include colloid and surface science, ceramic processing, and environmental ceramics.