ELSEVIER

Ceramics International 32 (2006) 521–525

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

The interaction of organic dispersant with alumina: A molecular modelling approach

H. Gocmez *

Ceramic Engineering Department, Engineering Faculty, Dumlupinar University, Kutahya 43100, Turkey

Received 2 February 2005; received in revised form 19 March 2005; accepted 1 April 2005
Available online 25 May 2005

Abstract

A molecular modelling approach has been used to screen and select appropriate dispersant for a given colloidal forming process. Seven dispersants with different molecular structure based on a benzene ring substitution with (–OH) and (–COOH) functional groups have been examined on the alumina surface. Theoretically computed interaction energy between dispersant and alumina surface and its correlation with adsorption amount of dispersant on alumina surface, which was obtained experimentally in the literature was studied. The simulation results showed that when functional groups increase in organic additives, the computed interaction energy between alumina surface and organic molecules increases. The proposed methodology based on molecular modelling computations, requiring no experimental data can be used to preliminary determine the most promising dispersants from large set of possible organic additives.

Keywords: Dispersant; Molecular modelling; Alumina; Functional groups

1. Introduction

The concept of colloidal ceramic processing has been successfully applied to the ceramic industry to produce high quality, high performance and reliable ceramic parts [1,2]. The stability of suspension during the colloidal processing has a significant influence on engineering properties of ceramic products [3,4]. A stable dispersion that requires the control of the interparticle forces in suspension can eliminate structural defects and stress centers in sintered ceramics [5,6].

Colloidal stability of ceramic powders in solution, typically in water, depends on ionic strength, surface charges, types and amount of dispersants, solid loading, pH value and temperature [7,8]. When the ceramic particles are added to suspending medium, particles are charged and thus van der Waals attraction force is generated on the surface of the particles, which result in the formation of agglomerate [9]. It is necessary to overcome van der Waals attraction force to keep particles as separate. Therefore, a repulsive force needs to be introduced to the colloidal system to disperse particles in the suspension. This force can be obtained in an aqueous solution by either electrostatic, steric or electrosteric stabilization. However, it is not easy to acquire well-stabilized, homogeneous and dispersed high solid loading suspension without dispersant [3]. An efficient use of inorganic or organic surface active dispersants controls the interparticle forces (van der Waals and repulsion) affecting the rheology of systems [10]. Organic dispersants exhibit several advantages over inorganic dispersants including greater stability, greater control of flocculation state and higher consolidated green density, less impurity and reduction in sintering temperature [11]. The absorption of organic dispersant on the surface of the alumina particles increases the surface charges, which improves repulsion force.

Hidber et al. [12] described the effect of the molecular structure of low molecular weight organic dispersants upon the adsorption and dynamic electrophoretic mobility behavior of alumina suspension. In their study, the number and position of (–OH) and (–COOH) functional groups of dispersant were systematically changed and their behavior compared with each other at different pH values. They found

* Tel.: +90 53374886676; fax: +90 2742652066.
E-mail address: hasangocmez@yahoo.com.

0272-8842/$30.00
doi:10.1016/j.ceramint.2005.04.005

that the adsorption and the dynamical electrophoretic mobility behavior of suspension depend on the nature, number and position of the benzene ring's functional groups on the properties of aqueous alumina suspensions. Likewise, this study has examined the effect of number and position of surface active groups of benzene ring's using molecular modeling approach based on theoretically calculated interaction energies between dispersant structure and alumina surface. In addition, the computed interaction energies were correlated with experimentally obtained absorption and electrophoretic mobility of dispersant on the alumina surface in the published literature.

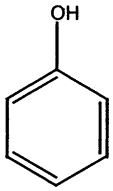
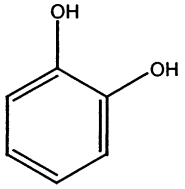
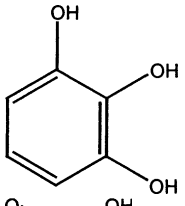
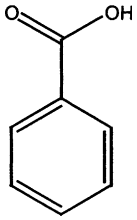
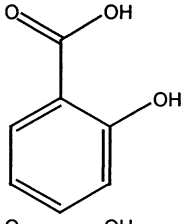
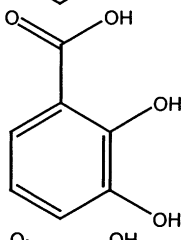
2. Molecular modelling methodology

The Cerius[2] program (Accelrys Inc., USA) at Highly Filled Materials Institute of SIT (USA) was used to model the α-Al_2O_3 surface-dispersant interactions by force field approach. The force field describes approximately the potential energy hypersurface in which the atomic nuclei move. The COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) has been chosen as a force field for all energy calculations. The COMPASS force field has broad coverage in covalent molecules including most common organics, small inorganic molecules, and polymers, which can be used to make accurate predictions of structural, conformational, vibrational, cohesive and thermophysical properties for a broad range of compounds both in isolation and in condensed phases [13]. Ewald long range summation method for electrostatic interactions (Coulombic) was selected and charges were calculated with charge equilibration (Q_{eq}) method based on electronegativity and geometry.

The method followed was similar to that reported by Pradip et al [14]. A surface cell was created from {0 0 1} cleaved plane of the α-Al_2O_3 unit cell. The surface was further extended to a periodic super lattice ($\sim$20 Å $\times$ 20 Å). Energy minimization (10,000 iterations) was applied to surface cell to optimize geometry in which potential energy is minimum. The atoms at the top layer were allowed to relax and the rest of atoms were constrained during the minimizations, because only top layer atoms have interactions with dispersant molecules.

Seven dispersants based on benzene ring substitution with (–OH) and (–COOH) were used for this study (Table 1). After the dispersant molecule was sketched, amorphous cell containing ten conformations of dispersant molecule was constructed and then optimized by minimization process. Then, the dispersant molecules were docked on the alumina surface. Dynamics simulation NVT (constant-volume/constant-temperature dynamics) was conducted to dispersant-alumina surface at 300 K with 30 ps. The NVT dynamics is modified to allow the system to fully equilibrate at a controlled temperature. The single point energy of total system, the alumina surface and the dispersant, was calculated after dynamic simulation. This was called total potential energy of system. The single point energy for the dispersant was calculated in a 3D lattice but without contributions from the alumina surface that was removed

Table 1
Molecular structure of the dispersants investigated in this study

Name	Molecular formula	Structure
Phenol	C_6H_6O	
1,2-Dihydroxybenzene (catechol)	$C_6H_6O_2$	
1,2,3-Trihydroxybenzene (pyrogallol)	$C_6H_6O_3$	
Benzoic acid	$C_7H_6O_2$	
2-Hydroxybenzoic acid	$C_7H_6O_3$	
2,3-Dihydroxybenzoic acid	$C_7H_6O_4$	
2,3,4-Trihydroxybenzoic acid	$C_7H_6O_5$