Molecular Dynamics Simulations of Al_2O_3-MgO-particles in order to find reliable DEM-potentials

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INTRODUCTION

The discrete element method (DEM) has been successfully applied for many powder suspensions and is established as an important simulation technique [1]. For improving ceramic processing, like the well-established sol-gel-process, the influence of the surfactants, liquid etc. [2,3] has to be studied in detail and the DEM calculations can help finding the best process parameters. For several materials and liquids empirical potentials have been found, but calculations on atomic level, like Molecular Dynamics (MD) presented in this paper, are appropriate for a better understanding of the particle interaction and their potentials. The goal of this research is, to predict the influence of the three important factors on the ceramic processing using aqueous slurries: 1) the polymers acting as precursors, 2) the pH-value due to the presence of ions in the solution, and 3) microstructural changes due to the small radius of nano-particles. For reaching this goal, MD-calculations in this work especially focused on the third topic are performed and compared to DEM potentials.

2. CALCULATION METHOD

The numerical Molecular Dynamics simulations were performed with the software "Moldy" [4] which allows the summation in reciprocal space and is especially suitable for ionic and covalent bonded materials. The Buckingham/Morse potential

$$E_R = \frac{z_i z_j e^2}{r} + f_o\left(b_i - b_j\right)\exp\left(\frac{a_i + a_j - r}{b_i - b_j}\right) - \frac{c_i c_j}{r^6} + D_{ij}\left(e^{-2\alpha_{ij}(r-r_{ij})}\right) - 2D_{ij}\left(e^{-\alpha_{ij}(r-r_{ij})}\right)$$

with f_o= 6.9511*10^{-11} N was used. The parameters for Al_2O_3, MgO and $MgAl_2O_4$ published previously [5] fit well to macroscopic properties, especially lattice constants, and thermal expansion coefficient of single crystal experiments and has been applied successfully [6]. The calculated energy values were normalized according to the number of mol of each phase, which allows direct comparison to the reaction enthalpy of each phase.

The particles used for simulation are the three ceramic materials in air and in water, and adapted with organic butan-chains as shown in fig.1. The later was constructed by placing CH_3-C_3H_6- chains rotated 20° to each other in each direction on the surface of a 1nm particle. The other particles have diameters from 0.5, 1 to 2nm and the distances were varied between

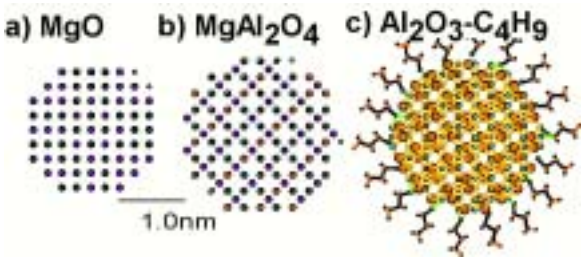

Fig.1 Some of the Nanoparticles for MD-Simulation a) MgO, b) $MgAl_2O_4$ c) Al_2O_3 attached with -C_4H_9

0 and 4 nm. The calculations were performed at room temperature (300K) at the N,p,T ensemble for a sufficient long time (>1ns). The DEM potential was applied in the usual form [1] including the VdW- and the repulsive term. The preexponential term *P* in the repulsive term is independent on the particle distance *h* and treated as one parameter *P*. It contains the dependence on the dielectric constant of the liquid ε_r, the Zeta potential of the particles Ψ. Hence, the DEM-potential depends on the six parameters r_1, r_2, A_H, κ, *P* and *h*.

3. RESULTS AND DISCUSSION

The Molecular Dynamics simulations showed that in the case of nano-particles the energy is increasing, if the radius of a single particle is below a critical particle size of 5nm (fig. 2). This can be explained by the surface relaxations, which affect almost all atoms

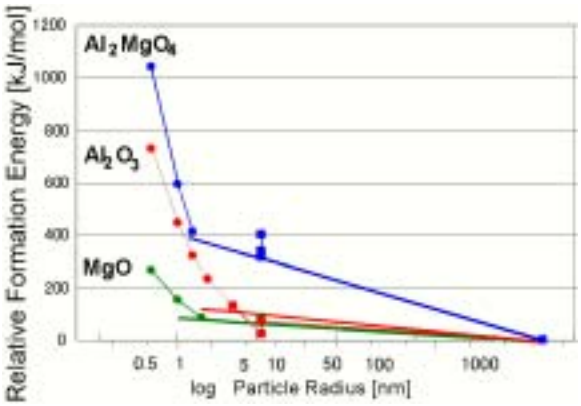

Fig.2. Energy for single ceramic nano-particles as a function of the logarithmic particle size

in these nano-particles. Particle with a radius of less than 2nm show an increase in their energy. The increase is steep for Spinel, less steep for Al_2O_3 or

MgO. The consequence from these different slopes is, that in the case of nano-materials the phase-diagrams have to be revised. The explanation of result is, that in the case of strongly ionic materials, like MgO, the nano-particles are stabilized by electric fields, while for materials with higher covalent bonding fraction surface relaxations occur. Nanoparticles with 0.5nm radius were unstable in any of the three materials.

The second goal of these MD-simulations is, to calculate the interaction potential between the particles, which can be used for modeling using the DEM technique. When distance between two nanoparticles is decreased, the relaxations affect larger regions of the particle (fig. 3). Interaction effects between the particles occur already at a distance of half the particle radius or more than 2nm.

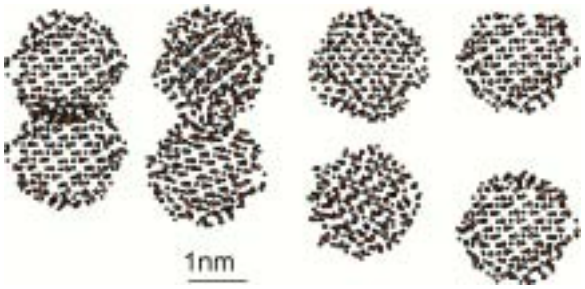

Fig. 3. Surface Relaxations at Al_2O_3-particles at different distances

The energy increases, when the interparticle distance (fig. 4) is reduced until a certain distance, then it decreases, but - in contrary to the singularity of the DEM-function- at zero it has a finite value as expected from physical laws. From this energy plot the DEM potential as a function of the distance can be evaluated by fitting. The DEM-parameters in the lines in fig 4 were r_1=r_2=1nm, A_H=70 10^{-20}J, κ=0.03 10^{-7} 1/m, P= 50 … 400 10^{-20}J. The dependence on the particle distance is low, since the particles in these simulations were uncharged particles.

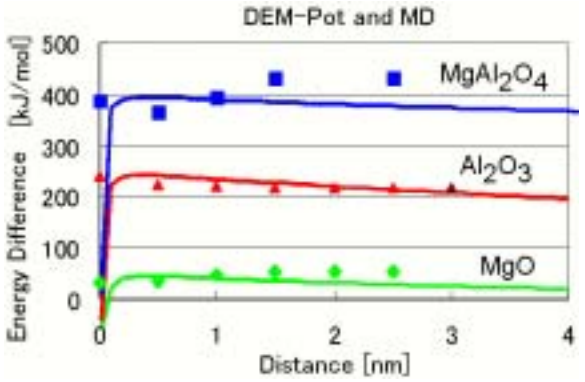

Fig. 4 Comparison between the energy difference for two 1nm-particles at a distance *h*, estimated a) by MD-simulations (data points), and b) by fitting to DEM-potentials (lines) for Spinel, Alumina and Magnesia in air

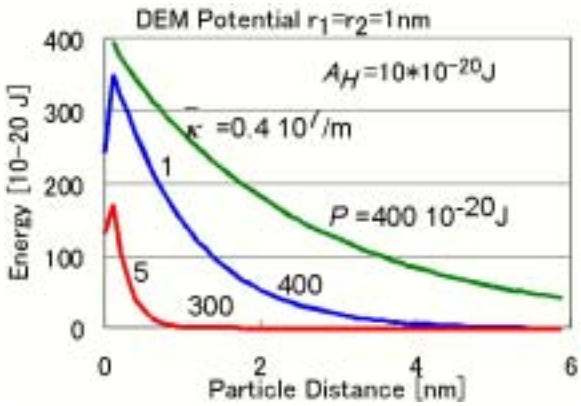

Fig. 5 Prediction of DEM-potentials for nanoparticles in strongly dielectric media

The goal of ceramic processing is to manufacture a colloidal crystal with a good balance between repulsive and attractive forces. To achieve a significant strong repulsive force for nanoparticles (1nm) we have two possibilities, as fig. 5 shows: The Debeye-Hueckel-Parameter κ can be increased or, as a second possibility, the repulsive term, that means increase the dielectric constant ε_r of the liquid media, the Zeta Potential Ψ of the particles or lowering the valency of the electrolyte.

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