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Sintering kinetics and mechanism of vitreous nanoparticles

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ABSTRACT

The sintering of vitreous nanoparticle doublets is investigated numerically by a volume of fluid method coupled to Hamaker summation and experimentally by a high-temperature sintering flow reactor as well as by doublet shape analysis in the transmission electron microscope. In particular, the characteristic differences between nanoparticulate and bulk sintering are studied. The sintering mechanism of vitreous nanoparticles is determined to be viscous flow with interparticle van der Waals interactions acting as additional driving force. The early stages of the nanoparticle sintering kinetics are inversely proportional to the square of the particle size, instead of an indirect proportionality to the first order of the particle size for the entire bulk process. The transition between nanoparticulate and bulk sintering is localised to primary particle diameters of approx. 200–300 nm.

1. Introduction

Nanoparticle sintering is important in various fields such as aerosol processing of materials (Kruis et al., 1998; Schmid et al., 2004, 2006; Artelt et al., 2005, 2006), rapid prototyping (Zhu et al., 2004; Casalino et al., 2002), emulsification (Lepers et al., 1999), spray processing (Mädler et al., 2002), atmospheric aerosol growth (Kulmala et al., 2004), green body sintering in materials engineering (Mawardi & Pitchumani, 2009), sintering of hollow bodies, including photonic fibres (MacChesney et al., 1998), and sub-cellular biology (Poste & Allison, 1973). Driving force for the process is the surface tension aiming to minimise the particle's surface area. The fundamental physical mechanisms determining the sintering process itself are viscous flow, volume, surface and grain boundary diffusion or evaporation and recondensation depending on the type of material under consideration.

The macroscopic size range, i.e. for the bulk where viscous flow is the predominant sintering mechanism for amorphous and vitreous materials, such as polymers and glasses (Kuczynski, 1949, 1980), was experimentally investigated by various authors (Kuczynski, 1949; Rosenzweig & Narkis, 1981; Bellehumeur et al., 1996; Kingery & Berg, 1955). Different phenomenological and analytical models for viscous flow sintering have been developed for spheres (Frenkel, 1945; Eshelby, 1949) and cylinders (Hopper, 1984, 1990). Numerically, various approaches in two and three dimensions have been reported such as boundary element, finite element and boundary integral methods dealing with the sintering of cylinders, doublets and multiparticle arrangements (van der Vorst et al., 1992; Ross et al., 1981; Jagota & Dawson, 1990; Hiram & Nir, 1983; Yadha & Helble, 2004; Zhou & Derby, 1998; Wakai et al., 2007; Kirchhof et al., 2009).

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So far, cluster and nanoparticle sintering has been investigated numerically for many materials by molecular dynamics simulations (Zhu & Averback, 1995; Lewis et al., 1997; Zachariah & Carrier, 1999; Lehtinen & Zachariah, 2001; Vishal & Cummings, 2005; Hawa & Zachariah, 2007), and complex model adaptation of the sintering kinetics from simulations of the gas-phase particle synthesis (Kruis et al., 1993; Ehrman et al., 1998; Johannessen et al., 2000). However, results of molecular dynamics simulations strongly depend on the applied force fields, especially for covalent-bonded systems (Guissani & Guillot, 1996; Roder et al., 2001; Schweigert et al., 2002), and the modelling of heat transfer to the surroundings (Zachariah & Carrier, 1999). Complex model adaptation from particle synthesis models shows problems arising from the complex coupling of very different kinetic processes and from the fact that the sintering kinetics is adapted to experimental aggregate particle synthesis results. Experimentally, nanoparticle sintering has been studied by hot-stage in-situ transmission electron microscopy (Easterling & Thölen, 1970; Kusonoki et al., 1993; Yeadon et al., 1998; Rankin, 1999), leaking in well-defined sintering conditions and unknown substrate's influence. Furthermore, aerosol methods such as differential mobility analyser reactor systems were applied to investigate the sintering kinetics by the change in electrical mobility of aggregates, so that the sintering can only be determined as an average over all particle sizes and aggregate morphologies (Schmitt-Ott, 1998; Seto et al., 1997; Kruis et al., 2000; Tsyganov et al., 2007).

In fact, in most particle applications the sintering process represents a multiparticle problem and often occurs in combination with other particle synthesis mechanisms such as coagulation and nucleation. Hence, many different sintering laws and strongly differing characteristic sintering times can be found in literature (Xiong, Akhtar, & Pratsinis, 1993; Ehrman et al., 1998; Johannessen et al., 2000; Schmid et al., 2006; Koch & Friedlander, 1990; Friedlander & Wu, 1994; German & Munir, 1976; Ulrich & Subramanian, 1977; Helble & Sarofim, 1989; Lehtinen et al., 1996). In a previous work we showed that the agglomerate/aggregate morphology has major influence on the sintering process itself (Kirchhof et al., 2009). Typically used aggregate characteristics such as fractal dimension cannot be used to describe the entire sintering process. In addition, interparticle forces such as van der Waals forces, that are supposed to influence the sintering of nanoparticles, depend on the local contact geometry of the single sintering contacts. Hence, for a fundamental investigation of the sintering process of nanoparticles, i.e. including the determination of the kinetics, the sintering process is analysed experimentally and numerically using doublets consisting of two spherical primary nanoparticles. By ensuring well-defined process conditions and by completely separating the sintering kinetics from all other sub-processes like particle growth or aggregation, we are able to avoid any ambiguity in data analysis and interpretation.

2. Methods

2.1. Theoretical approach

The sintering of two nanoparticles is investigated by computer simulations using an extended version of the method that already was applied for the investigation of bulk viscous flow particle sintering (Kirchhof et al., 2009). Sintering is simulated solving the Navier-Stokes equations, including free surface movement by a fractional volume of fluid method (Hirt & Nichols, 1981). The continuity and the momentum equations are used in the form

$$\partial\rho/\partial t+\nabla(\rho\,\mathbf{u})=0 \tag{1}$$

and

$$\partial\mathbf{u}/\partial t+(\mathbf{u}\nabla)\mathbf{u}=\mathbf{F}-1/\rho\nabla p+\eta/\rho\,\Delta\mathbf{u} \tag{2}$$

with the velocity vector $\mathbf{u}$, the pressure p, the density ρ, the dynamic viscosity η and the additional force $\mathbf{F}$ acting on a volume element. In the macroscopic case $\mathbf{F}$ represents the surface tension force. In the present case of nanoparticle sintering the surface tension force is extended by microscopic interparticle forces, i.e. van der Waals interactions between the two primary particles. The importance of interparticle van der Waals forces is shown by the fact that nanoparticles even made of stiff materials such as ceramics show a particle flattening in the contact region without sintering that can be described by JKR and DMT theories (Johnson et al., 1971; Derjaguin et al., 1975).

The spacial discretisation of the simulations is achieved using an unstructured tetrahedral computational grid representing the amorphous structure of vitreous materials. The node density of the grid equals the material's molecular density. The interparticle force is calculated by the van der Waals forces between the nodes of the two primary particles. Note that only *inter*particle forces are considered and not *intra*particle forces, because the latter already are considered by the surface tension force. This hybrid approach resembles the method by Zhou and Peukert (2008) for calculation of enhanced adhesion forces due to plastic deformation where FEM was coupled to the Hamaker summation based on the assumption of additivity of forces. In both cases a continuum model (FEM or CFD, respectively) is coupled to a discrete model for van der Waals forces.

During the sintering process the two initial spheres more and more coalesce to one particle, which in particular becomes obvious during the final stages when the sintering neck size reaches and exceeds the initial sphere size. During these final stages the newly formed particle cannot be considered as consisting of two primary particles any more. Hence, the summation method for the interparticle forces would lead to an additional contribution to the already considered surface tension that results from the intraparticle forces. Consequently, the present simulations are limited to the first sintering stages. However, these stages are the most important ones due to their rapid sintering kinetics.