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Nanobubble enhanced agglomeration of hydrophobic powders

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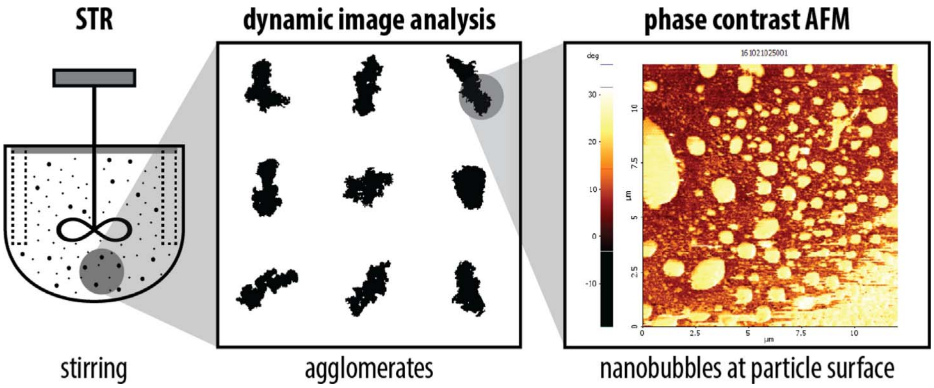
GRAPHICAL ABSTRACT



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ABSTRACT

Agglomeration of solid particles in aqueous liquid flows is generally influenced by the appropriate interacting forces. Between hydrophobic particles, these forces are dramatically increased compared to van der Waals forces due to the formation of capillary bridges, caused by nanobubbles located at the particle surface. In this study, both hydrophobic and hydrophilic agglomerates were generated in water with an agglomeration setup based on a stirred tank reactor. Variating the shear rate leads to different agglomeration sizes and provides information about the agglomerate strength. In principle, both stability and size of the hydrophobic agglomerates are larger than the hydrophilic ones. The presence of the nanobubbles is proved by applying atomic force microscopy to the particle surface.

1. Introduction

Agglomeration of fine particles plays a role in different industries. One major representative of hydrophobic (non-wetting) agglomeration is metallurgical processing, especially liquid metal cleaning by filtration and flotation. Non-metallic inclusions in metal melts are undesired for a high stability of the cast products. To increase the fatigue strength of these products, a filtration is applied to the metal melt during the casting process. Therefore porous ceramic foam filters, consisting of alumina, are used to separate the melt from inclusions. A depth filtration mechanism is assumed, because the pore diameter, where the inclusions enter the filter, are much larger than the inclusions themselves. If the inclusion attaches to the inner filter surface, the adhesion is provided due to van der Waals interactions, sintering and particularly capillary forces. Neither the inclusions nor the ceramic foam filter are wetted by the metal melt due to its high surface energy, which exceeds the surface energy of water about several magnitudes [1]. Gas reservoirs on the particulate inclusions as well as the filter surface are

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Abbreviations: AFM, atomic force microscopy; ASD, agglomerate size distribution; IEP, isoelectric point; PSD, particle size distributions; rms, root mean square

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caused by dissolved gas in the metal melt or during immersion. The reservoirs can also develop at the moment of particle-surface contact [2]. A capillary is formed and leads to a strong binding force of the inclusions resulting in the deposition within the foam filter. As it is known from the theory of depth filtration, inclusion particles are able to cross the filter without establishing contact to the filter surface, thus a pre-agglomeration of these particles is necessary to increase the contact probability and thus to purify the metal melt in the most efficient way.

Metal melts are opaque and solely treatable at high temperatures, that impedes investigations of inclusion agglomeration at the real system. Therefore, a room temperature model system is used, that mimics the poor wetting behavior of metal melts on nonmetallic inclusions and filter materials. In this model system alumina particles with a hydrophobic coating represent the inclusions while water is used as a non-wetting liquid. In the study, the agglomeration of hydrophobic powders is realized in a stirred vessel. To stimulate and control the hydrophobic agglomeration a novel approach is applied, which introduces defined nanobubbles in the system, to the particle surface respectively to increase the adhesion force between the particles dramatically due to capillary bridging [3,4].

In the recent past, similar investigations in this room temperature model system were done to understand and to improve the cleaning of metal melts. Saint-Raymond et al. investigated the agglomeration of fine alumina powders at different *p*H-values in water and in *n*-heptane [5]. Cournil et al. observed a higher agglomeration rate of hydrophobic particles than hydrophilic ones both theoretically [6] and experimentally [7]. Therefore, in situ measurements of turbidity in a stirred vessel at different agitation speeds were done [8]. Gruy et al. assumed the preexistence of nanobubbles on the particles and accomplished the agglomeration experiments at the *p*H-value of isoelectric point (IEP) and with dispersing the particles in a 15 vol.% ethanol-water mixture before the agglomeration starts [8].

This study has the aim to nucleate defined nanobubbles onto hydrophobic particles through a solvent exchange. A subsequent agglomeration of these particles in a non-wetting liquid is done. The emerged nanobubbles can be detected and qualified via AFM on comparable hydrophobic surfaces at corresponding physicochemical conditions. The hydrophobic agglomerates are compared with hydrophilic ones in size and stability, which were obtained in the same setup at the IEP. Also, high electrolyte concentrations were produced to reveal the enhancement of adhesion forces based on poor wetting property of the system.

2. Theoretical approach

The agglomeration of hydrophobic powders can be described with established techniques of flocculation, as used e.g. in waste water treatment. Agglomeration occurs if primary particles are both transported and attached to each other [9]. The transport requires a relative displacement (e.g. sedimentation, flow field, Brownian motion) and the attachment an attractive force between the particles.

Two components of interaction forces between particles immersed in polar liquids like water are known according to the DLVO-theory, which was established in the 1940s by Derjaguin, Landau [10], Verwey and Overbeek [11]. The van der Waals force represents the attractive component. This force is based on molecular dipoles of the different phases and scales with the distance to the negative power of three in the case of two colliding particles. The repulsive interactions is formed through the presence of the electrochemical double layer and decreases approximately exponentially relating to the distance.

A further force occurs between hydrophobic surfaces in aqueous solutions, which cannot be explained by the traditional DLVO theory [12]. This attractive hydrophobic force is commonly divided into two parts as well, the so called short range and long range hydrophobic force. The short range force is commonly described as structural formation of the water molecules at the solid-liquid interface and exhibits a range of a few nm while decreasing exponentially [13]. The most common explanation of the long range forces is due to the formation of nanobubbles onto the hydrophobic surface, which are leading to strong capillary interactions [14–16].

The behavior and the generation of nanobubbles at smooth surfaces is summarized already in literature [17,18]. Nanobubbles on solid surfaces can be produced via gas supersaturation in liquids that are achieved by electrolysis [19,20], perturbation [2] or heating the substrate or the liquid [4]. A widely used procedure to generate nanobubbles onto hydrophobic surfaces is the solvent exchange method [21–24]. This procedure was developed by Lou et al. [25] and Ishida et al. [26] to generate nanobubbles in a reproducible way. Here, the hydrophobic surface is firstly immersed in a wetting liquid, which is a good gas solvent. The next step is to exchange the solvent, e.g. ethanol, with a second poorly wetting liquid (e.g. water) which contains less dissolved air. In addition, the enthalpy of the ethanol-water-mixing causes local temperature gradients. Thus, a supersaturation of gas occurs in the mixing zone during the exchange. Nanobubbles are forming spontaneously at the surface and grow to a height of several hundred nm. Another important property of nanobubbles is their high stability. Actual, the bubbles should dissolve in microseconds, but they stay stable even for hours and days [22,27,28]. Although it is not totally clear, the most common explanations for the high stability is due to line pinning [29,30] and a dynamic equilibrium of gas flux at the liquid-gas interface [31]. The detection of nanobubbles is commonly possible via atomic force microscopy (AFM), whereby a soft cantilever is used at intermittent mode [18]. Furthermore, due to the colloidal probe technique, it is possible to measure adhesive forces between a single particle and a surface via AFM. Therefore, a spherical particle is glued onto a tipless cantilever [32] and after recording force-distance curves between this particle and a surface, the maximum adhesive force can be determined. Because real surfaces are rough, it is more practical to quantify the detachment forces by an adhesive force distribution, as described in [33].

The relative mobility of the particles is strongly influenced by the micro turbulence of a liquid movement. It is necessary to transport the particles to each other, but can also lead to break up induced by larger shear forces [34]. If these two processes are equilibrated, the size of agglomerates is reaching a constant value after a certain time *t*. Additional stress to the agglomerates could lead to a breakage and disabling this stress provides a regrowth ending up to the previous size of agglomerates [35,36]. The stability of agglomerates towards shear stress can be determined by observation of the size of the agglomerates at different shear conditions [37]. According to the theory of turbulence, the eddy size is distributed. Starting from the macroscopic eddies the dissipation of energy finally occurs in the smallest micro eddies. While stirring the liquid in the vessel, the energy is dissipating at a rate of the integral energy dissipation$\bar{\varepsilon}$. The latter can be evaluated from the difference in energy consumption between stirring with and without the liquid relative to its mass. By this, the character of turbulence can be estimated. The microscale η of Kolmogorov (Eq. (1)) gives the length scale of the smallest eddies, where the Reynolds number *Re* equals 1 [38].

$$\eta = \left(\frac{\nu^3}{\bar{\varepsilon}}\right)^{\frac{1}{4}} \tag{1}$$

Agglomerates with a size below the Kolmogorov scale are stressed by the dominating viscous shear forces and are consequently submitted to erosion. In this case, small parts in the size range of the primary particles detach. If the agglomerate size is significantly above the Kolmogorov scale, large scale fragmentation occurs due to dynamic pressures and the agglomerates decompose into several smaller agglomerates [37].

Camp and Stein [39] defined the global root mean shear rates $\overline{G}$ in a turbulent flow, which is related to the energy dissipation rate as well as