



Formation of hollow vitreous and semi-crystalline microspheres in slag flame spraying

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Abstract

Slags may be flame sprayed to produce hollow vitreous or semi-crystalline microspheres. Feedstock compositions, as well as the heating and cooling kinetics, determine the properties of the final product. These kinetics were estimated by finite element modeling of the thermal and kinematical history of different slags throughout a flame and compared with the morphology and crystallinity of the yielded microspheres. The formation mechanism of hollow spheres is also discussed.

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1. Introduction

1.1. Assessing vitreous and semi-crystalline microspheres for oil well drilling and cementing

Microspheres in the $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ system are considered as useful light weight puzzolanic [1] and torque/viscosity reducing additives in oil well drilling and cementing. Their diameter and morphology improve the flowability of the slurry and their composition and structure may improve their setting and mechanical properties [2,3]. Generally, such microspheres are obtained by flame or plasma spraying [1,4–5]. When particles are injected into a high temperature flow and melted through thermal transfer, the surface tension forces surpass the viscous flow and allow spheroidizing. This behavior arises for crystalline feedstock when the melting temperature is reached and particle heating is over

$$Q(T) = C_{p,solid}(T - T_{ambient}) + \Delta H_f. \quad (1)$$

where Q is the heat flow, C_p is the heat capacity of the crystal, T (K) is the heating temperature and ΔH_f is the enthalpy of fusion.

When the feedstock is vitreous, the glass transition is taken into account and spheroidizing may occur under the melting temperature. A “rounding” temperature has been approximated by Poirier et al. [4], for a $\text{SiO}_2\text{-CaO-Fe}_2\text{O}_3$ glass when the Ohnesorge number Oh is

$$Oh(T) = \frac{\eta(T)}{\sqrt{\rho(T)\sigma(T)D}} < 5.8 \times 10^5 \quad (2)$$

where η is the glass viscosity, σ its surface tension, ρ its volumic mass and D is the particle diameter.

It is possible to assess the thermo-kinematic history of this feedstock within a flame using the method developed by Vardelle [6]. This approach was simplified to 1 dimension, which allows limiting the experimental velocity and temperature measurements to the flame axis [4]. Such a method, in spite of its simplicity, yielded satisfactory results at assessing the rounding process of glass ceramic crushed particles. Viscosity, density and surface tension were known, and rounding was obtained at $\eta = 10^{5.5}$ Pa s. This corresponds to a higher temperature than the classic industrial softening value ($10^{6.6}$ Pa s) [7] and lower

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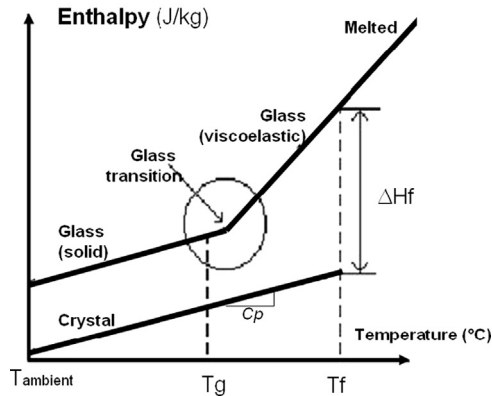


Fig. 1. Enthalpy vs temperature diagram for crystals and glasses.

temperature than the melting temperature for glasses ($\eta = 10^1$ Pa s). When a feedstock is semi-crystalline, which happens in some blast furnace slags and other slags, the approximation of hydrodynamic properties is suitable [8,9] but less reliable for calculating $Oh(T)$ because of the multicomponent character of the feedstock. However, it is possible to estimate the necessary particle heating for complete melting (temperature T_f), using Eq. 1 for mostly crystalline materials, or Eq. 3 for mostly glassy feedstocks (see Fig. 1)

$$Q = C_{p_{solid}}(T_g - T_{ambient}) + C_{p_{liquid}}(T_f - T_g) \quad (3)$$

Slags are inexpensive materials that can be obtained from several metallurgical processes. Their composition, structure and reactivity depend on the processing plant and cooling kinetics [10]. Slags with high content of glass forming oxides and under rapid cooling conditions are prone to develop more glassy phase and better cementing properties [11,12]. On the contrary, some metallurgical plants use slow cooling processes, which give rise to poorly vitrified and less reactive slags. This effect is more significant when few glass forming oxides are present. However, it is expected that flame spraying (at the end of the flame) produces higher cooling rates than most of the industrial processes; since fine particles exhibit more surface area than industrial, unmilled, feedstocks, and considering higher traveling velocities that yield higher heat transfer. Therefore, the flame spray spheroidizing technique may be able to reduce the crystallinity of the slag feedstock and produce glassy or semi-crystalline microspheres. This hypothesis has been confirmed by the thermal spraying of slag by Quercia et al. [1,5] and Saucedo et al. [13].

1.2. Structure of slags and their ability to produce hollow microspheres

Hollow microspheres also may be produced by thermal spraying of slag or glass. Their low density characteristics are useful for extenders and lightening materials in oil well drilling [14]. They are also interesting in other applications such as biomedical nano-carriers [15], hydrogen storage [16,17] and radiation shielding [18]. A pre-requisite for obtaining such hollow spheres is the presence of volatile elements within the feedstock, such as water, carbonates or sulfates [15,19–21],

which will supersaturate at high temperature within the material until they form bubbles. Navon [22], Lyakhovsky [23] and other authors [19,24] have described this phenomenon in volcanic materials such as basaltic, rhyolitic or andesitic glasses, starting with bubble nucleation by

$$\Delta F = \frac{16\pi\sigma^3}{3\Delta P^2} \quad (4)$$

where ΔF is the Helmholtz free energy required to form the curved bubble interface separating the gas from the melt; the excess pressure, ΔP , is the difference between the ambient pressure and the equilibrium vapor pressure of the melt. Bubble growth occurs because of the diffusion of the volatile species from the supersaturated melt, followed by the expansion of the yielded gas either by the release of more volatiles or by the increase of temperature (ΔP will depend on nRT). According to Bai [19,20], this bubble growth is initially controlled by viscosity near the glass transition where melt viscosities are high, and by diffusion at higher temperatures where viscous relaxation occurs rapidly: Lyakhovsky et al. [27] suggest a viscosity threshold of 10^4 Pa s in rhyolitic melts.

In natural samples, diffusion is expected to control bubble growth at near-liquidus temperatures. According to the Navier Stokes equation, the total pressure within the bubble (P_{gas}) is the sum of ambient pressure (P_{amb}) and the effect of surface tension (σ) and viscous stresses due to the deformation of the melt shell [25]. Thus,

$$\frac{dr}{dt} = \frac{(P_{gas} - P_{amb} - \frac{2\sigma}{r})r}{4\eta} \quad (5)$$

where r is the bubble radius, P_{gas} is the pressure inside the bubble, which depends on nRT . Since P_{gas} will increase linearly with temperature, whereas η and σ will decrease in exponential and linear ways respectively [4,26], the growth rate of bubbles within each particle should increase drastically through in-flight heating. As the amount of gas keeps on growing, bubbles may coalesce, which can significantly change the bubble size distribution. During the bubble growth stage controlled by viscosity, the bubble coalescence rate is slow. It increases significantly in the bubble growth stage controlled by diffusion [22].

Poirier et al. [4] estimated a similar phenomenon in SiO_2 – CaO – Fe_2O_3 glass microspheres with remaining carbonates. Saucedo et al. [13] observe such a phenomenon in slag microspheres produced by thermal spray methods, where sulfur bubbles coalesce and produce a particle size enhancement. However, such progressive behavior only seems to be possible in a material where the viscosity is high enough to hinder the bubble rising up [27]. This can be achieved more easily with glassy materials, because their viscosity progressively evolves with temperature. Therefore, the feedstock should be initially glassy, semi-crystalline or a glass–crystal composite [28]. A totally crystalline feedstock (Fig. 1), even with a consequent volatile content, would expel most of this content before it completely melts. Once melted, it would exhibit, at once, a rather low viscosity in comparison to the case of a glass [26]. This viscosity, as well as surface tension,

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