SMOOTHING IRON OXIDE-BASED GLASS PARTICLES WITH AN OXYACETYLENIC FLAME

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Abstract

Milled particles from a (SiO2-CaO-Fe2O3) glass were smoothed by flame spraying, focusing on the elimination of superficial roughness or angularity without reaching complete fusion of the glass. The purpose of this study is the further application to glass ceramic microspheres where avoiding thermal resetting of the second phase is needed. Finite element modeling of the thermal and kinematical history of glass particles throughout the flame was performed in order to predict the suitable size range of injected particles. Crushed and sieved glass powders were sprayed into oxyacetylenic flame and characterized by SEM, showing the importance of the diameter and anisotropic morphology of angular feedstock when discriminating between superficial smoothing and complete fusion in the glass.

Keywords: Flame spraying, Glass, Smoothing, Rounding, Anisotropy

Introduction

Glass or glass ceramics may be used in order to produce microspheres which are able to eliminate cancerigenous liver tumors by local radiation (classical case) [1,2,3] or hyperthermia [4,5]. The latter consists in including a crystalline ferromagnetic phase into the glassy matrix and produce local microheating by electromagnetic induction [5]. Moreover, the ferromagnetic behavior allows microspheres to be delivered to specific targets within the body [6]. Devitrifying iron oxide by adequate annealing fused SiO2-CaO-Fe2O3 glass is known as a safe way for introducing such a ferrimagnetic crystalline phase within the glassy phase [4,7,8]. However the resulting material still requires a controlled size and smooth surface in order to be injected through the blood vessels or directly to the tumor [6,9,10]. A typical range consists in particles between 1 and 100 μm [6,8,11], which can be yielded by
milling the fused and annealed glass. Yet, these particles show a rough and edged shape, which may damage or clog the blood vessels. Therefore, reducing the edges and superficial roughness of the glass or glass ceramic particles is mandatory. Producing perfect sphericity or, at least, yielding a smoother surface from these particles is possible through flame spraying [3, 12]. This process, which is used to produce radioembolizing as well as bone implant bioactive glasses (250-300 μm : [13]), is hardly predesigned or simulated by manufacturers [3, 14], mostly because trial and-error testing is sufficient to yield complete fusion of feedstock. In the present case, however, glass particles should keep a compromise of surface smoothing without reaching a complete bulk melting, since the active second phase within the glassy matrix should not be re-melted (“reset”) during flame spraying.

When the glass material within an angular particle is heated above its transition point (Tg), capillary forces (surface tension σ(T)) tend to yield the shape with higher stability and lowest surface/mass ratio, which is the sphere. Nevertheless, viscous flow (viscosity η(T)) acts as an opposite force to rounding. The Ohnesorge number is known to reflect this antagonism [15]:

\[
Oh(T) = \frac{\eta(T)}{\sqrt{\rho(T) \cdot \sigma(T) \cdot D}}
\]  

(Eq. 1)

where D is the particle diameter and ρ is the density of the glass.

Oh(T) decreases when the particle temperature increases, because η(T) decreases much faster than σ(T) does. Therefore, rounding the particles, or at least yielding a smoother surface, is made possible under a threshold value Oh, when T becomes higher than a limit Ts. Gamarra [16] observed that the variation of Ts vs D is reduced (about 25 K) over the studied diameter range [20-120 μm]. The purpose of the present work consists in predicting and experimenting the conditions where an angular particle is able to reach Ts without exceeding this temperature, and be rounded when heated through a flame jet.

**Experimental procedure**

The glass composition was previously obtained by mixing commercial powders of SiO₂, Fe₂O₃, CaCO₃ (respective brands and purities: Moliven C.A, BDH Chemicals Ltd, Riedel-de Haën; 98, 97, 99.9%). Each raw material was dried at 100 °C during 24 hours before weighing, mixing, melting in a platinum crucible in a Keith ESFK1700 furnace at 1550
°C for 2 hours. Air quenching was applied and the glass was milled (Spex Mill) for 2 minutes with hardened steel spherical media. Several size ranges were separated by dry sieving: (0-45; 45-53; 53-75; 75-90; 90-106; 106-150 μm). Sieved powders were injected into a Eutectic Castolin Terodyn 2000 oxyacetylenic gun. The gas flows were: Acetylene: 18 scfh, Oxygen: 22.5 scfh. The heated powder was collected in a metallic receptor. No deformation of fused particles could be attributed to this receptor.

The flame temperatures were determined along the longitudinal axis of the gun, using a type S thermocouple and applying the subsequent radiation correction. The gas velocity was calculated from the measured gas flow and applying equation 2:

\[
\frac{U(x)}{U(x=0)} = 12.6 \frac{R_0}{x} \quad \text{if } x > 20 R_0 \quad \text{Eq 2 [17]}
\]

where \(U\) is the gas velocity, \(x\) is the longitudinal distance from the nozzle tip and \(R_0\) is the radius of the nozzle orifice.

The selected composition was (wt%) 55SiO₂-35CaO-10Fe₂O₃ [7] and its thermal and hydrodynamic characteristics (glass transition temperature, viscosity, surface tension and specific heat vs temperature, see table 1) were taken or estimated from literature. As particles were mostly aspirated by the flame before being propelled [18], it was necessary to measure their velocity experimentally instead of calculating it. Therefore, a Kodak Motion Corder Analyzer PS110 SR-Ultra-C high velocity camera (exposure time: 3.33x10⁻⁴ second) was employed along the flame axis. The shape and size of the glass particles before and after heating through the flame gun were measured by Scanning Electron Microscopy (SEM: Jeol T300, 25 and 10 kV), in order to compare the experimental with numerical calculations.

<table>
<thead>
<tr>
<th>Value or formula</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical temperatures (K)</td>
<td></td>
</tr>
<tr>
<td>Glass transition (Tg : (\log(\eta) = 13)): 1006 K</td>
<td>[5,19,20,21]</td>
</tr>
<tr>
<td>Dilatometric softening ((\log(\eta) = 11.3)): 1056 K</td>
<td></td>
</tr>
<tr>
<td>Fusion temperature ((\log(\eta) = 2)): 1723 K</td>
<td></td>
</tr>
<tr>
<td>Viscosity (dPa.s)</td>
<td></td>
</tr>
<tr>
<td>(\log(\eta) = -5.65 + 9294.31 / (T - 507.56))</td>
<td>[5,19,20]</td>
</tr>
<tr>
<td>Surface tension (N/m)</td>
<td></td>
</tr>
<tr>
<td>(\sigma(T) = -2.109E-05 T + 0.4135)</td>
<td>[22,23]</td>
</tr>
<tr>
<td>Critical Ohnesorge value</td>
<td></td>
</tr>
<tr>
<td>(Oh_s = 5.8.10^5)</td>
<td>[16,20,24]</td>
</tr>
<tr>
<td>Specific Heat (J/kg/K)</td>
<td></td>
</tr>
<tr>
<td>(C_p(T) = 305 \ln(T) - 1038.9 \text{ si } T &lt; T_g)</td>
<td>[25]</td>
</tr>
<tr>
<td>(C_p(T) = 1435 \text{ J/kg/K si } T &gt; T_g)</td>
<td></td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion</td>
<td></td>
</tr>
<tr>
<td>At (T &lt; T_g) (\alpha = 11.3.10^{-6}K^{-1})</td>
<td>[20]</td>
</tr>
<tr>
<td>At (T &gt; T_g) (\alpha = 48.9.10^{-6}K^{-1})</td>
<td></td>
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</table>
### Results and discussion

The numerical simulations consisted in modeling the heating of particles injected in a hot gas [27]. The experimental fields of particle velocity, gas temperature, and calculation of gas velocity and hydrodynamic values were used as input data. The governing equations modeled the heating of the droplets, neglecting their evaporation, due to the low range of working temperatures compared to Tf. The temperature of the particles was calculated from an energy balance taking into account convective transfer and radiation emitted by the droplets. The particles were initially assumed to have a uniform temperature. The thermodynamic and transport properties of the flame mixture were determined using mixing laws from the properties of pure gases and composition of the gas system, using the ADEP software T&T Winner (Université de Limoges) [28]. The model projected the evolution of temperature in the particle, depending on its equivalent diameter.

Even though many simulations [16, 27, 29] assume the sphericity or, at least, the isotropy of the particles, SEM observations showed that milled particles presented a side more elongated than the others, thus approaching a cylindrical shape more than a spherical shape, (Fig. 1). Although the cylinder assumption does not describe the aspect of these particles in a fully satisfactory way, it represents a closer approach than the spherical representation, and highlights the following issue: the mass of glass to be heated strongly depends on the large side of these “cylinders”, but the heat penetration through the shallow side is much easier than in a spherical particle. Thus, an equivalent diameter ($D_{eq}$) may be calculated from the shape factor (average value of “cylindrical diameter”/length ratio ($X$=$d/L=0.595$)), measured by SEM on 49 particles within a 75 150 µm length range), using equation 3: [20, 30]

$$D_{eq} = \sqrt{d \times L + \frac{d^2}{2}} = L \times \sqrt{\left(X + \frac{X^2}{2}\right)} = d \times \sqrt{\frac{1}{X} + \frac{1}{2}}$$

Eq. 3

Therefore, when the model determines the thermal history of an isotropic particle with an equivalent diameter $D_{eq}$, the real length $L$ and diameter $d$ of the actual particle (considered as a cylinder) will have to be calculated.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Density</td>
<td>At 273 K: $\rho_0 = 3000 \text{ kg/m}^2$</td>
</tr>
<tr>
<td></td>
<td>$\rho(T) = \rho_0 / (1+\alpha)^3$</td>
</tr>
<tr>
<td>Emissivity</td>
<td>$\varepsilon=0.9$</td>
</tr>
</tbody>
</table>

Table 1: Thermal and hydrodynamic data of the selected glass composition
Figure 2 shows the evolution of velocity and temperature in flame and particle, at a given particle diameter: velocity increases gradually as angular glass particles enter the hottest zone of the flame. Therefore, temperature increases rapidly in the particle until a maximum value, and presents a reduction as the flame temperature goes down. If part of the curve for particle temperature (Tp) is above the rounding temperature (Ts), then smoothing of the angular particle surface is expected. If Tp grows up to the fusion temperature (Tf), complete fusion would be achieved, which implies complete resetting of second phase in case of devitrified glass as feedstock. Thus, for the purpose of smoothing the surface of glass ceramic particles, the latter case has to be avoided, as well as incomplete heating. According to the numerical simulation, 64 μm round particles should reach complete fusion, whereas particles above an equivalent particle diameter $D_{eq} = 90$ μm are unlikely to get smoothed or rounded (Tp=Ts). On the other hand, excessive heating and possible evaporation could be met with particles with an equivalent size $D_{eq} = 50$ μm or less.
When flame spraying is applied to the glass powder through the flame gun, an excessive loss of material is observed in the finest particles (< 53 μm), possibly because of strong evaporation. Cooler and faster flames (for example, using pressurized air as a shroud gas) reduce this loss, confirming the prediction made for small diameters by the model [20]. Figure 3 shows the morphology of glass particles after being milled, dry sieved and flame sprayed. It may be noticed that sieving efficiency was incomplete, for fine particles were found among much coarser particles. This effect is attributed to a tribocharging effect [31] during dry milling and sieving. Nevertheless, rounding is well discriminated, depending on the particle diameter. Above 110 μm, no microsphere is observed, whereas practically every particle under this size is smoothed or completely rounded. This equivalent spherical cut diameter D_{eq} (110 μm), which would correspond to actual particles with d=74 μm and L=125
μm, is different by 20% from the calculated spherical size (90 μm). However, the shallower side (d) of the corresponding actual particle is much smaller, before being rounded into a broader sphere (D_{eq}), and could allow for easier thermal transfer. Applying a correction factor range (relating d to D_{eq}) could be a relevant way to consider the rounding ability of the studied anisotropic powder by flame spraying. The variations observed in d/L, and the low accuracy of the cylinder hypothesis would justify the use of a range instead of a determined value for this correction factor.

The hypothesis of a better thermal transfer through the shallower side of the particles implies that the thermal conductivity in the glassy material would be a limiting stage when heating the particle. As a matter of fact, the value of Biot number (Bi: thermal conductivity ratio between flame and particle) was calculated over the whole temperature range, giving values between 0.03 and 0.04 [20], which means that uniform temperature is not reached immediately within the core of the particles (case when Bi>0.01 [32]), although their surface is highly heated, or even smoothed. This effect could explain the higher experimental smoothed diameter in the present study, and would allow to consider the application of this process to glass ceramic angular particle that require only superficial rounding, in order to maintain enough underheated second phase within the glassy matrix.

Many smoothed particles exhibit a higher diameter than the upper limit of the sieved, unheated particles: they changed from near cylindrical shape to full sphere geometry during flame spraying, yielding a higher final diameter (eq. 4). For example (fig 4d), spherical particles with a 90 μm equivalent diameter (D_{eq}) were produced from particles which could pass through a 75 μm sieve, thanks to a shallow, cylindrical diameter d=70 μm (according to equation 4).

On the other hand, some voids were observed in the spherical particles under 65 μm (Fig. 4d). This phenomenon is attributed to releasing of gaseous microbubbles during in-flight heating, as glass viscosity and surface tension decreased enough to allow the diffusion and expulsion of gas throughout the particle thickness. According to the numeric simulation, this effect seems to occur when maximum temperature of the particles exceeds 1700 K (ie near Tf), which corresponds to viscosities under 10^{2.4} dPa.s (table 1). The similarity (in chemical, thermal and hydrodynamic terms) with the fining process in industrial glass kilns [33] is explained by the probable presence, before flame spraying, of residual CO\textsubscript{2} within the glass.
composition. The decomposition of CaCO$_3$ in the crucible at 1550°C allowed the expulsion of almost all the volatiles products. However, the smallest CO$_2$ bubbles could not travel along the thickness of fused bath and could not be expelled. A dissolved (and possibly a non dissolved) amount of this gas remained until the glass was milled into fine particles and melted again. This effect is known as “reboiling”.

These morphologic observations confirm most of the predictions of the model, with respect to the probability of smoothing, rounding, fusing, or even evaporating the edged glass particles by flame spraying.

![Fig. 4: SEM photographs of sieved, flame sprayed glass particles depending on the selected feedstock size: (a) 106-150 μm (b) 90-106 μm (c) 75-90 μm (d) 53-75 μm. Circles in fig. 4d show the voids in the reboiled spheres](image)

**Conclusion:**

SiO$_2$-CaO-Fe$_2$O$_3$ glass edged particles were smoothed or rounded by flame spraying, which included reboiling or evaporation effects when the flame was hotter or slower and the particles were finer. These results suggest the feasibility of producing rounded glass ceramic
particles without “resetting” their second phase. However, a good control of their diameter by an improved crushing and sieving (non tribocharging) method and an adequate flame temperature distribution are mandatory. The numerical simulation proposed in the present work has proved to be a useful tool to globally assess the in-flight behavior of the edged particles to be selected by the manufacturer, although feedstock anisotropy and low thermal conductivity of the glass influenced the experimental results and required a modified interpretation of the model. On the basis of results of these results, designing non-agglomerated, finer, Fe-richer, glass ceramic microspheres is suggested in the future.

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References:


