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Processing of Glass in Space

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Abstract

NEW glass compositions should result from space processing.[1,2] To make a glass, a liquid must be cooled rapidly enough to prevent nucleation of crystals and the elimination of container walls, a common source of nucleation, should lead to new glass-forming compositions. Rapid heat transfer is important in glass forming; the special conditions of heat transfer in space processing must be carefully controlled for successful melting of easily crystallized glasses. Fining and homogenization are important problems in making glasses, but they present no special problems for glass melting in space.

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Nucleation

If a glass is formed from a liquid, it must be cooled below its melting point so fast that the supercooled liquid does not crystallize. Either the rate of nucleation or of crystallization can limit the formation of crystals. The rate of crystallization is usually a maximum for molten silicates at an undercooling between 50 and 100 deg. The rate of nucleation has a broad maximum, usually at a somewhat lower temperature. Many glass-forming silicates have maximum crystallization rates of 10^{-4} cm/s or higher. With this rate, it is necessary to cool the glass through the temperature range of maximum crystallization rate in less than 10^{-2} s to prevent growth of crystals larger than 100*A* in diameter. This time is too short for most practical conditions, so a low rate of nucleation must be limiting the formation of crystals in most silicate glasses. Since nucleation of crystals in glasses almost always occurs at their free surface or the interface with vessel walls, it is necessary to cool these interfaces rapidly enough to prevent nucleation of crystals at a temperature where they can grow.

Impurities are the most important source of nucleation at free surfaces. As the molten glass cools, dust particles adhere to the glass surface, giving preferred nucleation sites. Other impurities, such as alkalis and even water, can corrode the surface, giving lower liquid-vapor surface energies and enhanced nucleation. In space melting the glass batch will probably be premelted in a container and then remelted in space; the history of the glass surface will be an important factor in its tendency to nucleate crystals. Impurities from grinding, dust, and chemicals from treatments of the surface are all potential nucleating agents. Careful studies will be necessary to achieve surfaces with minimum nucleation tendencies.

One way to partially remove potential nuclei at the glass surface would be to melt, cool, and remelt the glass several times in the space chamber. Each successive melt could dissolve and disperse some of the surface impurities into the bulk of the glass.

Rapid Cooling

Consider a sphere of glass of diameter D, density p, and heat capacity C in J/g·K. The sphere is immersed in a gas of thermal conductivity k and does not touch any solid surface. The gas and the walls of the surrounding vessel have the same temperature Tg. At first, the sphere will be assumed to be at a uniform temperature throughout and heat transfer from the surrounding gas and radiating surfaces treated. Then heat transfer in the glass will be discussed. Two contributions to cooling the glass are conductive heat transfer from the glass to the gas, and radiative heat transfer to the surrounding surfaces. These factors are expressed in the equation

$$\frac{DpC}{6}\frac{\mathrm{d}T}{\mathrm{d}t} = h(T-Tg) + \sigma E(T^4 - Tg^4) \qquad (1)$$

for the cooling rate $\mathrm{d}T/\mathrm{d}t$. In the equation, h is a convective heat transfer coefficient, σ the Stefan-Boltzmann constant of $5.67\ (10)^{-12}$ W/cm^2·deg, E the emittance of the glass, and T the temperature of the glass. If the Reynolds number of the gas is low, that is, if it is not in turbulent motion, $h = 2k/D$. This relation should be valid in absence of gravity, where the gas is quiescent. Then the first term on the right-hand side of Eq. (1) represents conductive heat transfer.

First consider the sphere 1 mm in diameter at 1000°C. Other parameters are $p = 2.5$ g/cm^3, $k = 1.2\ (10)^{-3}$ J/g· deg and $E = 0.3$ If the walls and gas are at room temperature (25°C), the conductive term becomes 23 J/cm^2·s, and the radiative term 4.5 J/cm^2·s. However, if the diameter of the sphere is a more practical 10 cm, the conductive term is reduced to 0.23 J/cm^2·s. Thus, the relative importance of radiation and conduction depends critically on the size of the sphere.

For the 1 mm sphere with walls and gas at 25°C, the rate of cooling $\mathrm{d}T/\mathrm{d}t$ at 1000°C is 553°/s, and at 500°C is 236°/s. Heat transfer inside the glass sphere can be estimated from the thermal diffusivity $Q = K/pC$ in cm^2/s. For glass $Q \approx 0.06$ cm^2/s at 1000°C and decreases to about 0.006 cm^2/s at 25°C. An estimate of the average distance X of heat flow in time t is possible from the equation $X^2 = 2Qt$. For $X = 0.05$ cm, the time is about 0.02 s for $Q = 0.06$. Thus, it is reasonable to assume that the temperature is nearly constant in a 1 mm glass sphere at 1000°C; however, for a much larger sphere, such as one 10 cm in diameter, there will be a gradient of temperature from the sphere surface to its interior, and the gradient will be greater for a lower temperature because the thermal conductivity of the glass decreases at lower temperatures.

Even if the interior of a glass sample is not cooled rapidly, the surface layers can be cooled at quite a rapid rate (greater than 500°/s), but this cooling results mainly from conduction from the gas surrounding the sample. The radiative flux from a glass sphere at 1000°C to walls at low temperature is about 5 J/cm^2·s or less, which is not enough to cool a large sample very rapidly. Radiative cooling will not take place just at the sample surface, because the glass is partly transparent to the radiation. Thus, rapid cooling of the glass surface, essential for preventing nucleation of easily crystallized glasses, requires conductive cooling from a surrounding gas. Any gas in contact with the glass surface must be carefully cleaned of

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dust and aerosols to prevent their acting as catalysts for surface nucleation.

Another problem is that a large temperature gradient in a cooling glass leads to stresses in the glass, and can crack it if its coefficient of thermal expansion is too high. Thus, it may be necessary to work with glass compositions of low thermal expansion for space processing. An alternative is to use small samples (less than a few mm in diameter), or different geometries, such as planar, to provide at least one small dimension and more rapid stress-free cooling.

One possibility to increase the rate of radiative cooling of the glass surface would be to add an absorbing oxide, such as iron, nickel, chromium, or another transition metal oxide that absorbs in the near infrared. This addition would make the glass more like a black body in the infrared, raising its emissivity and reducing radiative transfer from the sample interior, so that a larger sample would cool only at its surface.

Homogeneity and Fining

Some homogenization is achieved in commercial glass tanks by convection caused by gravity. Small melts are sometimes stirred to mix them. However, by far the most important element in melting a homogeneous sample of glass is thorough mixing of the powders of the raw materials for the melt. This mixing is best achieved by starting with fine powders (about 10μ in dimension, or less, if possible) and suspending them in an organic liquid. After thorough mixing, the liquid is evaporated away to give the starting mixture. If this mixing is properly done, crushing and remelting the glass is not necessary.

Bubbles in glass disappear in two different ways. If the bubble is large enough, it will rise to the glass surface by buoyancy, but if the bubble is smaller than about 0.1 mm in diameter, its rate of rise is too slow, and it can be removed from the melt only by dissolution of the gas in it into the glass melt, the rate of which is controlled by diffusion of the gas in the glass. In a gravity-free environment, only the dissolution mechanism is possible. The rate of dissolution of gas is often enhanced by adding "fining agents" such as arsenic or antimony oxide to the glass; the mechanism by which these agents enhance fining is controversial.

In laboratory glass melts it is unlikely that the glass is in turbulent motion. In a melt of 10 cm dimension and a viscosity of 100 P, a velocity of more than 4000 cm/s would be required to give a Reynolds number of 1000 and incipient turbulent motion. Under these conditions, as in space processing, it is unlikely that convective motion of the glass contributes appreciably to gaseous transport in the glass.

Even if a glass has been melted and cooled to a bubble-free state, it can release gas and form new bubbles when it is reheated to glass melting temperatures. This "reboil" can be controlled by proper cooling cycles and additives, depending upon the composition, melting history, and raw materials of the glass.

References

[1] Happe, R.A., "Implications of Zero Gravity for Producing New Glasses in Space," *Journal of Non-Crystalline Solids*, Vol. 3, 1970, p. 375.

[2] Neilson, G.F. and Weinberg, M.C., "Outer Space Forming of a Laser Host Glass," *Journal of Non-Crystalline Solids*, Vol. 23, 1977, p. 43.