

Composites of Bubble Encapsulated Silver or Gold Spheres in Oxide Glasses

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Bubble-encapsulated silver or gold spheres ranging in size from less than 1 to about 500 μm in diameter can be prepared in quenched oxide glasses. High metal concentrations ($> 1\%$ Ag_2O , Au_2O_3 , etc. equivalent), imperfect batch mixing and melting procedures, and melt viscosities between 10 and 5000 poise, all favour metal sphere formation over either complete agglomeration or colloidal dispersion. The release of the latent heat of fusion when the metal freezes can, apparently, expand either small amounts of residual gases or the small void created by metal solidification to form a bubble. Rapid quenching appears to freeze the bubble. In contrast, subsequent slow cooling below the melting point of the metal may allow each bubble to collapse around its sphere.

1. Introduction

The preparation, properties, and possible structures of silver and thallium germanate glasses were described recently [1]. Initial attempts to prepare the silver germanate glasses from AgNO_3 and GeO_2 were hindered by the formation of unwanted quantities of silver metal. The use of Ag_2SO_4 and appropriate reaction conditions partially solved that problem [1]. Microscopic examination of the quenched silver germanate glasses prepared from AgNO_3 , has revealed two unusual characteristics of some of the silver present. First, the dispersed silver is present in spherical form, in contrast to the usual colloidal suspensions found in glass [2-4]. Second, each silver sphere is completely surrounded by a bubble.

The sphericity of the dispersed silver is not entirely unexpected, since silver melts at 960°C and these glasses are generally quenched from above 1200°C . Thus, at the glass-melting temperatures used, the silver formed at much lower temperatures from the decomposition of AgNO_3 and Ag_2O is molten. The molten metal can be present, either as suspended droplets of varying size, or as a relatively large pool in the bottom of the crucible.

In contrast, the encapsulating bubble around each silver sphere seems unexpected. Further experiments proved necessary in order to explain more completely these two phenomena, potentially useful from a materials point of view. This

paper describes some of those experiments and postulates operationally important parameters that may control the formation of bubble-encapsulated spheres of silver or gold in a variety of glass compositions.

2. Experimental and Results

Baker Reagent Grade AgNO_3 , Na_2CO_3 , K_2CO_3 , and Al_2O_3 , Matheson Coleman and Bell Reagent CaO , Fisher $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, Eagle Picher Electronic Grade GeO_2 , and Morgan 200-mesh SiO_2 of low Fe_2O_3 content, were used. All glass-melting reactions involving either silver or gold salts were performed in recrystallised alumina crucibles or boats. The soda-lime-silica glass (73 mole % SiO_2 , 17 mole % Na_2O , 10 mole % CaO) and the potassium germanate glasses had been previously prepared in platinum containers. All melting experiments were performed in an air atmosphere in a silicon carbide muffle furnace.

Fig. 1 shows a typical size distribution of bubbles, each one containing a silver sphere. They were obtained by mixing a 10 g batch of AgNO_3 and GeO_2 in a one-to-two weight ratio, heating for 1 h at 275°C to achieve melting of the AgNO_3 into the GeO_2 , fusing at 1300°C for 2 h, and air-quenching to room temperature. The resultant glass might contain from 1 to 25 mole % Ag_2O , depending on total mass, time, melt surface area, etc. The larger spheres in fig. 1 are from 25 to 30 μm in diameter. Note that the

ratio of bubble to sphere diameters varies from 1.20 to 1.40.

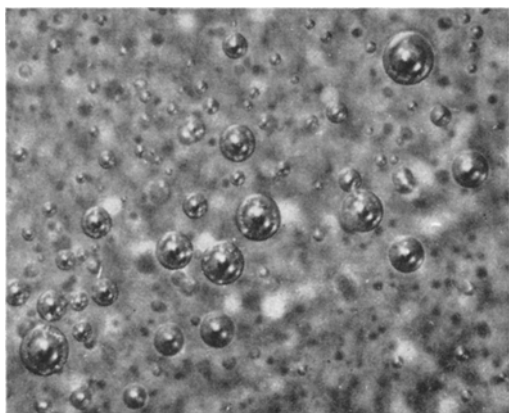


Figure 1 Distribution of bubbles containing silver spheres embedded in quenched silver germanate glass. The larger spheres are 25 to 30 μm in diameter.

The above results are readily reproduced using 5 g batches of AgNO_3 and the soda-lime-silica glass. Mixtures containing 3 to 6 mole % Ag_2O were melted at temperatures between 1250 and 1400°C for times of 1 to 2 h. Figs. 2a and b show typical, well formed silver spheres (74 and 56 μm diameter respectively) with their encompassing bubbles (dark in the photographs), embedded in the quenched glass. The bubble-to-sphere diameter ratios are 1.48 and 1.60 respectively.

Gold, with a melting point of 1063°C, and salts and oxides which decompose at much lower temperatures, were chosen to examine the generality of these phenomena. Experiments were performed with 1 to 5 g batches, with salt-to-glass weight ratios of about one to five, for 25 mole % potassium oxide/germanate and for soda-lime-silica glasses. Melting temperatures ranged from 1200 to 1400°C for times of 0.5 to 1 h.

As with silver, well formed gold spheres, encased in bubbles, are dispersed throughout the quenched glass. Figs. 3 and 4 show such arrangements in the soda-lime-silica glass. The five largest well defined spheres in fig. 3 range from 65 to 250 μm in diameter while the four largest spheres in fig. 4 range from 50 to 220 μm in diameter. The small dark circles that appear at various positions on some spheres are merely reflections of other gold spheres located higher up near the surface of the glass. The bubble-to-sphere diameter ratios lie between 1.27 and 1.53.

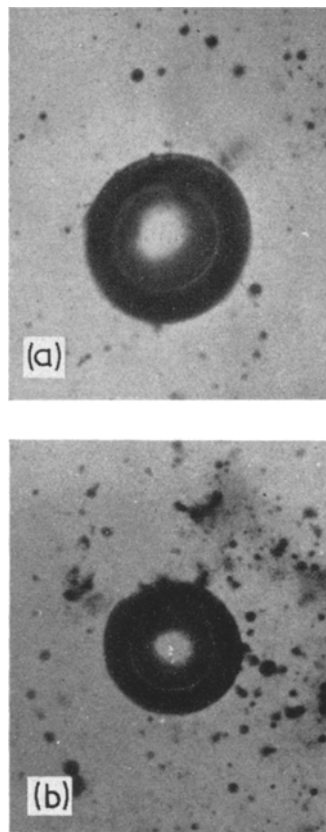


Figure 2 Individual silver spheres and their encompassing bubbles (dark regions) embedded in a quenched soda-lime-silica glass (a and b spheres are 74 and 56 μm in diameter respectively).

3. Discussion

3.1. Sphericity of the Metals

Colloidal suspensions of noble metals in glasses are generally achieved by deliberately dispersing relatively small amounts (less than 1 wt or mole %) of the metal in question. Dispersal can be accomplished either by mixing the metal salt with the glass batch, or by adding an aqueous salt solution [3]. Reducing gas mixtures, which control the oxygen potential, can also be used to obtain grey dispersions of 0.05 to 0.25 wt % silver [5]. More recently, applied voltages have been used to form colloidal silver alloys that colour a glass [6]. The "striking" or sudden appearance of colloidal metal colour in a glass can occur either on cooling from the molten state, or during careful reheating. The latter may occur at lower temperatures because the precipitation (removal from a saturated solution of metal in glass) of the colloiddally dispersed

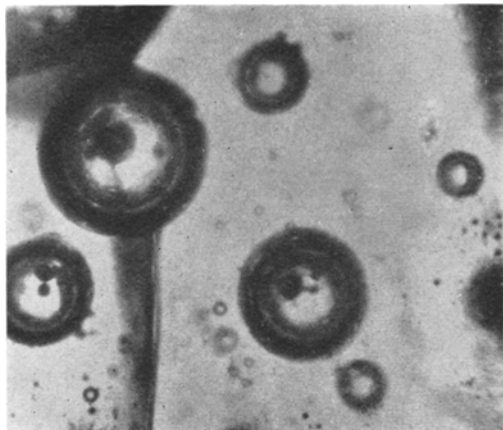


Figure 3 Gold spheres, with encompassing bubbles, embedded in a quenched soda-lime-silica glass. Largest gold sphere is 250 μm in diameter.

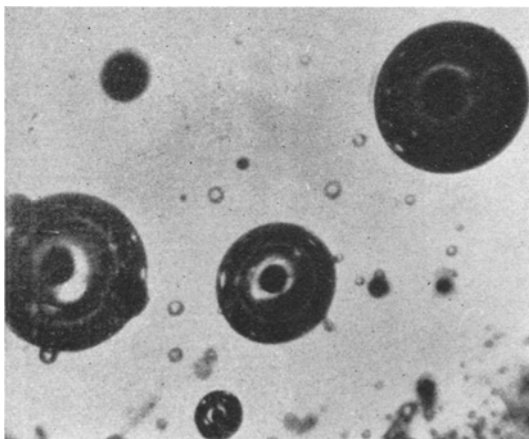


Figure 4 Gold spheres, with encompassing bubbles, embedded in a quenched soda-lime-silica glass. Largest gold sphere is 220 μm in diameter.

metal can accelerate the conversion of oxidised to reduced metal [4]. These colloidal crystals can possess well developed faces.

In contrast, the previously described experiments obviously do not achieve a homogeneous dispersion of the metal. This incomplete dispersion results in a distribution of particle sizes ranging up to a maximum of about 500 μm in diameter. The factors that appear to be responsible for this are described below.

First, the initial concentration of silver and gold salts are considerably larger than those normally used to develop colloidal dispersions. Second, "melting in" of AgNO_3 at 275°C and

mechanical mixing of gold salts tends to produce local silver and gold concentrations that are relatively high compared to their bulk concentrations in the glass batches.

The above factors were examined by dispersing small amounts of a dilute aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (equivalent to 0.05 wt % Au_2O_3 in the glass batch) throughout powdered soda-lime-silica glass samples. The mixtures were then melted at temperatures between 1170 and 1350°C. The resultant glasses contained brown ruby gold dispersions of a rather large number of extremely small gold particles. Very few gold spheres were observed. In contrast, mechanically mixed and similarly melted salt/glass batches of higher gold content (equivalent to about 1.5 wt % Au_2O_3) yield large numbers of well formed gold spheres.

A third factor that appears to influence the efficiency of metal dispersion is the viscosity of the host glass melt. If spheres are to exist at all, the glass transition region ($T_g \equiv 10^{13.0}$ to $10^{14.5}$ poise) must lie below the melting-point of the metal. Otherwise, the glass would be rigid *before* the metal froze to a solid. This would produce irregularly shaped metal particles. Fortunately, there are numerous glass compositions that fulfill the stated T_g requirement.

The influence of viscosity on the dispersion of gold at higher temperatures was examined with several simple glasses for which viscosity information is readily available. For example, 1 g batches of gold salt and powdered GeO_2 glass (about 5 wt % Au_2O_3 equivalent) were melted for 0.5 to 1 h at temperatures between 1200 and 1500°C. The only samples to exhibit a reasonable degree of sphere formation are those held at 1500°C, where the viscosity is about 2000 poise. Even then, a considerable fraction of the gold is present as a finely divided colloidal dispersion. Similar results were obtained for soda-lime-silica glass melts held at $\sim 1120^\circ\text{C}$ where the viscosity is about 1500 poise.

In contrast, several experiments with 3 g batches of gold salt/potassium germanate glass (about 1 to 3 wt % Au_2O_3 equivalent), that were melted at temperatures between 1150 and 1250°C (viscosities of 4 and 3 poise respectively), gave different results. Only a few larger gold spheres, with some smaller ones, were observed. These tended to collect at the bottom of the melts.

One can conclude that glass-melt viscosity definitely plays an important role in noble metal sphere formation. Viscosities much greater than 5000 poise appear to severely impede metal

agglomeration and hence favour colloidal dispersion. Viscosities under about 10 poise appear to be too small to prevent the metal from agglomerating into either one large pool and/or several larger spheres.

The present technique of silver or gold sphere-formation differs considerably from previous methods which have generally aimed at preparing free metal spheres. Thus, the helium plasma torch can yield silver spheres up to 1000 μm in diameter [7] while the use of graphite crucibles *in vacuo* can give silver spheres in the 50 to 500 μm range [8]. Very small spheres ($< 0.1 \mu\text{m}$) are produced by condensation in free space [9] while 0.03 μm particles are obtained from the pyrolysis [10] of silver salts in flames [11].

3.2. Formation of the Encapsulating Bubbles

The average ratio of bubble to sphere diameter for the silver and gold spheres is approximately 1.45. Translated into volumes, it becomes obvious that each metal sphere occupies only one-third of the volume of its encapsulating bubble. This raises the question of the source of the other two-thirds of the volume of a given bubble.

One possibility would be that the contraction of the metal that occurs during its solidification and subsequent thermal shrinkage is considerable. However, this is not the case. The total volume shrinkage for silver and gold, from their respective melting points to room temperature, is only about 11% [12].

A second possibility is that the bubbles represent entrapped gases that are produced during the thermal decomposition of the metal salts. Visual observations strongly suggest that most of these gases are released quite early in the heating and fusion processes. Using the sphere in fig. 2a as an example, one can calculate the weight of metal in the $2.14 \times 10^{-7} \text{ cm}^3$ sphere (2.24 μg) that is surrounded by $4.71 \times 10^{-7} \text{ cm}^3$ of "empty" space. The total amount of N_2O_5 and O_2 given off by the 2.08×10^{-8} mole of AgNO_3 , assuming ideal gas laws and 1 atm. pressure at 1300°C, would occupy a volume that is several thousand times larger than the specified amount of "empty" space.

Either *all* of this gas could be retained close to the silver or gold and be under high pressure or only a small proportion of it, if any, is retained. The previously cited visual evidence for early gas evolution suggests the latter interpretation to be the more likely of the two. This raises the

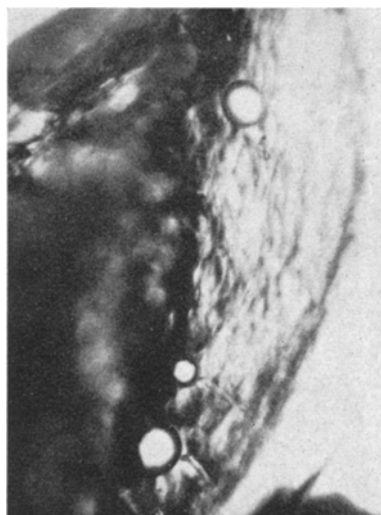


Figure 5 Silver spheres embedded in slowly cooled silver germanate glass. Note absence of encompassing bubbles. The largest sphere is 50 μm in diameter.

possibility that some other phenomenon could cause a bubble to be associated with each metal sphere in the quenched glass. This was tested by altering the cooling schedule of some metal sphere/glass mixtures.

Thus, several 5 g batches of AgNO_3 and GeO_2 (one-to-two weight ratios) were reacted for 1 h at 275°C and then for 1 h at 1250°C. Instead of being quenched directly to 25°C, they were held for several hours at about 920°C and then either quenched or slowly cooled through the T_g region to room temperature. Fig. 5 shows three silver spheres embedded in such a glass that had been quenched directly from 920°C. Note the complete absence of encapsulating bubbles. This behaviour was typical of all samples so treated. These silver spheres in fig. 5 closely resemble other unmelted spheres that can be embedded in glass to form composites [13, 14]. This finding suggests that the bubbles may disappear at temperatures just below the freezing point of the metal if sufficient time is allowed for the glass to collapse back around the spheres. It also suggests that any gases in the bubble are not likely to be under very high pressure.

A simple calculation of the latent heat evolved [15] during solidification of the mass of silver in fig. 2a reveals the "sudden" availability of about 5.6×10^{-5} calories. That is about 5000 times as much energy or PV work as would be required to expand just $1 \times 10^{-9} \text{ cm}^3$ of residual gas to a

final volume of $4.71 \times 10^{-7} \text{ cm}^3$ (the "empty" space in the bubble). Most of this "excess" energy would probably be required to work against the rather viscous surroundings during the expansion. For example, the viscosity of the soda-lime-silica glass would be about 45000 poise at 960°C when the silver droplet solidifies. Since the process, as visualised, occurs within a small temperature/time interval during rather rapid cooling, there would normally be little opportunity for the increasingly viscous molten glass to collapse back around the now solid metal sphere.

Another possibility, in addition to any small amount of residual gas at the sphere/melt interface, is the creation of a small spherical void, because of the slight contraction of the metal at the instant of solidification. This spherical, low-pressure void could then be expanded by the release of the heat of solidification.

The final result would be a surrounding bubble, most of which was created at the instant of solidification of the metal droplet. In this regard, bright flashes of light were generally observed, particularly for colourless glass melts, from numerous melt locations, after removal from say 1200°C , but obviously long before the glass became rigid at T_g . This flashing is therefore quite probably associated with metal droplet solidification, and may be associated with reflectance changes during the process of solidification and bubble formation.

4. Conclusions

It is possible to prepare a variety of quenched oxide glasses which contain bubble-encapsulated silver or gold spheres that range in size from colloidal to $500 \mu\text{m}$ in diameter. The experimental evidence suggests several factors which may contribute to the formation of metal spheres instead of colloiddally dispersed crystals. These are (a) relatively high metal salt concentrations, (b) batch-mixing and melting procedures that

favour metal agglomeration, and (c) glass melt viscosities in the range of 10 to 5000 poise for the temperature region above the melting point of the metal.

The encapsulating bubbles appear to form when the liquid metal droplets freeze. The sudden release of the latent heat of fusion may be responsible for rapidly forming a surrounding bubble from small amounts of residual gases, or from the small empty volume initially created by the contraction of the metal during solidification. Further cooling at a rapid rate may then "freeze in" the enlarged bubble, while further cooling at a very slow rate may allow the bubble to collapse back on the now solid metal sphere.

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Received 11 May and accepted 21 May 1971.