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FABRICATION OF GLASS SPHERE LASER FUSION TARGETS*

C. D. Hendricks, A. Rosencwaig, R. L. Woerner
J. C. Koo, J. L. Dressler, J. W. Sherohman,
S. L. Weinland and M. Jeffries

University of California
Lawrence Livermore Laboratory
Livermore, California 94550

ABSTRACT

We have developed processes at LLL for mass producing the high quality glass microspheres required for current laser fusion targets. Here we describe the methods and the materials used in our liquid-droplet and dried-gel systems. Glass microspheres ranging from 70-600 microns O.D., with walls from 0.5 to 18 microns thick and which satisfy the exacting surface and symmetry specifications of targets for high density experiments are now produced routinely.

INTRODUCTION

Current laser fusion experiments require hollow glass microspheres filled with 1-10 MPa of equimolar deuterium and tritium (DT). Depending on the fusion experiment the microspheres range from 50 to 500 μm in diameter with wall thicknesses from 1 to 20 μm .

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For exploding pusher targets in which the laser energy is delivered to the entire thickness of the shell in a short time, literally causing the shell to explode, the quality of the glass shell is not extremely critical. Variations in wall thickness, surface irregularities, and some bubbles or voids in the wall can be tolerated. However, even with such relaxed tolerances only a few in 10^6 to 10^9 of the commercially produced shells are acceptable. Even then only shells with limited thicknesses ($0.5 \mu\text{m}$ - $1.5 \mu\text{m}$) and diameters ($40 \mu\text{m}$ - $250 \mu\text{m}$) are available.

For the ablative experiments designed to achieve a high density implosion the criteria for the target microspheres are very stringent. Sphericity and wall uniformity all must be better than 5%, which translates to no more than a $0.2 \mu\text{m}$ deviation for a $4 \mu\text{m}$ wall. The surface finish, as well, must be better than $0.2 \mu\text{m}$ peak to valley. Finally, we need batches of these microspheres which are suitable for coating with additional ablative layers. To produce a sufficient yield of acceptable coated spheres not only must the initial batches contain a high percentage of quality microspheres but also the wall thicknesses of the microspheres must fall within a narrow thickness range. Such microspheres, let alone batches are simply unavailable commercially.

Thus, to provide high quality microspheres in the desired sizes and quantities and further, to control the composition, we developed

two techniques for producing hollow glass microspheres. The liquid-droplet method which we describe first has been particularly successful in producing quality batches. The dried-gel method described second gives us added flexibility in available sizes and composition. Spheres made by both processes have similar compositions and are subjected to the same surface treatment to obtain the necessary smooth surfaces.

LIQUID-DROPLET PROCESS

The liquid-droplet method of making microspheres⁽¹⁾ starts with an aqueous solution of water-soluble glass-forming compounds, such as sodium silicate. Subjecting drops of this solution to elevated temperatures traps water vapor within the drops as a gel membrane forms on the surface.

The encapsulated water vapor is an internal blowing agent and with the appropriate temperature-time profiles we can make hollow glass microspheres that are exceptionally spherical and symmetrical. Most importantly, by using acoustic disintegration of a liquid jet to produce uniform drops⁽²⁾ of the solution, microspheres with specified diameters and wall thicknesses can be produced in a controlled fashion.

Liquid-droplet tower

Figure 1 schematically represents the liquid droplet tower consisting of a liquid droplet generator on top of a vertical furnace. Uniform aqueous droplets $\sim 200 \mu\text{m}$ in diameter are introduced into the long vertical drop furnace by a piezoelectrically-driven liquid droplet generator.^(3, 4) The percentage of solids in the solution and the size of the orifice in the liquid-droplet generator determine the diameter and wall thickness distributions of the resultant microspheres.

The 5 m furnace consists of 6 segments of quartz tubes 7.5 cm in diameter, 3 mm thick heated by insulated heater strips and GLOBAR multi-zone ovens. We drive the various heaters in the furnace with thermocouple-controlled power supplies. The furnace is well sealed and insulated throughout the heated regions. The amount of air drawn into the furnace is carefully controlled by a vacuum vent in the collector section. The air flow affects the transit times of the droplets during the various stages of transformation into a hollow glass microspheres. We estimate that vertical velocities of the droplet range from $\sim 500 \text{ cm/sec}$ near the top to as low as $\sim 5 \text{ cm/sec}$ at the bottom of the drying region.

Microsphere formation

The formation of a hollow glass microsphere from a water droplet is a dynamic process occurring in a reasonably short time, and because the droplet is travelling through a long opaque furnace, we cannot directly observe the processes that occur. Nevertheless we have been able to infer the physical and chemical events that take place in the liquid-droplet process by observing the system output as a function of furnace temperature profile and air flow.

The stages that occur during the transformation of the aqueous droplet to the final hollow glass microsphere can be divided into four separate events; encapsulation, dehydration, transition, and refining. These stages are shown schematically in relation to the drop furnace in Figure 1. The lengths and temperatures of the furnace sections given in Figure 1 were established according to the discussion given below.

Encapsulation and dehydration

As the water droplet enters the first zone a rapid evaporation of water occurs from the outer surface and a skin, or gel membrane forms. This gel membrane then encapsulates the rest of the water droplet in an elastic outer surface through which the water vapor can diffuse. The second section dehydrates the gel microsphere

sufficiently so that it can be properly fused into glass. Although we want to form and dry the gel sphere as quickly as possible to minimize furnace length, the temperature must be kept low enough to prevent rupture of the membrane due to excessive water vapor pressure.

If the transit time in the second zone of the drying region is long enough, and the remaining furnace sections are turned off, the output of the furnace is a hollow sphere as large as 2 mm in diameter with gel membranes about 0.1 μm thick. The walls of the gel microspheres are quite hard and not readily deformable. Also, because furnace gases diffuse readily into the cavity of the gel sphere, special gases such as argon can be encapsulated. This is discussed in an accompanying article.⁽⁵⁾

Transition and refining

Upon leaving the dehydration region, the gel microsphere enters the transition region where the transformation to glass begins. Here the gel wall turns to liquid, its viscosity drops, and the microsphere begins to collapse due to surface tension. This is the most crucial step and the glass formation chemical reaction must occur rapidly so that the gel microsphere will collapse uniformly while remaining hollow and spherical.

Below the transition region is the refining region where the chemical reaction comes to completion and any pockets of incompletely reacted material within the wall turn to glass and the wall becomes uniform. The gases trapped within the microsphere diffuse out at a rate determined by the glass composition and temperature. Simultaneously, if the viscosity of the glass is low enough at the maximum temperature of the refining region, any defects in sphericity will be eliminated by the surface tension of the molten glass. Higher viscosity glasses or lower refining region temperatures result in a large fraction of nonconcentric spheres.

By controlling both the temperature and transit time through the transition and refining regions, we can obtain batches of spheres with high yields of glass microspheres with the desired geometric parameters and with excellent sphericity and concentricity as illustrated by the interference micrograph in Figure 2.

DRIED-GEL PROCESS

The liquid-droplet technique has two constraints. First the glass forming compounds must be in solution. Some compositions we tried quickly formed a gel and were therefore not usable. Second, the maximum mass of the glass microsphere is limited. A larger drop of the solution than we normally use would require a drying column longer

than our space currently permits. Also, increasing the solution concentration eventually causes the droplet generator to cease functioning properly because of the increased viscosity of the solution. Thus, to expand our range of compositions and available sizes we use a dried-gel process in addition to the liquid-droplet method to make hollow glass microspheres.^(6, 7) In Figure 3, the sphere sizes we have produced using both methods are compared with those available commercially.

In the dried-gel process a solution containing glass-forming oxides is dried and ground into fine particles. The powder, after sieve cutting for the appropriate size granules, is dropped through a furnace. The water of hydration in the gel is encapsulated and the oxide particles blow and fuse into hollow glass shells.

The dried gel tower consists of a particle injector mounted on a vertical furnace. The injector is simply a fluidized bed with a small hole in the bottom through which particles occasionally fall. For some applications we can use a furnace similar to that shown in Figure 1. Usually, however, there is no "drying" section as in the liquid-droplet furnace because the dried-gel contains only water of hydration. Thus we can have a long refining section in which we can make relatively thick microspheres of high quality. In general, we find that the longer and hotter the furnace the better the sphericity and concentricity of the microspheres.

Gel particles and the resultant microspheres are shown in Figure 4. Note that a wide distribution of spheres are produced due to the varying particle size. Unlike the droplet system, sieve cutting the spheres will give a narrow diameter range but the thicknesses will still vary since gel particles with different masses can result in spheres with the same O.D. We are trying to make spherical gel particles so that a more uniform powder can be injected into the furnace.

For our initial experiments we used a glass composition similar to that employed in the liquid droplet systems. The main advantage being that we can produce more massive spheres by using large gel particles ($\sim 140 \mu\text{m}$ O.D. X $20 \mu\text{m}$ thick). By adding urea which acts as an additional blowing agent we can produce large-diameter, thin-walled spheres ($\sim 500 \mu\text{m}$ O.D. X $.5$ to $1 \mu\text{m}$ thick). Now that we have the dried gel process under control we are experimenting with lead and other high-Z glass compositions to meet the future needs of the fusion program.

GLASS COMPOSITION

Amongst the various glass-forming compounds, only the alkali silicates are water soluble to any significant degree, and of these

the $\text{Na}_2\text{O-SiO}_2$ binary system most easily forms a glass at relatively low temperatures. We use $\text{Na}_2\text{O-SiO}_2$ in the weight percent ratio of approximately 71% SiO_2 and 22% Na_2O . This particular composition has been chosen because it is close to the eutectic in the $\text{Na}_2\text{O-SiO}_2$ phase diagram, thus resulting in a low melting temperature.⁽⁸⁾ In addition, a eutectic composition reduces the possibility of devitrification.⁽⁹⁾ Another reason for choosing the $\text{Na}_2\text{O-SiO}_2$ system is that this particular alkali glass has a lower viscosity at temperatures below 1200°C than do the other alkali glasses. A low viscosity is essential to ensure high sphericity and concentricity of the microspheres.

We are unable to use a pure $\text{Na}_2\text{O-SiO}_2$ system, since this alkali glass is highly susceptible to deterioration due to the water in the atmosphere. It is believed that the primary mechanism for this deterioration is the rapid formation of NaOH at the glass-air interface and the subsequent etching of the underlying glass by the NaOH .⁽¹⁰⁾ This deterioration is further enhanced by the relatively high mobility of Na^+ ions in the glass structure.

We alter the $\text{Na}_2\text{O-SiO}_2$ system by adding small amounts of glass network modifiers such as K_2O and Li_2O , as well as glass network formers such as B_2O_3 . The network modifiers Na_2O , K_2O and Li_2O disrupt the continuity of the SiO_2 network, thereby

decreasing the softening point markedly from its value of 1600°C for pure SiO_2 and reducing the Na^+ ion mobility.⁽¹¹⁾ Network formers, such as B_2O_3 , join the network structure of the pure silica glass, reducing the viscosity⁽¹²⁾ but not affecting the softening point significantly or adversely affecting the thermal expansion and durability. Thus the addition of B_2O_3 , K_2O and Li_2O has little adverse effect on the low melting temperature and viscosity of the basic $\text{Na}_2\text{O-SiO}_2$ system, while considerably increasing the durability of the glass.

To date, we have obtained the best results using aqueous solutions of sodium silicate, boric acid, potassium hydroxide and lithium hydroxide. The relative composition of the glass-forming oxides in the solution and in the final glass is given in Table I.

Table I. Glass Compositions (weight %)

	SiO_2	Na_2O_3	B_2O_3	K_2O	Li_2O
Sol.	66.3	22.7	2.9	8.0	0.1
Sphere	70.6	21.9	2.0	5.4	0.1

The composition of the resultant microspheres is slightly different from that of the solution. This difference is primarily due to loss of some of the alkali by vaporization in the hot fusing region of the oven.

SURFACE TREATMENT

Once the glass microspheres are produced, it is imperative that they be carefully washed to remove all of the reactive alkali from the surface. A conventional acid wash such as an HCl or HF wash results in clean surfaces but does not prevent the surfaces from deteriorating within a matter of days when exposed to humid air.

We have developed an acid wash procedure that not only cleans the reactive alkali from the surface, but also significantly inhibits deterioration.⁽¹³⁾ This procedure involves several cycles of washes with a 0.5 N HNO₃ + 0.1 NH₄F solution heated to 90°C, followed by washes with hot distilled water, acetone, and finally ethanol. Microprobe analysis indicates that this wash procedure etches out a significant amount of the alkali (primarily Na) from the first micron of the microsphere wall. This alkali depletion inhibits the deterioration process at the surface.

There is no sign of deterioration on spheres treated in this manner even after being left in humid air for several weeks. Figure 5 shows a SEM photograph of a washed LLL microsphere. Surface smoothness is obviously much better than the required 2000 Å. Thus, with such smooth surfaces and the variety of available sizes we can meet the laser fusion target requirements.

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LIQUID-DROPLET SYSTEM

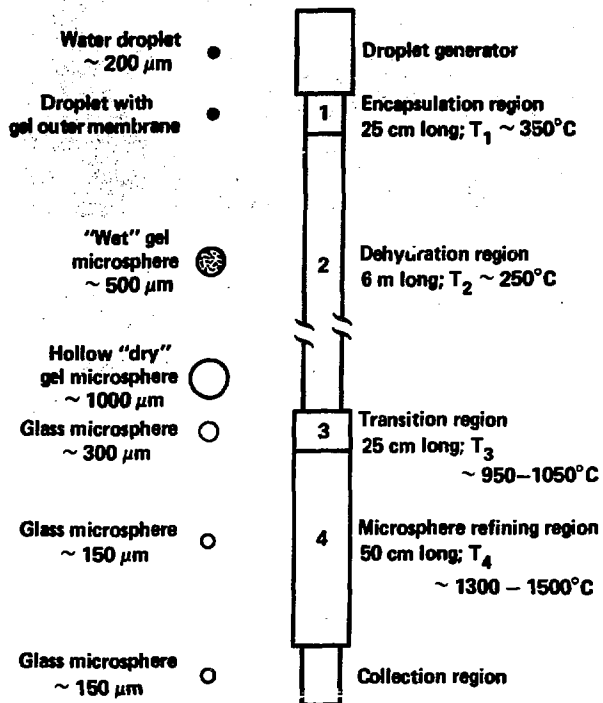


FIGURE 1. A schematic diagram of the vertical-drop furnace.

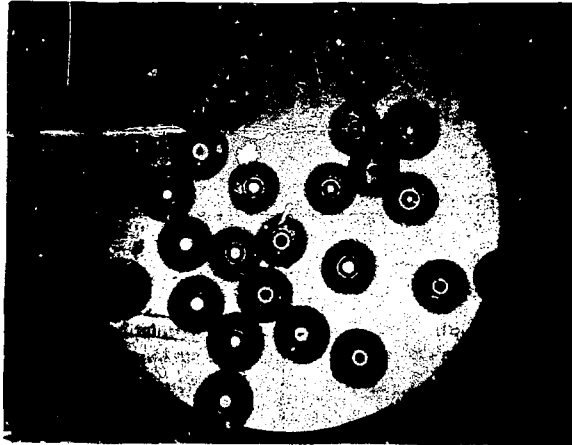


FIGURE 2. An interference micrograph of hollow glass microspheres that have excellent concentricity, wall uniformity and a narrow thickness distribution. Over 90% of the spheres in this batch meet the specifications for ablative targets. These spheres are $140 \mu\text{m}$ in diameter with $5 \pm .5 \mu\text{m}$ thick walls.

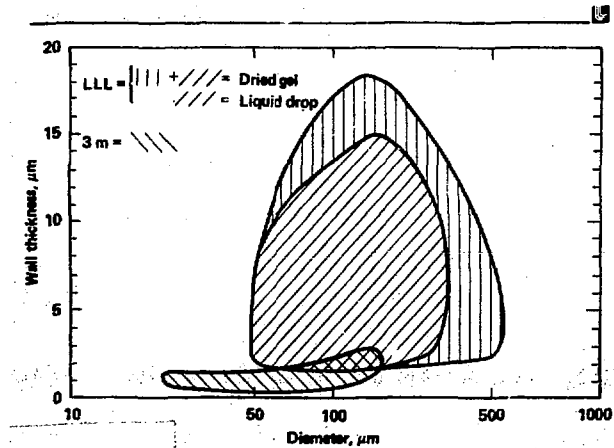


FIGURE 3. Comparison of available sphere sizes.

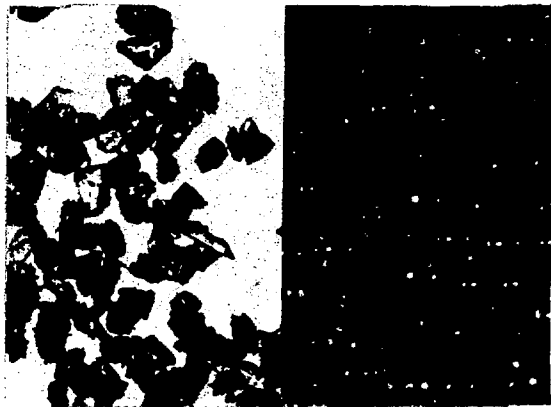


FIGURE 4. Gel particles and resultant microspheres.

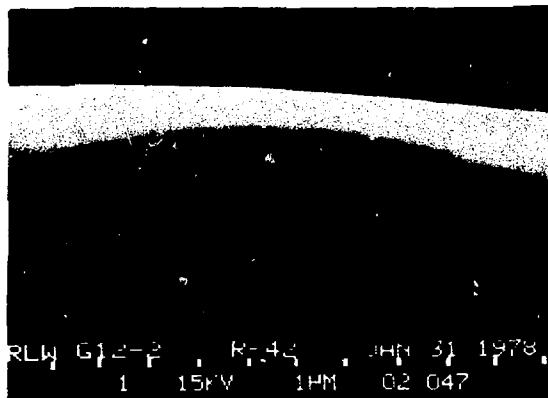


FIGURE 5. SEM photograph of a washed LLL microsphere with a 100-200 Å surface finish.