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FABRICATION OF THE GLASS MICROBALLOON LASER TARGET

P. C. Souers
R. T. Tsugawa
R. R. Stone

September 26, 1974

MASTER

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Symbols

a	outer radius of microballoon (m)
$\bar{a}$	average outer radius in a batch of microballoons (m)
A	outer surface area of microballoon (m^2)
D	diffusion coefficient (m^2/s)
D_0	diffusion coefficient intercept (m^2/s)
F_i	mole percent of i^{th} constituent oxide in a given glass (%)
F_{Si}	mole percent of SiO_2 in a given glass (%)
G	mole percent glass formers ($SiO_2 + B_2O_3 + P_2O_5$) (%)
k_i	number of oxygen atoms in the formula of the i^{th} constituent oxide in a given glass
K	gas permeability coefficient ($m^3[STP] \cdot m/m^2 \cdot s \cdot Pa^n$, where $n = 1$ for glass/silica and $n = 1/2$ for metals)
K_0	gas permeability intercept ($m^3[STP] \cdot m/m^2 \cdot s \cdot Pa^n$, where $n = 1$ for glass/silica and $n = 1/2$ for metals)
t	wall thickness of microballoons (m)
$\bar{t}$	average wall thickness of a batch of microballoons (m)
m	mass of gas (kg)
m_g	mass of glass microballoons (kg)
M	molecular weight (kg/mol)
M_i	constituent oxide in a given glass (kg/mol)
n_D	refractive index at the sodium D line
P	perfect gas pressure (Pa)
P_1	perfect gas pressure inside microballoon (Pa)
P_2	perfect gas pressure outside microballoon (Pa)
P^c	gas pressure corrected for compressibility (Pa)
P_m	experimentally measured gas pressure (Pa)
P_{max}	maximum perfect gas pressure inside microballoons (Pa)
P_∞	maximum experimentally measured gas pressure (Pa)
Q	gas permeability exponential ($^{\circ}K$)
Q_D	diffusion coefficient exponential ($^{\circ}K$)
Q_S	solubility exponential ($^{\circ}K$)
r_i	refractive index constant for the i^{th} constituent oxide in a given glass (dimensionless)
R	gas constant ($8.314 J/^{\circ}K \cdot mole$ or $m^3[STP] \cdot Pa/^{\circ}K \cdot mole$)
S_0	solubility intercept ($m^3[STP]/m^3 \cdot Pa^n$, where $n = 1$ for glass/silica and $n = 1/2$ for metal)
t	time (s)
T	temperature ($^{\circ}K$)
V	volume of gas ($m^3[STP]$)
V_0	constant, volume of gas at STP ($22,414 \times 10^{-6} m^3$)

V_i	volume constant for i^{th} constituent oxide in a given glass - used in glass density calculation (m^3)
W_i	weight percent of i^{th} constituent oxide in a given glass (%)
Z	gas compressibility (dimensionless)
$Z_{\text{B/O}}$	ratio of boron to oxygen atoms in a given glass (dimensionless)
$Z_{\text{Si/O}}$	ratio of silicon to oxygen atoms in a given glass (dimensionless)
β	temperature dependent component in first virial coefficient for gas compressibility ($\text{m}^3/\text{kg} \cdot ^\circ\text{K}$)
β_0	constant component in first virial coefficient for gas compressibility (m^3/kg)
λ	tritium decay constant ($1.780 \times 10^{-9} \text{ s}^{-1}$)
ρ	density of gas (kg/m^3)
ρ_g	density of glass (kg/m^3)
ρ_T	density of tritium atoms (atoms/m^3)
$\sigma_{1/2}$	hoop stress for half breakage of a given batch of glass microballoons (Pa)
τ	gas permeation time constant (s)

FABRICATION OF THE GLASS MICROBALLOON LASER TARGET

Abstract

The fabrication of the first LLL laser target designed for neutron yield is described. Glass microballoons loaded with hydrogen gas were used as targets. It was found that hydrogen permeability in glass decreased exponentially as the temperature and silica content decreased.

Loaded hydrogen was measured destructively, but absolutely, with an ionization chamber; it was measured nondestructively, but relatively, with a proportional counter. The diameter and wall thickness of the microballoons were measured by helium fill of a batch, individual metallographic sectioning, and refraction and light interference techniques.

I. Foreword

INTRODUCTION

One of today's most exciting technical goals is the achievement of laser-induced thermonuclear fusion. To reach that goal, a high-energy, short-pulse laser beam would have to induce thermonuclear burn by compressing a DT fuel pellet a thousand-fold. The resulting energy could supply the power needs of the next generation.¹

The impetus for laser fusion at LLL has come from the theoretical work of Nuckolls, Wood, and other LLL scientists.^{2,3,4} Under the direction of C. Haussmann and J. Emmett, a large program in laser construction has been initiated at LLL.¹ One goal of this program is to demonstrate the scientific feasibility of laser fusion by obtaining "break-even" by 1978. Break-even is

achieved when thermonuclear burn produces the same amount of energy as that contained in the incident laser beam.

DESCRIPTION OF THE TARGET

Nuckolls' A-Division group has designed a laser target to test laser-fusion theory and computer calculations. The target has been specifically designed for a significant neutron yield in the initial low-energy laser regime of 50 J and 100 ps. We believe that it has a good chance of producing more than 1000 neutrons (which is the threshold of the neutron detectors). It is not the break-even target, but it is intended to be the first step along the way.

Basically, this class of target generates multi-keV electrons at the laser photon-material interface. The particles

Table 1. Target design guidelines.

Design parameter	Initial delivery specification	Final objective	Analytical method
Microballoon o. d.	70 to 80 $\pm$ 2 μ m	70 to 80 $\pm$ 1 μ m	Direct optical
Microballoon wall thickness	1 $\pm$ 0.2 μ m	1 $\pm$ 0.1 μ m	Interferometry
DT fill	8 $\pm$ 4 kg/m ³	5 $\pm$ 1 kg/m ³	Tritium counting
D/T ratio	1.0 $\pm$ 0.4	1.0 $\pm$ 0.2	Mass spectrometer
Suspension	30 ng within 100 μ m	10 ng within 100 μ m	Optical

Fig. 1. DT-filled glass microballoon glued to a 5- μ m glass fiber (note human hair).

transport energy around and through the target. The subsequent explosion-implosion of a low Z shell compresses a DT fill which burns slightly when proper densities and temperatures are obtained.

The heart of this type of target is a glass microballoon with a 70 to 80- μ m diam and about a 1- μ m wall thickness. DT gas is permeated through the walls at

high temperature and trapped when returned to room temperature. Table 1 shows the basic specifications for the target. The wall thickness uniformity (and hence, sphericity) seems to be the most important theoretical parameter, and it is also the most difficult to measure experimentally. Figure 1 shows the gas-filled microballoon glued to a 5- μ m glass fiber.

USING GLASS FOR THE MICROBALLOON SHELL

In constructing the neutron target we have tried to purchase the best possible commercial microballoon as the starting unit. Only four materials are available in microballoon form: glass, nickel-manganese, plastic, and carbon. Glass was selected for its strength in holding gas pressure, its transparency to optical inspection, its apparent sphericity, and, from theoretical considerations, its relatively low atomic number. Recently, the transparency of glass to 1.06- μ m laser radiation was seen as a further bonus, since the effect of precursor pulses have been recognized as a problem. The

relative merits of these microballoon types are described below.

Two companies make glass microballoons as a light-weight filler for plastics.⁵ They are made in ton quantities by a highly random flash furnace process. Basically, a blowing agent is mixed into the glass on nearly an atomic scale and the resulting mixture is ground and passed through an air-flow furnace. Some particles are blown by chance into microballoons and are swept out by the air flow. Size and wall thickness are roughly set by production conditions, but the spread of the product is wide and the manufacturing methods are empirical. The manufacturing processes for both companies have been patented and are proprietary.^{5,6}

The Emerson & Cuming glass microballoons have an outer diameter of 5 to 300 μm with 40 to 80 μm being the most common. The walls are 1/2 to 2 μm thick. The manufacturing process is said to start with an aqueous slurry of sodium borosilicate, with "oxide compositions" of 70.7 wt% SiO_2 , 22.2% Na_2O , and 7.1% B_2O_3 . An organic blowing agent, possibly 1% urea, is mixed in at the slurry

stage. Residual gases inside the blown product are said to be under 0.02 MPa (3 psi) of CO_2 and N_2 .⁷

The basic Emerson & Cuming glass microballoon has a composition close to 3M's; i.e., similar to that of window glass (72% silica). Their industrial grades (IG) have this composition, although they may be surface-treated to improve flow properties. The company leaches out the sodium and claims to replace it by ion-exchange with another material.⁷ The resulting SI grade contains about 93% silica and is sold as a stronger grade of microballoon.

The 3M glass microballoons are made by permeating gas into solid glass particles.⁶ Again, inclusion of the blowing agent is on an atomic scale. The finished microballoon is said to contain 0.034 MPa (5 psi) SO_2 and O_2 .⁸ All 3M microballoons are chemically similar to window glass in that they contain 75 to 80% silica plus calcium and sodium. All grade are said to be surface treated with DuPont Voland, an organo-chromium complex that improves the flow of the product.⁸ The o.d. ranges from 20 to 100 μm , with 50 to 70 μm the mean. 3M literature describes the microballoon strength in terms of 14-MPa (2000-psi) hydrostatic tests.

Early work was performed at LLL on Emerson & Cuming SI-grade microballoons in 1970-71. Ekstrom et al., glued unloaded 35- μm o.d. microballoons to glass stalks.⁹ Otsuki and Stribling permeated deuterium into the microballoons at room temperature, finding about 16-hr first order decay ($1/e$) time.¹⁰

⁵ Emerson & Cuming, Inc., Dielectric Materials Division, Canton, Massachusetts 02021, and 3M Company, Special Enterprises Department, St. Paul, Minnesota 55101.[†]

[†]Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Atomic Energy Commission to the exclusion of others that may be suitable.

OTHER TYPES OF MICROBALLOONS

Certain plastic microballoons are among the most spherical. Many encapsulate, on a small scale, such products as perfume, ink, explosives, and fertilizer. Plastic microballoons are created if the product is able to permeate out (which is certainly not the intent of those who make the product). The sizes tend to be small: 5 to 60 μm o. d., with walls 0.1 μm thick. They are quite weak in relation to glass: perhaps holding up to 0.35 MPa (50 psi). Too many firms make such plastic products to warrant a list here; however, such materials may be found generally listed under "plastic microencapsulation."

Carbon microballoons are made in Japan⁴ by blowing petroleum pitch

⁴Kureha Chemical Co., Lt., Tokyo, Japan. American outlet:
Kureha Corporation of America
116 East Alondra Blvd.
Gardena, CA 90248

Fig. 2. As-received carbon microballoons.

particles in a flash furnace followed by high temperature carbonization.¹¹ Sizes are said to be controllable from 40 to 400 μm o. d., with walls 1 to 20 μm thick. The material is offered as a competitor to the glass microballoons and the company claims they are just as strong. A 150- to 200- μm o. d. sample obtained by us showed the particles to generally be somewhat football-shaped. The product, of course, is black and opaque and was not convenient for our optical methods. Figure 2 shows the appearance of this type of microballoon.

The only metal microballoon product, to our knowledge, is the Solacel "hollow metal powder,"[†] which is approximately 70 wt% Ni and 20% Mn. It is possibly the same material that was patented as a stainless steel brazing alloy for use in the B-70 bomber.¹²⁻¹³ The sizes range

[†]Solar (Aircraft), P. O. Box 80966, San Diego, CA 92138

Fig. 3. As-received Solacel nickel microballoons.

from 150 μm o. d. to several mm, with walls 2 to 5 μm thick. The sphericity is generally poor and only a fraction are leak tight. However, experiments at

LASL¹⁴ and Bendix, Kansas City¹⁵ have succeeded in loading selected Solacel balloons with tens of MPa (thousands of psi). Figure 3 shows the Solacel balloons as received.

II. Composition and Predicted Properties of Glass Microballoons

GLASS COMPOSITION^{16,17}

Glass has an amorphous atomic arrangement and lacks a sharply defined melting point. It is composed of basic materials called "glass formers" that form networks of metal-oxygen units. The mole% of glass formers (G) determines how "glassy" the network is. By varying the glass formers, we can alter the physical properties of glass. The major glass formers are SiO_2 , B_2O_3 , and P_2O_5 .

When modifying oxides are added, e.g., Na_2O , K_2O , and CaO , the glass-forming network is somewhat broken up but manages to incorporate the modifying oxygens into its structure. As long as the atomic ratio of oxygen to glass-forming metal is three or less, the compound remains a stable glass.

Glass is usually analyzed just for the metals, and the results are stoichiometrically paired with oxygen as though all components were oxides. Actually, carbonates, sulfates, and fluorides may be present.

When glass is placed in even a weak acid solution, the modifying metal cations are leached out to perhaps a depth of 10 μm . It is thought that the corresponding oxygens in the glass are left behind, although this is not clear. Almost all work is understandably done on the metal ions. We may postulate the following surface reaction:

The sodium hydroxide in this example reacts with the acidic solution and is removed from the area. The sodium has been leached. Another cation could be introduced, e.g., K^+ , and such ion exchange to a larger cation is often done to provide compressive surface strength.

Emerson & Cuming state their use of leaching and ion exchange on some of their products, initially made from an aqueous slurry. Hence, the probability of finding hydroxyl groups in E & C glass would seem to be quite high. 3M states that they do not leach their finished products.

Table 2. Inventory of glass microballoons mentioned in this report. (The list is in order of increasing advertized strength.)

3M		
Grade	Lot number	Experimental or commercial
B12AX	P-8144-2	E
B15BX	P-0745-8	E
B18A	P-9151-7	C
B22A	P-9339-9	C
B35D	P-0097-1	C
B35D	P-8705-6	C
Emerson & Cuming		
IG-101	1297	C
IG-25	1311	C
R	713	C
SI	10208014	E
SI	10303019	E
SI	339-S	C
SI	355-S	C

but do treat them chemically. Consequently, hydroxyls may also be present in their products.

BATCH ANALYSES OF UNSIEVED GLASS MICROBALLOONS

Because there are a large number of glass microballoon grades, Table 2 lists each batch mentioned in this report. Tables 3 and 4 list the results of all analyses actually run. As is customary for ease and expense, only metals have thus far been analyzed. Tables 5 and 6 relist the major components in mole% oxides.

The analytical data is recompressed to yield the first two columns in Table 7. The first column shows the mole% of

glass formers (G): $\text{SiO}_2 + \text{B}_2\text{O}_3 + \text{P}_2\text{O}_5$. The second column shows the average atomic number of the glasses — all are close to 10, reflecting the fact that there are no heavy metals.

Finally, microballoon samples were checked by x-ray diffraction, and all showed an amorphous, glassy structure on a ball-by-ball basis. The batches checked were: 3M — B35D-P-0097-1 and P-8705-6; Emerson & Cuming — SI-10208014, 10303019, 339-S, and 355-S.

ATTEMPTS AT INDIVIDUAL MICROBALLOON ANALYSIS

Preliminary work with the electron microprobe had indicated ball-to-ball differences in chemical composition.

Table 3. Average batch chemical analyses in wt% of as-received 3M glass microballoons.

Component	Batch ^a						Analytical method ^b
	R12AX P-8144-2	B15BX P-0745-8	B18A P-9151-7	B22A P-9339-9	B35D P-0097-1	B35D P-8705-6	
SiO ₂	—	—	74.1	73.0	76.8	—	1
Ca	6.75	6.37	6.69	6.40	6.52	6.07	2
Na	2.82	3.34	3.18	4.35	5.06	4.21	2
B	—	—	1.2	1.5	0.70	0.59	3
K	0.5	0.5	0.5	0.5	0.168	0.095	2, 4
Mg	0.2	0.5	0.5	0.1	0.2	—	4
Al	0.05	0.1	0.3	0.2	0.14	0.081	2, 4
P	0.2	0.2	0.2	0.2	0.3	0.3	4
Zn	0.03	0.02	nd<0.003	0.5	0.88	0.90	2, 4
Fe	0.1	0.2	0.2	0.1	0.041	0.049	2, 4
Cr	0.2	nd<0.003	0.2	0.3	0.1	0.1	4
Li	0.1	0.1	0.1	0.1	0.066	0.0315	2, 4
Mn	0.001	0.992	0.993	0.992	0.140	0.050	2, 4

^a An average of all the batches has also been made. Detected: Ti, Zr < 0.02; Ba < 0.015; Sr, Pb < 0.01; Ni, Cu < 0.0003; Ag < 0.0002. Analytical Method: 4. Not detected: Cs, Rb < 0.03; Cd < 0.01; Bi, Mo, Nb, Sb, Sn < 0.003; Co < 0.0003, Be < 0.0001. Analytical Method: 4.

^b Analytical Methods: 1. Gravimetric Na₂CO₃ fusion/perchloric acid. 2. Atomic absorption. 3. Barium borotartarate precipitation. 4. Emission spectroscopy.

Table 4. Average batch chemical analyses in wt% of as-received Emerson & Cuming glass microballoons.

Component	Glass grade/lot ^a				Analytical method ^b
	Grade IG-101 1297	Grade IG-25 1311	Grade R 713	SI grade 10303019	
SiO ₂	74.2	—	—	—	1
Na	17.5	16.1	10.74	4.91	2
B	1.35	0.7	0.24	0.48	3
Ca	0.8	—	0.023	0.04	2, 4
Al	0.2	—	—	0.06	2, 4

^aAn average of all the batches has also been made. Detected: Fe < 0.05; Ba < 0.04; K, P < 0.03; Ti, Pb < 0.02; Mg, Cr < 0.01; Zn < 0.006; V, Cu < 0.005; Ca, Zr < 0.003; Mn < 0.002; Li, Ni, Sr, Ag < 0.001. Analytical method: 2, 4. Not detected: Cs, Rb < 0.03; Cd < 0.01; Bi, Mo, Nb, Sb, Sn < 0.003; Co < 0.0003; Be < 0.0001. Analytical method: 4.

^bAnalytical methods: 1. Gravimetric Na₂CO₃ fusion/perchloric acid, 2. Atomic absorption, 3. Barium borotartarate precipitation, 4. Emission spectroscopy.

Table 5. Summary analyses in mole% of as-received 3M glass microballoons. (All analyses are converted to stoichiometric oxides.)

Component ^c (mole%)	Glass grades/lots					
	B12AX P-8144-2	B15BX P-0745-8	B18A P-9151-7	B22A P-9723-9	B35D P-0097-1	B35D P-8715-6
SiO ₂	(82.1) ^a	(81.7) ^a	79.3	77.4	79.2	(82.2) ^a
CaO	10.1	9.6	10.7	10.2	10.1	9.1
Na ₂ O	3.7	4.4	4.4	6.1	6.8	5.6
B ₂ O ₃	(2.8) ^a	(2.8) ^a	3.6	4.4	2.0	1.6
Other ^b	1.3	1.5	2.0	1.9	1.9	1.5
Total - wt%	(100.0) ^a	(100.0) ^a	94.6	95.7	98.1	(100.0) ^a

^aParentheses indicate estimates: 1 wt% B and SiO₂ by subtraction.

^b"Other" oxides are considered to have an average oxide-to-metal mass ratio of 1.5 and an average molecular weight of 100.

Variations of about a factor of two were seen in Ca and Na for 3M (B35D, P-0097-1) and in Na for E & C (SI, 10303019). We now believe that these results are incorrect based on our readings from the curved surfaces of microballoons.

A second attempt was made with the emission spectrometer. Individual balls were selected from 3M (B35D, P-0097-1). One ball at a time was run to obtain the Na-to-Si ratio. The National Bureau of Standards glass sample Nos. 91

Table 6. Summary analysis in mole% of as-received Emerson & Cuming glass micro-balloons. (All analyses are converted to stoichiometric oxides.)

Components (mole%)	Reported starting composition	Glass grades/lots			
		IG-101 1297	IG-25 1311	R 713	SI 10303019
SiO ₂	71.9	72.5	(<76.6) ^a	(<85.0) ^a	(<91.9) ^a
Na ₂ O	21.9	22.3	21.3	14.1	6.5
B ₂ O ₃	6.2	3.7	1.9	0.7	1.3
Other ^b	-	1.5	(>0.2) ^a	(>0.2) ^a	(>0.3) ^a
Total ~ wt%	100.0	103.9	(100.0) ^a	(100.0) ^a	(100.0) ^a

^aParentheses indicate estimates: SiO₂ by subtraction.

^b"Other" oxides are considered to have an average oxide-to-metal mass ratio of 1.5 and an average molecular weight of 100.

Table 7. Summary of glass properties.

Company	Grade and lot No.	Glass formers, mole%	Average atomic No.	Theoretical bulk density, kg/m ³	Theoretical refractive index (NaD)	Theoretical gas permeability exponent, K	
						He/glass	H ₂ /glass
3M	B12AX, P-8144-2	≤84.9	≥10.2	≥2.41	≥1.51	≥4340	≥6480
	B15BX, P-0745-8	≤84.5	≥10.2	≥2.42	≥1.51	≥4390	≥6530
	B18A, P-9151-7	82.9	10.2	2.43	1.51	4590	6740
	B22A, P-9339-9	81.8	10.1	2.44	1.51	4730	6880
	B35D, P-0097-1	81.2	10.2	2.44	1.51	4810	6950
	B35D, P-8705-6	≤83.8	10.2	≥2.42	≥1.51	4480	6620
E & C	IG-101 1297	76.2	9.8	2.43	1.50	5440	7590
	IG-25, 1311	≤78.5	≥9.9	≥2.41	≥1.49	5150	7300
	R, 713	≤83.7	≥10.0	≥2.34	≥1.48	4240	6380
	SI, 10303019	≤93.2	≥9.9	≥2.27	≥1.47	3300	5420
Pure fused silica		100.0	10.0	2.202	1.458	2440	4550

(borosilicate glass) and 93 (opal glass) were used as standards. We concluded from the emission spectrometer work that no significant differences in the Na/Si ratio existed. However, the results were close to the error of the method, and the high cost of individual analysis has precluded further attempts.

CALCULATION OF GLASS DENSITIES AND REFRACTIVE INDICES

Given the composition of a theoretically dense (i.e., annealed) glass, it is possible to calculate the bulk density and refractive index (at the sodium D line).¹⁸ The Huggins method has a theoretical basis to the extent that volumes representing the components are added together. However, the method is actually empirical, and it has been fitted to a large number of glass compositions.

We first calculate the ratio of silicon to oxygen atoms in the glass:

$$Z_{\text{Si/O}} = \frac{F_{\text{Si}}}{\sum_{i=1}^n k_i F_i} \quad (2)$$

where F_{Si} is the mole% of SiO_2 , k_i is the number of oxygens in the formula of each constituent oxide, and F_i is the mole% of that oxide. All this data, normalized to 100% closure, may be obtained from Tables 4 and 5. For "other" oxides, we take k to be 2. This is taken from the 12 oxides that were averaged in the analytical treatment into "other," with an average molecular weight of 100 and an oxide/metal mass ratio of 1.5.

For our glasses, $Z_{\text{Si/O}}$ will lie between 0.40 and 0.50. Table 8 shows that V_i , which is needed for the next calculation, can have two values, depending on whether

$Z_{\text{Si/O}}$ is in the range 0.40 to 0.435 or 0.435 to 0.50. The purpose of Eq. 2 is to tell us which column of V_i to use.

Next, our mole% compositions must be converted to wt% with 100% closure. (This generally is not the experimentally obtained values, which rarely close to 100%.) The wt% of the j^{th} oxide is:

$$W_j = (100) \frac{F_j M_j}{\sum_{i=1}^n F_i M_i} \quad (3)$$

where M_i is the molecular weight of the i^{th} oxide.

We may then calculate the bulk density for annealed glass of this composition:

$$\rho_G = \frac{1}{\sum_{i=1}^n V_i \cdot W_i} \quad (4)$$

Finally, the refractive index at the sodium D line is obtained:

$$n_D = 1 + \rho_G \sum_{i=1}^n r_i \cdot W_i \quad (5)$$

The results of these calculations for our various glasses are shown in Table 7, with some preliminary density data on

Table 8. Constants used in calculations of glass densities and refractive indices.

Component	V_i		r (sodium D line)
	$Z_{\text{Si/O}}$ 0.40-0.435	$Z_{\text{Si/O}}$ 0.435-0.50	
SiO_2	4.41×10^{-6}	4.34×10^{-6}	2.08×10^{-6}
CaO	2.31×10^{-6}	1.84×10^{-6}	2.26×10^{-6}
Na_2O	3.24×10^{-6}	2.81×10^{-6}	1.94×10^{-6}
H_2O ^a	4.60×10^{-6}	3.45×10^{-6}	2.15×10^{-6}
(Other) ^b	2.9×10^{-6}	2.3×10^{-6}	2.55×10^{-6}

^a10 values used in Ref. 18. (Our glasses all have $Z_{\text{Si/O}} > Z_{\text{H}_2\text{O}} = 0.5$.)

^bEight of the twelve major "other" components used in the analytical calculations were averaged for these values.

^cThe added correction of source 3 has been ignored (0.1%).

crushed microballoons that will be discussed in the next chapter.

HELIUM PERMEATION IN GLASS

The permeation of helium as a function of glass composition has been pretty well worked out in two comprehensive papers.^{19,20} Altomose,²⁰ especially, made an extensive comparison and suggested that helium permeability decreases exponentially with increasing mole percents of modifiers. His equation for helium in annealed glasses is:

$$K = (3.45 \times 10^{-15}) \exp \left\{ -\frac{1}{T} (15,040 - 126 \cdot G) \right\} \times \frac{m^3 \text{STP} \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{Pa}}, \quad (6)$$

where G is the mole% of glass formers. Altomose maintains the same intercept and modifies only the exponential. For He in pure silica, Q is 2440°K. The experimental data used for this correlation lies between G 's of 65 to 100%. The effect of leaching on this relation is unknown. The calculated Q 's from Eq. (6) for our batches of glass are listed in Table 7.

The permeation of helium in glass is unchanged by pressure up to 100 MPa (15 kpsi) compression²¹ or by shear stress up to 0.004.²² However, an increased helium permeation has been seen with 0.02 to 0.04-m diam Pyrex ($G = 94$) bulbs at room temperature.^{23,24} Permeation rate increases of 50% were seen at hoop stresses of 35 MPa (5 kpsi)

in one case²³ and 140 to 210 MPa (20 to 30 kpsi) in the other.²⁴ The effect was thought to be related to the breaking stress of the glass rather than the absolute stress.²⁴ The cause is postulated to be the opening of microcracks in the glass walls.²³ The tension effect was not observed for helium in Pyrex and fused silica at 200°C, for helium in Pyrex at room temperature, or for deuterium in Pyrex at 200°C.²⁴

To summarize, for helium (and perhaps hydrogen), we may expect a tension-increased permeation rate starting at about half the crushing stress of our microballoons. The effect diminishes with increasing temperature and increasing mole% of glass formers (G). For our 75 to 80% G 's, we might expect such an effect even as high as 400°C. However, even if present, the effect may not be important.

PERMEATION OF HYDROGEN IN GLASS

The passage of hydrogen through glass conforms to a first power relationship with pressure. This is attributed to molecular hydrogen diffusing interstitially.^{25,26} It has been extensively studied in pure fused silica, where it occurs as the primary form of activity below 500°C.

Unfortunately, little work has been done on glasses with lower silica concentrations. The literature is summarized in Table 9, which represents a data compression covering essentially five different compositions varying from G 's of 72 to 100%.

We have arranged the data of Table 9 into an Altomose-type expression for hydrogen permeation in glass:

The intercept, K_0 , is $1.84 \times 10^{-6} \text{ cm}^3 \text{STP} \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{atm}$.

Table 9. Summary of literature on hydrogen permeation through glass.

Type of glass	G (mole%) SiO ₂ +B ₂ O ₃ +P ₂ O ₅	Isotope	K ₀ $\frac{m^3[\text{STP}] \cdot \text{cm}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}}$	Gas permeability exponent, K	Experimental temperature range, °C	Reference
Soda lime	72	H ₂	2.72×10^{-14}	9520	250°-450°	37
Soda lime	80	H ₂	2.79×10^{-15}	7430	250°-450°	37
Sodium borosilicate	92.6	D ₂	7.23×10^{-16}	4655	150°-500°	38
Pyrex 7740	94	D ₂	2.74×10^{-15}	4980	110°-280°	39
Vycor	99	H ₂	2.06×10^{-5}	4450	300°-1000°	28
Vycor	99	D ₂	1.05×10^{-15}	4190	25°-500°	40
Fused silica	100	H ₂	1.83×10^{-15}	4570	300°-1000°	25, 27, 28
Fused silica	100	D ₂	1.90×10^{-15}	4590	300°-1000°	25, 27, 41

$$K = (1.82 \times 10^{-15}) \exp$$

$$\left(-\frac{1}{T} (17\,330 - 127.8G)\right)^*$$

$$\times \frac{m^3[\text{STP}] \cdot \text{cm}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}}. \quad (7)$$

For fused silica, G = 100% and the exponential is 4550°K. The intercept is constant at the fused silica value. This equation fits the small amount of available data about as well as any could. The calculated Q's from Eq. (7) for our batches of glass are listed in Table 7.

THE PERMEATION OF HYDROGEN AND WATER IN GLASS

The two subjects listed in the title are mentioned together because it appears that they may be the same. Hydrogen permeation of 99.9% fused silica above 500°C becomes anomalous, with the solubility of the gas increasing far above that expected by molecular processes, according to mass spectrometer outgassing

studies.²⁵⁻²⁸ This work has been correlated to infrared hydroxyl signals over the temperature range 470° to 1000°C.^{27,28} The resulting hydroxyl form is stable, as shown by no loss of infrared signal for a sample pressurized with H₂ at 750°C and then stored under room conditions for 2 yr.²⁶

Outgassing of hydrogen-pressurized, fused silica at 700°C or above produces a nonexponential result, more as though two exponentials with very different time constants had been overlaid.²⁵⁻²⁸ The break in slope occurs somewhere between 90 and 99% of the total gas out.

Researchers studying the permeation of "water" in fused silica at high temperatures (>1000°C) found that it dissolved according to a half-power relation of water vapor – and infrared showed the presence of hydroxyl groups.^{29,30} Then, the heating of dry silica glass with hydrogen at 800° to 1050°C produced hydroxyl groups in a concentration about that of previously reported hydrogen solubilities at these temperatures.³¹ It was suggested, for the first time, that water and hydrogen

*The intercept, K₀, is 3.5×10^{-6} cm³[STP]·cm/cm²·s·atm.

reactions in silica glass are intimately related, at least at higher temperatures.

Another important new discovery is the so-called transformation (temperature) range. Above 1000°C, "water" diffuses in silica glass with a particular exponent; below 900°C, it diffuses with another, larger exponent.³² The temperature range from 900 to 1000°C, is called the transformation range, for which the diffusivity shows an extraordinarily large exponent. The reason for this phenomenon is unknown, but it appears also in 72 to 75 wt% silica glass at 460° to 500°C.^{33,34} The importance of this phenomenon is that it is our only correlation between fused silica and soft glass. It suggests that the fused silica reactions may occur some 500° lower in soft glass. Since fused silica starts to react with hydrogen at 500°C, we may find soft glass reactions in the 25° to 300°C range.

The reactions involved in all this are unknown, except that a hydroxyl group is formed in fused silica from 460°C up (not

looked for yet in soft glass). The most commonly written reaction is²⁹:

Others include:

Note that Eq. (8) may be run backwards, by the addition of hydrogen as a catalyst, to pull off the hydroxyl groups. Leached or slurry-formed glass might contain a large amount of hydroxyl even at the start.

Other components of glass might be even more reactive. The following reaction, suggested for calcium, would probably hold for anything.²⁸

Table 10. Literature summary of water permeation in glass below the transformation range.^a

Glass composition, wt%	Diffusion		Diffusion conditions	OH SiO ₂	Solubility conditions	Known formation range?	Reference
	D ₂ ^o (m ² /s)	Q _D (°K)					
72 SiO ₂ , 14 Na ₂ O, 9 CaO	2.3 × 10 ⁻¹⁰	6 050	380°-480°C			Yes	34
75 SiO ₂ , 15 Na ₂ O, 10 CaO	1 × 10 ⁻⁸	11 200	370°-460°C			Yes	33
99% + calica	6.4 × 10 ^{-11b}	8 960	600°-1200°C, transformation range not evident	S _O = 5.2 × 10 ⁻² Q _S = -2160	600°-1200°C, transformation range not evident	No	29
5400 Å silica film (100% SiO ₂)				0.14% inside, 1% surface ^c	200°C, shown to depend (equilibrium?)	No	36

^a72 to 75% SiO₂ < 460°C; 99.9% SiO₂ < 900°C.

^bAverage absorption and removal values.

^cP_H - corrected to 0.1 MPa (1 atm).

A reduction of Fe^{3+} , Ce^{4+} , and Sn^{4+} to Fe^{2+} , Ce^{3+} , and Sn^{2+} has been carried out in soda lime glass by hydrogen reduction.³⁵

Table 10 summarizes the literature data concerning water diffusion and solubility at temperatures below the transformation range. The data conflict and perhaps, do not even describe the same thing. Some of it was taken without a knowledge of the transformation range phenomenon.

III. Batch Separation and Characterization of Glass Microballoons

AS-RECEIVED SIZE DISTRIBUTIONS

Commercial glass microballoons arrive with diameters ranging from 10 to 250 μm (Fig. 4). Before sieving a given cut, it is desirable to have some idea of the percent of microballoons that fall in this size range. This measurement is obtained from a Model 720 Quantimet (Image Analysing Computers, Ltd.; Cambridge, England). The Quantimet has a TV camera that peers through a microscope at a batch of microballoons laid on a slide. The TV picture is cast onto a screen to aid the operator. The Quantimet breaks the picture into 650 000 picture points, with 720 horizontal lines. The picture points are analyzed for grayness, one by one, and the data fed through digital circuitry at a rate of 10.8 frames per second. Up to 31 channels of data may be taken across a given size range with two significant digits being available in the logic.

Figure 5 shows as-received distributions for various batches. The microballoons were spread in oil in order to darken their interiors and make a better contrast for the electronics. Hence, the interior walls are actually the measured edges. The Quantimet was run in the area measurement mode (rather than chord length) for better accuracy. Channel increments were set to increase logarithmically in anticipation of log-normal statistics. However, it seemed more useful to plot the final data with a linear diameter scale, even though the as-

received batches do appear to be log-normal in their distribution.

The Quantimet was calibrated by a 74.9- μm o.d. glass reference microballoon, scanned both in air and oil. The number of picture points in the projected area of the reference microballoon then set the standard for all other picture point-area conversions. The reference microballoon was mechanically measured, as described by R. R. Stone elsewhere in this report.

WASHING AND SIEVING

The first microballoons were taken as received and dry-sieved to standard 15- μm cuts. Static charges resulted in many small microballoons remaining in the center cut.

Next, the microballoons were washed in water and then reagent grade ethanol,

Fig. 4. As-received glass microballoons (3M).

Fig. 5. Quantimet diameter distributions of as-received 3M glass microballoons.

dried in a vacuum at 110°C, washed again in pentane, then hexane, and then dried again. The purpose of the pentane is to sink all microballoons with a density less than $0.63 \times 10^3 \text{ kg/m}^3$. This removes the small 10- to 20-μm microballoons, which tenaciously resist separation by sieving. The final wash with highly pure hexane is intended to achieve a free-flowing product, but flow characteristics are unpredictable. Some 3M grades impart a greenish color to the washing solution. This is caused by the organo-chromium layer (Volland from DuPont), which is applied to improve flow properties.⁴²

The sieving is done with 20-cm Buckbee-Mears screens, rated to $\pm 2 \text{ μm}$. The standard cut is 70 to 75 μm, cor-

responding to the dimensions listed in Table 1, Chapter I. However, 40- to 45-μm and 20- to 25-μm cuts have since been initiated. The two screens, with top and bottom pans, are loaded with about $50 \times 10^{-6} \text{ m}^3$ of washed microballoons in the bottom pan. The screen unit is then plunged into a sonic bath of ethanol, which forces the low density microballoons upward. Hence, the sieving proceeds large to small from bottom to top. The sonic vibration helps to clear the blockage at the screens as well as break up aggregations of electrostatically-charged microballoons. An aspirator is used to suck off the top (small cut periodically. Figure 6 shows sieved microballoons.

Fig. 6. Glass microballoons after a wet sieving to a nominal 70 to 75 μm cut (3M).

Considerable artistry is required to satisfactorily sieve glass microballoons, and a suitable separation becomes ever more difficult as the diameter drops. Figure 7 shows the Quantimet distributions for sieved 70- to 75- μm cuts. The half-widths are just slightly larger than the 5- μm nominal screen differences

SECTIONING GLASS MICROBALLOONS

Following sieving, our first dimensional measurements on glass microballoons

Fig. 7. Quantimet diameter distributions of 70 to 75- μm sieved glass microballoons.

were made by the destructive method of sectioning and optically measuring. The more recent nondestructive optical techniques are discussed by R. R. Stone in another chapter of this report.

To begin the sectioning process, a small sample of sieved microballoons is placed in viscous Shell type 815 epoxy and pressed into the surface with a glass slide. The epoxy is hardened and polished with 1- μ m diamond on nylon cloth. Since the epoxy is opaque, the sectioned microballoons are photographed by reflected light at 200 to 1000 X through a Zeiss Ultraphot. The microballoons selected for photographing are those that present large views so that the cross section is close to the equator of the microballoon. Perhaps two dozen representative photographs are taken. The pictures taken are next cast onto the TV screen of the Epidiascope of a 1967 Model Quantimet (Metals Research Ltd., Cambridge, England). Eight wall thicknesses per ball,

in symmetrical positions, are hand measured with calipers, after centering each measurement area in the center of the screen. Four diameters per ball are also measured with the naked eye and calipers. All dimensions are measured parallel to calibrated grids so that no error occurs in horizontal-vertical amplification differences on the TV screen (see Figs. 8 and 9).

Table 11 shows the summary of sectioning data on glass microballoons. The wide spread in radius/wall thickness ratios shows the statistical nature of the manufacturing process. Sphericity is indicated conservatively by the percent deviation of the worst single wall thickness from the average for a given microballoon. Most microballoons are worse than $\pm 20\%$ out-of-roundness; only a few meet the $\pm 10\%$ specifications.

The sectioning gives the first evidence of asymmetries in the glass microballoons, as shown especially by the wall thickness

Fig. 8. Typical sectioned glass microballoons.

Fig. 9. Sectioned glass microballoons with measuring lines.

Table 11. Summary of glass microballoon sectioning.

Material	3M				E & C			
	B75B, P-0745-1	B78A, P-0151-7	B35D P-0097-1		S ^a 10363019		SJ 10208014	
Stave cut, μm	70-7	70-75	45-60	70-75	60-75	75-104	88-105	124-149
No. of samples	15	24	56	23	22	30	12	10
Mean o.d., μm	65	69	53	72	67	86	102	136
Mean wall thickness, μm	0.6	0.8	1.4	1.7	1.0	2.4	2.5	3.1
Mean radius: wall ratio	57	47	19	23	20	18	22	25
Radius: wall: standard deviation of mean, %	25	18	18	20	31	14	21	36
Mean maximum wall deviation, % ^a	29	21	22	29	23	23	37	33
Samples with $\leq \pm 10\%$ maximum wall deviation, %	8	16	3	0	14	5	0	19

^a Deviation of the worst single wall thickness from the sample average for a given sample.

variations. Caliper measurements of the outer diameters made directly from the photographs show that at least 95% of the microballoons are round to 0.5%, the resolution of the measurement. For a 100- μm microballoon with a 2- μm wall, this uncertainty is 0.50 μm or 25%. We cannot tell, therefore, whether the observed wall asymmetry is on the inner or outer surface of the microballoons.

Besides the destructive aspect, sectioning has other limitations. It is quite difficult to see walls thinner than 1 μm , and resolution — limited by edge fuzziness — is probably $\pm 0.25 \mu\text{m}$ on any given measurement. It has also been suggested that microballoons will float with the thickest end down, thus presenting an unusually symmetric cross section upon grinding. Finally, the operator is called upon to select representative samples in a relatively small number.

Note that the percent of spherical microballoons (e.g., $\leq 10\%$) is found to be much higher in the sectioning technique

than in the optical techniques described in another section.

GASES FOR DENSITY SEPARATION

A sink/float method of batch separation involves using a fluid with a density comparable to that of glass microballoons. The least dense convenient liquid, under room conditions, is n-pentane ($0.63 \times 10^3 \text{ kg/m}^3$) which can only float microballoons with diameters of about 20 μm or less. A lighter fluid is required for larger microballoons, and LASL was the first to experiment with a density separator using SF_6 .⁴³

A sink/float unit has been built at LLNL. It is a 20-cm long stainless steel cylinder, with a 2-1/2-cm diameter. It is divided a quarter of the way from the top into two sections by a ball valve operable from the bottom. Microballoons that float to the top can be sealed into their upper compartment by closing the ball valve. Initial tests have shown electrostatic

sticking problems similar to those of sieving. Vibration problems have been handled by adding transducers.

The gases that LASL used in this apparatus had densities of 0.2 to 0.6 $\times 10^3$ kg/m³, corresponding to gas pressures of 3 to 10 MPa (500 to 2000 psi). Pressures that high can break the microballoons and can require additional safety procedures as well. Thus, while we want to achieve the highest density per unit pressure possible at room temperature, we also want to keep the pressure low. The gas equation

$$\frac{\rho}{P_1} = \frac{M}{ZRT} \quad (1)$$

shows two ways to do this: select a fluid with the highest possible molecular weight (M) and the lowest possible compressibility (Z). The latter effect occurs at the critical point, where the compressibility falls below 0.3.⁴⁴ The suggestions of SF₆⁴³ and C₂F₆⁴⁵ use compounds of sufficiently high molecular weight so that critical temperature is close to room temperature. Table 12 shows a number of suitable compounds with their critical values.

The sink/float method will be far from simple. For xenon at the critical point,

gravitational layering causes density gradients of up to $\pm 15\%$ (of the critical density), but this effect may be removed by moving 2° or more above the critical temperature.^{46,47} Even off the critical point itself, compressibilities can vary from 0.5 to 0.8 with slight changes of temperature and pressure. Using a Hougen-Watson chart,⁴⁴ we have estimated compressibilities and pressures for the fluids of Table 12 at various densities applicable to glass microballoons. The results are shown in Table 13, where compressibilities range as low as 0.5.

It will be difficult to calibrate the density if slightly supercritical fluids are used, since pressure-volume data are generally scanty in this region.

PRELIMINARY CRUSHING EXPERIMENTS

Two sieved 70- to 75- μ m cuts of 3M (B18A, P-9151-7) were pressurized under helium and argon to various pressures between 1.7 (250) and 34.5 MPa (5000 psi). The broken and unbroken microballoons were separated by liquid flotation. The results indicated that about 50% (by weight) broke at 6.9 (100) to 8.6 MPa (1250 psi). Sectioning of 24 samples of this cut

Table 12. High density fluids suitable for glass microballoon sink/float.

Gas	Molecular weight, kg/mole	Critical temperature, °C	Critical pressure, MPa (psi)	Critical density, kg/m ³	Reference
Kr	83.8×10^{-3}	-63.8	5.50 (798)	0.95×10^3	49
CF ₄	88.0×10^{-3}	-45.7	3.74 (543)	0.62×10^3	49, 50
CClF ₃	104.5×10^{-3}	28.8	3.87 (561)	0.58×10^3	49, 50
Xe	131.3×10^{-3}	16.6	5.88 (853)	1.09×10^3	49
C ₂ F ₆	138.0×10^{-3}	24.3	3.31 (480)	0.66×10^3	51
SF ₆	146.0×10^{-3}	45.6	3.76 (545)	0.74×10^3	52

Fig. 13. Estimated sink/float pressures and compressibilities for various fluid densities.

Density, 10^{-3} kg/m^3	Approximate pressure, MPa (psi)			Approximate compressibility		
	0.1	0.2	0.4	0.1	0.2	0.4
C_2F_6 at 30°C	1.4 (210)	2.5 (360)	3.5 (510)	0.8	0.7	0.5
SF_6 at 60°C	1.7 (240)	2.8 (400)	3.9 (570)	0.9	0.7	0.5
Xe at 25°C	1.7 (250)	3.1 (450)	4.8 (700)	0.92	0.8	0.6
CF_4 at 25°C	2.6 (370)	4.5 (650)	7.6 (1100)	0.9	0.8	0.7
Kr at 25°C	2.8 (410)	5.3 (770)	9.6 (1400)	0.86	0.9	0.8

showed a mean outer diameter of $69 \mu\text{m}$ and a mean wall thickness of $0.8 \mu\text{m}$ (mean of $(a/l) = 47$). The hoop stress at half breakage is, therefore,⁴⁸

$$\sigma_{1/2} = \frac{P}{2} \left(\frac{a}{l} \right). \quad (2)$$

We obtain a hoop stress for half breakage, $\sigma_{1/2}$ of 180 MPa (26,000 psi). This allows us to roughly estimate the half-breaking pressure for other sizes of glass microballoons. For a $1\text{-}\mu\text{m}$ thick wall, we obtain:

Outside diameter (μm)	Estimated half breaking pressure, MPa (psi)	
20	3.6	(5200)
40	1.8	(2600)
70	1.0	(1500)
100	0.7	(1000)
200	0.35	(500)

It cannot be estimated at this time whether the crushing results represent integral spherical shells, as implied above, or the effects of flawed shells.

IV. Permeation of He, H₂, and D₂ into and out of Glass Microballoons

PRESSURIZING EQUIPMENT

We have built an apparatus to permeate gases through microballoon walls at elevated temperatures. The system is capable of pressurizing He, H₂, or D₂ to 20 MPa (3000 psi).

The pressure vessel is a pencil-sized container made of 316 stainless steel, with an o. d. of 6.35 mm, an i. d. of 2.3 mm, and a 7-12-cm hot zone. It is heated in a metal block by a 100-W Hotwatt heater, which is controlled to $\pm 2^\circ\text{C}$ by an off-on controller and an iron-constant thermocouple. The vessel is monitored for pressure with a 0 to 140-MPa (0 to 200-kpsi) Taber-Teledyne transducer. The gas coming out of the microballoons is measured for pressure using a 0.13-MPa (1000-mm) Baratron head. This gas is also collected into a calibrated glass burette for $\pm 1\%$ PVT measurements.

To pressurize the gas, we pour 50 000 to 500 000 microballoons, of a given sieve cut, directly into the pressure vessel. (A glass capillary had been used as a container until we realized that it absorbed hydrogen and perturbed the measurements.)

A small mass of quartz wool is placed over the microballoons so that application of a vacuum will not cause them to be sucked out. The system is sealed and the microballoons are outgassed at several hundred degrees C in a vacuum for several hours to overnight. The pressure vessel is heated to the desired temperature and either helium or hydrogen gas is

admitted. When some of the gas has permeated the microballoons, the heater is turned off. This traps the gas inside the microballoons, since permeability drops exponentially with the temperature of the external atmosphere. Next, this atmosphere is pumped out to 1.3×10^{-4} Pa (10^{-6} Torr). The loaded microballoons may now be brought to an elevated temperature slowly so as to permit observation of outgassing, or quickly so that the internal gas permeates out for a volume measurement. The final collected gas, especially from a long outgassing experiment, is usually checked on a mass spectrometer for air leaks. The H/D ratio may also be obtained in this manner.

Stainless steel is not the best material for pressure vessels because hydrogen can permeate it. According to the literature, hydrogen permeates 304 SS (similar to 316 SS) as follows:

$$K = (9.1 \times 10^{-10}) \exp \left(-\frac{6040}{T} \right)^{(53,54)} \\ \times \frac{\text{m}^3[\text{STP}] \cdot \text{m}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}^{1/2}} \quad \text{measured} \quad (1) \\ 125^\circ\text{--}375^\circ\text{C}$$

Helium, however, does not permeate stainless steel as readily as hydrogen. For example, at 850°C , helium permeates 304 SS at a rate 6×10^{-8} slower than hydrogen.⁵³ Blank pressurizations and outgasings show that more hydrogen than helium has permeated SS for similar conditions, confirming the difference in

⁵³The permeation intercept is $2.9 \times 10^{-3} \text{ cm}^3[\text{STP}] \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{atm}^{1/2}$.

permeability. Furthermore, we have noted that the vessel pressure drops with time for hydrogen but not for helium, indicating greater hydrogen permeation. This difference between hydrogen and helium distorts our initial data. To remove the hydrogen permeability problem, we are now building impermeable beryllium tubes.

HELIUM GAS FILL AND AVERAGE WALL THICKNESS

An average wall thickness for a sieved batch of microballoons may be determined by helium permeation. Helium is convenient because it permeates through glass much faster than hydrogen, and because it does not permeate into the stainless steel pressure vessels.

To determine average wall thickness, we permeate helium into glass microballoons for 1 to 6 h at 250° to 300°C. No large drop in chamber pressure is noted, indicating that the helium has not been absorbed by the stainless steel pressure vessel. The sample chamber is allowed to cool, trapping the helium inside the glass. The pressurizing atmosphere is pumped off and the sample reheated. The helium permeates out and the total amount is measured. The volume of the pressure vessel is always much larger than the void volume of the microballoons so that all gas is presumed to have permeated out.

Next, we assume our sieve cut is composed of identical microballoons of an average radius and wall thickness. The mass of gas in the microballoon void volume, which is measured experimentally, may be related to the mass of glass in the microballoons. Also required is the

density of the trapped gas, derived from the loading pressure and temperature, assuming 100% fill equilibrium. The experimental mass ratio for gas to glass is

$$\frac{m}{m_g} = \frac{\rho}{\rho_g} \left[\left(\frac{1}{\frac{\bar{a}}{a} - \bar{f}} \right)^3 - 1 \right] \quad (2)$$

This may be solved for the average wall thickness

$$\bar{f} = \bar{a} \left\{ 1 - \left[\frac{1}{1 + \left(\frac{m_g \cdot \rho}{m \cdot \rho_g} \right)} \right]^{1/3} \right\} \quad (3)$$

This method is used with helium for 1- to 24-h loads at 200° to 400°C and 5.9 MPa (1000 psi). Several runs with different parameters are made to ensure complete fill. For 3M (B35D, P-0097-1, 70 to 75 μm), helium fill yields an average wall thickness of 1.5 to 1.6 μm . This may be compared with the 1.7- μm value obtained from 23 metallurgically sectioned samples (Table 11).

SIMPLE THEORY FOR GLASS MICROBALLOON PERMEATION

It is generally accepted that hydrogen and helium will permeate through glass or fused silica in a manner directly proportional to the driving pressure,⁵⁵ providing that no chemical reaction takes place. This last possibility may indeed be present in our hydrogen experiments, especially for soft glass above 400°C, but the low-temperature no-reaction behavior may be given by Fick's First Law as,

$$\frac{dV}{dt} = \frac{KA}{f} (P_2 - P_1) \quad (4)$$

If the microballoons are loaded to a pressure, P_1 , and an outgassing run is

made, we may take P_2 to be zero since the pressure vessel volume is much larger than the microballoon void volume. K is the product of the diffusivity and the solubility, and usually is assumed to have the temperature dependence⁶

$$K = K_0 \exp (-Q/T). \quad (5)$$

We now use the perfect gas equation to convert the left side of Eq. (4) to pressure.

$$\frac{dP_1}{dt} = \frac{RT}{V_0} \cdot \frac{KA}{\ell} (P_2 - P_1) \\ \frac{1}{\tau} (P_2 - P_1), \quad (6)$$

where

$$\tau = \frac{V_0}{3RT} \frac{a\ell}{K}. \quad (7)$$

We have made the exchange of $(3/A)$ for (A/V) , which is true for spherical balloons with thin walls.

For the outgassing of loaded microballoons into a vacuum ($P_2 = 0$), the internal pressure should decay as

$$P_1 = P_{\max} \exp (-t/\tau). \quad (8)$$

In the experiment, we look at the buildup of pressure outside the microballoons. This reverse view is just

$$P_m = P_{\infty} [1 - \exp (-t/\tau)], \quad (9)$$

Recently, J. E. Shelby of Sandia, Livermore, CA, has redefined this function for He in fused silica as being, $K = K_0 T \exp (-Q/T)$. It is not yet known if this will be widely applicable to all glasses. J. E. Shelby, *J. Amer. Ceram. Soc.*, **55**, 61 (1972). We shall continue to use the more widespread form of Eq. (5) since the uncertainties involved are probably small compared to those of our problem.

where calibration of the equipment will be needed to relate the pressures of Eqs. (8) and (9).

GAS COMPRESSIBILITY EFFECTS

To determine what effect compressibility has on permeation, we must first learn to what extent the gases used deviate from the perfect gas behavior assumed in the preceding section. The imperfect gas pressure, P^* , may be related through the compressibility, Z :

$$P^* = Z \cdot \rho \frac{RT}{M}. \quad (10)$$

For gas densities up to only 0.1×10^3 kg/m³, we may expand Z using only the first virial coefficients. We write Z in the form

$$Z = 1 + (B_0 + B T) \rho. \quad (11)$$

The constants for the gases of interest are listed in Table 14 (values in parentheses are estimates).

This first virial coefficient is to be used only to densities of about 0.01×10^3 kg/m³, whereupon higher order coefficients are needed. At this density, the values in Table 14 yield compressibilities within 1½% error for temperatures from 0°C to the measured maxima: 600°C for He⁴ and 150°C for H₂ and D₂. The compressibility decreases with temperature for helium, and amounts to about a 3% correction to the perfect gas equation at 0.01×10^3 kg/m³. The compressibilities for H₂ and D₂ increase with temperature, and amount to about 5% at 400°C and 0.01×10^3 kg/m³. In any case, compressibility may generally be neglected in our low density studies of gas permeation in glass microballoons.

RESULTS OF THE OUTGASSING EXPERIMENTS

The purpose of the outgassing work is to find if microballoons do, in fact, obey the expected permeation equations of bulk glass, or whether special "surface" considerations dominate their behavior. If microballoons can be shown to act like bulk glass, then credence may be placed in the probable filling of a typical microballoon, even though no individual measurement was made on that microballoon.

Obtaining good hydrogen decay curves has so far been complicated by the stainless steel permeation problem. From 300°C and up, a semi-log plot of $(1 - P_m/P_0)$ vs time shows a bend instead of the straight line predicted by Eq. (9). This curve may be broken into two exponentials, as is commonly done with mother and daughter radioisotope decay. The faster decaying component is assigned to hydrogen permeation from the microballoons; the slow component is from the stainless steel. Subtracting the two, we obtain the fast decay. Figure 10 shows a fast decay, which is quite exponential. The zero-time height agrees with the amount of gas expected from helium gas

loading. The 1/e-time of 45 m at 325°C agrees with the 72-m value calculated from the chemical composition and average dimensions. The hydrogen outgassing at room temperature cannot be broken down as to its origin, but it shows the gas to be effectively trapped.

Table 15 shows the measured 1/e time, along with the calculated values. The agreement is good, indicating that hydrogen and helium seem to permeate through glass microballoon walls as expected from bulk properties.

Fig. 10. Deuterium outgassing from glass microballoons.

Table 14. Constants used in converting gas density to compressibility for helium and hydrogen.

Gas	Molecular weight, (10^3 kg/mole)	β_0 , (10^{-3} m ³ /kg) ^a	β , (10^{-6} m ³ /kg·K)	Reference
He ³	3.016	(4.22)	(-1.1)	56, 57
He ⁴	4.003	3.163	0.812	56, 57
H ₂	2.016	4.695	7.73	58, 59
D ₂	4.029	2.293	3.70	58, 59
DT	5.032	(1.82)	(2.9)	59

^a β_0 may be converted to cm³/g and β to cm³/g·°K by multiplying by 10^3 . Using a gas constant, R , of 1205.9 cm³[STP]·psi/K·mol, the final pressure will be in psi.

Table 15. Summary of outgassing runs of glass microballoons. (The faster exponential data is presented.)

Sample	Isotope	Outgassing temp, °C	Faster experimental 1/e time	Calculated decay time
3M, H351D, P-0097-1, 70-75 μ m	He	200	17.0 m	17.0 m
		201	14.0 m	17.0 m
		301	3.3 m	2.2 m
	D ₂	400	28.0 m	25.0 m
		402	34.0 m	24.0 m
		460	30.0 m	8.6 m
3M 50-55 μ m	H ₂	25	140 d	years
		325	1 h	1.2 h
	D ₂	325	1 h	1.2 h
3M 45-60 μ m	D ₂	300	1 h	2.1 h
E. & C, IG-101, No. 1297 60-75 μ m	H ₂	325	45 m	72 m
	D ₂	25	>1 year	years

V. The Permeation of DT into Glass Microballoons

THE DT PRESSURIZER

A special apparatus has been designed and constructed to fill glass microballoons with DT gas. It is designed for extremes of 500°C and 70 MPa (10 000 psi). The pressurizer is shown in Figs. 11 and 12. A schematic of the system is shown in Fig. 13. Helium and deuterium are used to check the system for leaks before each DT run. The DT reservoir is a previously pumped high pressure bottle, whose pressure is monitored by a 140-MPa (20 000 psi) Taber-Teledyne pressure transducer at valve V1. The glass microballoons are poured into a 316 SS pressure vessel, which is surrounded by two 100-W heaters imbedded in a rod of 304 SS. A Leeds & Northrup Series 60 controller monitors the sample temperature. Valve V2 controls the DT pressure in the pressure chamber, and a second transducer monitors the pressure. Valve V2 is cooled by a welded water jacket.

Fig. 11. DT pressurizing system.

Fig. 12. Detailed view of the pressure vessel, transducer, heater, and secondary container.

The high pressure lines are made of 316 SS tubing (6.35 mm o.d., 2.08 mm i.d.) with a maximum working pressure after weld of 140 MPa (20 000 psi). All high pressure valves are Autoclave type with welded seals and a maximum working pressure of 140 MPa (20 000 psi). The input pressure transducer and the pressure vessel-heater-transducer system are both secondarily contained in the event of a leak. Argon gas is admitted to the pressure vessel secondary container to aid in the heat transfer to the sample.

The gas recovery system consists of a DT recovery tank (0.04 m^3), a D_2 flush recovery tank (0.035 m^3), and an abort tank (0.035 m^3) for the pressure transducer. An activated uranium trap with a capacity for 0.018 m^3 of D_2 is incorporated into the system to getter the DT gas remaining in the lines after a D_2 flush. A Wallace and Teirnan pressure

Fig. 13. DT pressurizer for glass microballoons (Valves V1 and V2 are mentioned in text).

gauge (0.2 MPa [0-30 psi]) measures the gas pressure in all the tanks.

Blank experiments on the pressure vessel show the amount of tritium in the secondary container to be about one-tenth that expected from the permeation formula (1) in Chapter IV. This effect could be caused by surface oxides on the stain-

less steel pressure vessel, the probable nonequilibrium for the first 24 hr of pressurization, and the plausible expectation that tritium permeates more slowly than hydrogen. In any case, the effect reduces activity in the pressure vessel secondary container.

Table 16. Conditions for DT pressurization of glass microballoons.

Run	Pressurization date	Grade & lot	Sieve size, μ m	Mass-pressurized, kg	Average temperature-time history	Average pressure-time history, MPa (psia)
1	10-22-73	B33-D P-0097-1	70-75	4.17×10^{-6}	360 C for 7.2 h	2.61 (378) for 7.2 h
2	1-10-74	B22-A P-9339-9	70-75	4.22×10^{-5}	422 C for 8.0 h	4.23 (613) for 1.8 h; 7.00 (1016) for 5.2 h
3	1-22-74	B22-A P-9339-9	70-75	2.91×10^{-5}	422 C for 70.6 h	4.11 (593) for 2.6 h; 6.99 (1014) for 67.0 h
4	2-7-74	B22-A P-9339-9	34-45, 70-75	1.13×10^{-5} 1.37×10^{-5}	422 C for 8.0 h	5.09 (738) for 2.0 h; 10.29 (1492) for 6.0 h
5	2-14-74	B22-A P-9339-9	20-30, 34-45	1.25×10^{-5} 1.37×10^{-5}	420 C for 8.0 h	5.16 (748) for 1.8 h; 10.72 (1554) for 6.2 h

DT PRESSURIZATIONS OF GLASS MICROBALLOONS

Five DT runs have been carried out to date. Table 16 lists the operational details of each run. All runs were one working day (8 h) except for a single 71-h run (Run No. 3). One temperature was 360°C; all others were 420°C. All glass microballoons were 3M brand.

Table 17 shows the analyses taken by a high resolution mass spectrometer. The actual data on the DT feed gas were corrected to the amount of He^3 expected on the day of pressurization. The first four runs were carried out with an "old" feed bottle containing 8 to 9 mole% He^3 ; a fresh bottle was substituted for run No. 5. The D/T ratios are all close to one.

Table 18 shows the mass spectrometer results taken on small batches of DT-loaded microballoons mechanically crushed some days later. Because of the small sample sizes, only the D and T measurements are acceptable, and they show the D/T ratio to have increased. This probably indicates a slightly faster deuterium permeation during pressurization, and incomplete equilibration, even in the 71-h

Table 17. Mass spectroscopy of gas used in DT pressurization of glass microballoons.

Run, mole%	Gas, mole%				D/T ratio
	H	D	T	He_3	
1	0.2	45.2	46.9	7.7	0.965
2	0.2	45.0	46.0	8.8	0.977
3	0.2	44.9	45.9	9.0	0.979
4	0.2	44.9	45.7	9.2	0.981
5	0.6	49.2	50.1	0.1	0.981

run. (Room temperature permeation after pressurization cannot be greatly involved, or the mix would be tritium rich.) The 71-h run shows the lowest D/T ratio of the first four runs, as expected. However, run No. 5, with low He^3 content in the feed gas, has the lowest D/T ratio of all the runs. The reason for the low ratio is that the helium atoms are physically filling part of the permeation space inside the glass and thereby slowing the hydrogen permeation. Since He^3 permeates through glass at a rapid rate, even at room temperature, one would expect to see the mole fraction of He^3 diminish with the number of days since pressurization. Run No. 3 (71 h) appears especially out of place in this

Table 18. Mass spectrometer results taken after crushing DT-filled microballoons.

Run	Mass crushed, kg	Days since pressure	Gas, mole%				D/T ratio
			H	D	T	He ₃	
1	$<7 \times 10^{-8}$	51	1.7	51.7	46.6	0	1.18
2	2.2×10^{-7}	4	0	50.8	46.9	2.3	1.08
3	4.5×10^{-7}	6	1.0	47.6	45.7	5.7	1.04
4	6.4×10^{-7} (70 to 75 μm)	28	0.6	50.8	47.5	1.1	1.07
5	6.7×10^{-7} (34 to 45 μm)	7	0.7	49.7	49.0	0.6	1.01

regard, although the He³ data is not accurate. The glass microballoons also appeared somewhat crazed by the long No. 3 run, suggesting a chemical reaction of the DT with the glass. Such a reaction seems reasonable based on the considerations discussed in Chapter II.

The mass spectrometer was not calibrated to yield quantitative microballoon gas fill data, and the work to be described attacks this problem.

DESTRUCTIVE TRITIUM COUNTING OF GLASS MICROBALLOONS

An individual microballoon crusher has been used to determine whether our pressurization procedure loaded microballoons to the expected gas density.

Figure 14 shows the system schematic, with a blow-up of the crusher. A single DT-loaded microballoon is photographed under a microscope to obtain its diameter, and then it is placed underneath the crusher. Electrostatic attraction suffices to hold it in place. The system is assembled and evacuated to 1.33×10^{-4} Pa (10^{-6} Torr). The microballoon is manually crushed and valve V2 is opened, admitting the DT gas to the ionization chamber. Argon is admitted through

valve V3 until a pressure of 0.1 MPa (760 Torr) is reached. A potential of -600 V is applied to the ionization chamber and the current reading* is taken on a sensitive electrometer. The circulating pump is critical in moving the DT gas from the crusher to the ionization chamber. The circulating pump is a Bellows Model No. 110-10, the pressure sensor a Baratron model 145AHS-1127, and the electrometer a Victoreen 475 BR femto-meter. The total internal volume of the system is $(1165.4 \pm 0.3) \times 10^{-6} \text{ m}^3$, with the ionization chamber being 10^{-3} m^3 .

The ionization chamber is a special model developed at LLL by Colmenares for low-level tritium detection.⁶⁰ A special problem in conventional chambers is the absorption of tritium into elastomeric seals. This chamber is made of stainless steel with sapphire insulators isolating the collecting electrode. To prevent absorption of tritium into the stainless steel (very low at room temperature), a mirror finish of sputtered gold is applied to all interior walls. Since there are no plastic or elastomer

* Caused by the tritium decay ionizing the argon gas.

Fig. 14. Destructive tritium counting equipment for glass microballoons.

parts, the entire ionization chamber and entrance tubing is baked out at 300°C under vacuum before starting a series of runs. This type of ionization chamber allows measurement of tritium levels of

less than 4×10^7 disintegrations $\text{s} \cdot \text{m}^3$ [STP] ($< 1 \text{ mCi/m}^3$ [STP]).

Colmenares has estimated the efficiency of his improved ionization chamber design^{60,61} in terms of energy loss of

the beta particles to the fill gas, back-scattering of the betas from the chamber walls, and losses in charge collection resulting from ion pairs recombining. He concludes that his chamber geometry and electric potential will yield a theoretical efficiency of 97.8% compared to the generally expected 99%.

Table 19 shows the results of the individually crushed microballoon-ionization chamber runs. The outer diameter was measured for each sample. The wall thickness for the 70 to 75- μ m samples is a batch average obtained from helium fill, as described in Chapter IV. The 1/2- μ m wall thickness for the 30 to 45- μ m diameter microballoons is an estimate. These dimensions are combined with the

calculated gas densities (see next section) to calculate the expected tritium activity, assuming 100% fill.

The last column of Table 19 shows that the comparison of calculated and measured tritium values are especially good, considering that individual wall thicknesses are not included. The mean ratio of measured to calculated tritium ratios for the fifteen 70 to 75- μ m microballoons is 102%. We may conclude that 3M glass microballoons are almost completely gas-filled after 8 h at 420°C, and that several weeks' storage at room temperature does not affect the count.

The gas fill of the glass microballoons is too great to truly measure the DT permeation. However, assuming that an

Table 19. Ionization chamber results on individually crushed glass microballoons.

Run No.	Assumed average wall thickness, μ m	Sample	Measured outer diameter, μ m	Tritium, 10^{-4}		Measured/calculated ratio, %	Days since pressurization
				disintegrations/s C.A.C.	Meas.		
1	1.4	1	73.7	8.62	8.14	94	113
		2	71.6	7.89	7.59	96	
		3	72.6	8.20	7.99	97	
2	1.0	4	75.0	22.8	23.1	101	33
		5	70.5	18.9	20.0	106	
		6	76.2	23.9	24.8	104	
		7	74.1	22.3	23.2	117	
3	1.0	8	71.3	19.8	19.0	96	19
		9	73.2	21.4	22.6	106	
		10	74.8	22.9	24.3	106	
		11	71.8	20.2	20.9	103	
4	1.0	12	69.6	26.4	27.2	103	5
		13	72.2	29.5	28.0	95	
		14	70.6	27.5	29.2	106	
		15	73.4	32.4	33.3	103	
4	1/2	16	37.4	4.10	4.40	107	5
		17	42.4	6.05	6.44	106	
		18	45.2	7.36	7.99	109	
5	1/2	19	42.4	7.01	6.66	95	11
		20	38.0	5.09	5.29	104	
		21	37.6	4.92	5.29	108	
5	1/2	22	29.6	2.35	2.59	110	11
		23	31.7	2.91	2.92	100	
		24	29.7	2.39	2.41	101	

8-h pressurization is five time constants (99+% fill), we find, for the 70 to 75- μm microballoons, that the permeability at 420°C must be greater than $8 \times 10^{-21} \text{ m}^3 [\text{STP}] \cdot \text{m}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$. The permeability calculated from the chemical composition is indeed larger by an order of magnitude: $9.1 \times 10^{-20} \text{ m}^3 [\text{STP}] \cdot \text{m}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$.

DETAILS OF THE DT GAS DENSITY CALCULATION

To calculate the percentage of gas fill, we must convert from measured temperature and pressure calculations to tritium-decay density calculations. We have used an algorithm that assumes a single chemical component and corrections have been added to agree with experimental modifications.

First, the experimental pressures have been reduced to an average value. In fact, these pressures have varied as much as $\pm 5\%$ because of hydrogen permeation into the stainless steel pressure vessel, requiring periodic pressure resets. The mass spectrometry data of Table 16 is then used to subtract out the He^3 effects, thus obtaining a mole percent and average partial pressure of hydrogen. This is converted to density in kg/m^3 , using the compressibility-corrected DT Eq. (11) of Chapter IV.

This may be converted to the density of tritium atoms for a 50-50 mix, using Avogadro's number and the DT mole weight of $5.032 \times 10^{-3} \text{ kg}/\text{mole}$. From Table 16, we obtain the D/T ratios for the filled microballoons, and convert these to at. % tritium. These percents are used to adjust the tritium atom density from the basic 50-50 mix to the actual final conditions. Table 20 summarizes these calculations for the five DT pressurization runs. The He^3 is subtracted, the pressure- and compressibility-corrected density of pure DT is calculated, and the result is corrected for the true percentage of tritium inside the microballoons. The last column displays the tritium decay density where the decay constant for tritium⁶² is $1,780 \times 10^{-9} \text{ s}^{-1}$. We calculated the tritium disintegrations that appear in the ionization chamber results of Table 18 by the above method.

NONDESTRUCTIVE TRITIUM COUNTING OF GLASS MICROBALLOONS

The destructive method of tritium counting is sufficient to show that glass microballoons are gas-filled on a statistical basis. However, it is desirable to nondestructively count the tritium on the specific microballoons that will be used as laser targets. To this end, we

Table 20. Calculated DT data for gas fill of glass microballoons.

Pressurization run	DT feed gas, mole%	DT partial pressure, MPa (psi)	DT gas density Z-corrected, kg/m^3	Tritium after fill, at. %	Tritium density, $10^{26} \text{ atoms}/\text{m}^3$	Tritium-decay density ($10^{18} \text{ disintegrations}/\text{m}^3 \cdot \text{s}$)
1	92.1	2.40 (348)	2.28	47.4	2.59	0.46
2	91.0	6.38 (925)	5.44	49.0	6.25	1.11
3	90.8	6.35 (921)	5.42	49.0	6.36	1.13
4	90.6	9.32 (1352)	7.88	48.3	9.11	1.62
5	99.3	10.64 (1543)	8.96	49.6	10.7	1.91

have employed a proportional counter technique, first used by Fries and Farnum⁶³ on DT-loaded microballoons.

Our DT-loaded microballoons were counted by C. Prevo, R. Griffith, and L. Anderson of Hazards Control. They used a Nuclear-Chicago system, capable of automatically counting a stack of one hundred 5-cm planchets. The detector is a gas flow proportional counter comparable to the present model 1152B. The counting gas is P-10: 90% argon and 10% methane, operated at 1750 V. The gas detector window has a 5-cm diameter and it is covered with a metalized Mylar window with a mass density of less than 15×10^{-12} kg m² (150 μ g/cm²). The system is highly shielded and possesses a plastic scintillator guard detector coupled to a phototube. The guard detector output is matched in anti-coincidence with the proportional counter output to reduce counting of cosmic rays or other extraneous radiation. The background is about 1.0 counts/min.

Double-sided masking tape was attached to the planchets, and one microballoon (sometimes more, by accident) transferred to the top surface of the tape. Each sample was counted for 20 min and

Because an ionization chamber operates at low voltages, no multiplication of the ionization current occurs. At higher voltages, the proportional region is entered: current multiplication occurs due to electron avalanching, but the pulse height at fixed voltage is proportional to the amount of ionization caused. At still higher voltages, the Geiger region is entered: high current multiplication occurs but all pulses saturate at the same height, whatever the ionization of the charged particle. See, for example, G. Friedlander and J. W. Kennedy, Nuclear and Radiochemistry (John Wiley, New York, 1957), pp. 224-236.

stored at room temperature between counts. Since the count rate was several hundred counts/min, the low background feature of the equipment was non-essential.

Table 21 shows the results of the proportional counting on DT-loaded glass microballoons. The background counts have been subtracted from the counts/min columns. Note that 14 of the 16 samples show little decline in count rate for periods of 50 to 100 days. Since the error in counting is greater than the rate decline, the only way to estimate a room temperature permeation decay time from this data is to base it on the chemical composition. The two exceptions are sample Nos. 3 and 4, where it appears that perhaps one of the three microballoons is leaking in each sample. The counts have not yet dropped to the point where it appears that more than one microballoon is involved. We may optimistically state that only two of thirty-two microballoons used in the nondestructive counting appear to be faulty (94% good).

The proportional counter method cannot be internally calibrated, and the crusher/ionization chamber must be used for absolute calibration. Individual microballoons have not yet been doubly counted, but we may compare the count rates of Table 21 with the expected DT gas densities from Table 20. Table 22 is a comparison of the results for the 70 to 75- μ m microballoons, for which the dimensions are fairly well known.

DISCUSSION OF THE NONDESTRUCTIVE TRITIUM COUNT

H. Shay of LLL predicted that most of the tritium beta particles would be stopped

Table 21. Nondestructive tritium counts on DT-loaded glass microballoons (background counts subtracted).

DT pressurization run	Sample	Number of microballoons	Days since pressurization			
1			46 days	56 days	77 days	142 days
			Counts/min ^b			
	1	1	158	159	151	152
	2	2	275	287	267	285
	3	3	415	414	390	334
	4	3	500	466	451	403
2			6 days	22 days	25 days	62 days
	5	2	815	783		821
	6	1	433	418		423
	7	1	344	339		324
	8	1 ^a	740	708		748
	9	2	802	799		828
	10	2	638	612		640
	11	3	965	935		967
	12	4	1 501	1 446		1 456
	13	1		370	357	383
3			8 days	11 days	48 days	
	14	1	382	381	381	
	15	1	423	420	422	
	16	2	875	879	873	

^aLarge: o. d. > 100 μ m.

^bStandard deviation: at 200 counts/min: $\pm 4.0\%$; 300: $\pm 2.7\%$; 500: $\pm 2.3\%$; 800: $\pm 1.5\%$. 1500: $\pm 1.2\%$.

Table 22. Comparison of the results for 70 to 75 μ m microballoons.

DT pressurization run	Mean measured microballoons (counts, s)	Measured microballoons (10^{-5} counts/calculated disintegrations)
1	2.15	3.0
2	6.12	3.0
3	6.72	3.3

in the glass microballoon walls, and that much of the counted radiation would be silicon soft x rays, even though the electron to x ray conversion is very low.⁶⁴ The x rays have a low absorption and pass easily through the thin glass walls. Shay used the SANDYL code on a hypothetical pure silica microballoon (40 μ m i. d., 2- μ m-thick walls, 2.5 kg/m³ of DT gas inside). He obtained predicted

ratios of x ray to beta particle production of 8×10^{-4} for the average beta particle and 2.5×10^{-3} for the end-point (18 keV) beta particle. This may be compared with the previously cited experimental values: 3×10^{-5} for 70- μ m i. d., 2.5 to 3.5 kg/m³ DT, and 1 to 1.4- μ m-thick walls.

Consequently, Camp of LLL Radiochemistry counted a DT-loaded microballoon with a solid-state lithium-drifted silicon crystal operating at liquid nitrogen temperature.⁶⁵ Three microballoons were individually mounted on polyethylene backings with a thin ($\approx 0.1 \mu$ m) film of VYNS (polyvinylchloride-acetate copolymer in cyclohexanone)^{66,67} deposited on top, between the sample and the detector.

Only one sample survived, and its peak (2.7×10^{-16} J (1.7 keV) silicon K_{α}) is shown in Fig. 15. The integrated peak amounts to 248 counts/m with the background subtracted. A second peak of about 22 counts was seen at about twice the energy. It is not presently known whether this smaller peak is the calcium peak (5.9×10^{-6} J [3.7 keV]) or a double count sodium satellite (5.4×10^{-16} J

[3.4 keV]). This sample was counted as No. 13 in the proportional counter, yielding a mean of 370 counts/min for three runs. Finally, proportional counter samples 5 and 6 were counted with a second 6- μ m-thick aluminized Mylar window between the samples and the proportional chamber. In both cases the counts were reduced by almost exactly one-third. This is about the difference between the

Fig. 15. X-ray fluorescence from DT-filled glass microballoons.

Fig. 16. Beta particle escape from DT-loaded silica microballoons (calculation: SANDYL code by H. Shay).⁹

Si(Li) and the proportional counter results for the microballoon counted both ways.

To summarize, two-thirds or more of the proportional counter results are due to soft x rays, as H. Shay predicted. Up to one-third may be due to the few highest-energy beta particles that pass through the glass walls and the detector. These betas were presumably stopped by the positioning of the second window. The importance of the betas in the count total is that, unlike the soft x rays, their numbers are an extreme function of the wall thickness.

Shay has simulated the beta particle effect,⁶⁸ using the SANDYL code for a

hypothetical microballoon of pure silica (40 μm i.d., 7.5 kg/m^3 of DT gas inside, 0.8 and 1.2- μm -thick walls). He approximated the beta-particle energy spectrum with a nine-step function, extending to 2.9×10^{-15} J (18 keV). The output spectra for the two wall thicknesses are shown with the input spectrum in Fig. 16. Note that integrated counts for the 1.2- μm wall are about one-third those of the 0.8- μm wall. It may well be, given extensive calibration, that the average wall thickness of a given microballoon may someday be measured using this beta-particle effect.

VI. Nondestructive Geometric Certification of Microballoons

INTRODUCTION

Since symmetrical microballoons are necessary to obtain maximum compression we have placed close absolute tolerances on the geometry of microballoons. The absolute allowable error on the outside diameter of microballoons must be no more than $\pm 2 \mu\text{m}$ with $\pm 1 \mu\text{m}$ preferable (see Table 1). The variation in wall thickness must be less than $\pm 0.2 \mu\text{m}$ with $\pm 0.1 \mu\text{m}$ preferable. In our search for microballoons that met our specifications, we selected balls with symmetric walls before measuring the outside diameter because the former was the more difficult task.

MEASUREMENT OF THE WALL THICKNESS

Two nondestructive methods have been developed at LLL to measure the thickness of microballoon walls. One method,

developed by R. Reedy of Technical Photography,⁶⁹ measures microballoon refraction. In this method, parallel light enters the glass microballoon and is refracted at each glass-air interface (Fig. 17). When the light exits the microballoon it subtends angles whose size depends on wall thickness, index of refraction, and outside diameter. The angle size also depends on where the light ray enters the microballoon. Each microscope objective (Fig. 17) has a fixed acceptance angle that limits the light received to exit angles less than the acceptance angle. Since the light rays exiting the ball at an angle greater than the acceptance angle are blocked, a dark ring is seen in the image plane. For example, ray X on Fig. 17 would normally follow the path indicated by the dashed line, but it is blocked by the microscope aperture. If the outside diameter, index of refraction, and distance H (objective to

Fig. 17. Refractive measurement of wall thickness.

Fig. 18. Width of refractive black ring vs microscope acceptance angle.

focal plane) are known, the thickness of the black ring indicates the wall thickness. Thus, we can theoretically calculate the width of the black ring vs the wall thickness. Figure 18 shows the results of one such calculation.

A more precise measurement of the black ring image can be obtained by using a scanning photometer. The photometer, by being moved along the diameter of a microballoon, indicates how symmetrical it is. For example, if a photometer plot were made of Fig. 19, it would look like Fig. 21. The microballoon in Fig. 19 has nonconcentric inner and outer walls and that is reflected in the asymmetrical plot shown in Fig. 21. The lack of symmetry indicates the difference in wall thickness across the diameter. On the other hand, if a photometer plot were made of Fig. 20, it would look like Fig. 22. The microballoon in Fig. 20 is symmetrical and so is the plot in Fig. 22. From these plots the thickness of the black ring can be determined and this is then converted to wall thickness by using the plot shown by Fig. 18.

Fig. 19. Photomicrograph of a black ring showing a microballoon with nonuniform walls.

Fig. 20. Photomicrograph of a black ring showing a microballoon with symmetrical walls.

Another method of nondestructively measuring the wall thickness of transparent microballoons was conceived by Gregg.⁷⁰ He used a commercial

Fig. 21. Light intensity vs location for a microballoon with nonuniform walls (see Fig. 19).

Fig. 22. Light intensity vs location for microballoon with symmetrical walls (see Fig. 20).

interference microscope to interfere with the light rays that exit the microballoons. A schematic of the basic optical system of the microscope is shown in Fig. 23. To obtain the necessary optical quality, matched objectives are used. Mirrors M_1 and M_2 are cut from the same reflecting surface, such as an aluminum-coated microscope glass slide. This allows an excellent match in reflectivity, which increases the sharpness of the interference pattern. The microballoons to be inspected by this optical system are placed on one of the mirrors

and an interference pattern is obtained (Fig. 24). Further adjustment is made until the mirror appears to be perfectly flat [this spreads out the pattern (Fig. 25)]. A microballoon that appears to have a concentric interference pattern is selected and the magnification of the microscope is increased. The ball can then be inspected at a high power for defects (Figs. 26 and 27). To increase the accuracy of the pattern measurement as well as speed up the process, a scanning photometer coupled to an intensity-vs-displacement recorder is used.

If a microballoon, with a known outside diameter, is placed on one of the mirrors and adjustments are made so that the light at the middle of the microballoon is at maximum brightness, the wall thickness can be determined by measuring from the center radially to the first minimum brightness (Fig. 28). The optical path lengths of rays 1 and 2 differ because of the increased amount of glass ray 2 travels through. When the difference is $\lambda/2$, there is a 180° phase change in ray 2 relative to ray 1. A correction to straight line travel for ray 2 must be made because of the refractive properties of the shell.

In practice, it is difficult to determine when the middle is at maximum brightness, so two measurements are required. Any two interference bands can be measured and since the optical path difference is known, the wall thickness can be determined. For example, if a measurement is made from the 1st minimum to the 2nd minimum, the optical path difference is λ or $0.535 \mu\text{m}$ (thallium light source). A particular set of measured

Fig. 23. Optical design of interference microscope.

Fig. 24. Interference pattern before adjustment.

Fig. 25. Interference pattern after adjustment.

Fig. 26. Interference pattern of a uniform microballoon.

values can only exist for one wall thickness and outside diameter. Values were calculated for various outside diameters and wall thicknesses, relating planar radius and optical path differences.

OUTSIDE DIAMETER MEASUREMENTS

We can use both a Talystep mechanical probe (accurate to $\pm 0.3 \mu\text{m}$) and an image-splitting eyepiece to measure the outside diameter of a microballoon. In the first method, a probe is placed on a glass slide, which is used for a reference, and the system is zeroed. A microballoon is then placed between the probe and the glass and another measurement is taken. The difference between the two values is the outside diameter of the microballoon.

The microballoon diameter may also be measured by an image splitting method. In this method, an eyepiece is used to split the image into two tangent images (Fig. 29). The amount that the image is shifted to produce the tangent microballoons is the diameter. The repeatability

Fig. 27. Interference pattern of a uniform microballoon with constructive interference in the center.

Fig. 28. Interference method of measuring microballoon wall thickness.

of this method is shown by Table 23. One problem with this method is that the microballoon waist image must be distinct. But, since we are measuring dimensions of about 100 μm , we need to magnify the image about 200 times. At this power, the microballoon edge is not clearly defined because of the diffractive effects of light. However, by focussing the microscope above and below the waist while observing the inner ring pattern, we can determine when the waist is in focus (Figs. 30-32).

CALIBRATION OF REFRACTION AND INTERFERENCE

To determine the accuracy of refraction and interference methods, we compared the image splitting outside diameter measurements against those taken on Talystep.

Next we measured wall thickness with Talystep and a scanning electron microscope by breaking and measuring microballoon walls. These probe measurements were taken on a scale that reads out to

$\pm 0.3 \mu\text{m}$, but an error can be introduced by having any dirt or broken glass under the broken shell. This error would always give an apparent increase in thickness. After measuring with the Talystep, the same broken pieces were taken to a SEM and photographs at high magnifications were taken. The results of the SEM and Talystep measurements are listed in Table 23. The blank spaces in this table result from the loss of the microballoons during the calibration process. The prime wall thickness measurement was to be the SEM, but all the microballoons except two were lost before measurements were taken. The spread of wall thickness measurements for any one method indicates that a microballoon with nonconcentric walls may have been initially selected for calibration.

Table 23 shows that it is possible to meet the outside diameter specifications using the image splitting eyepiece. Further work is indicated for the refractive and interference techniques. The range of reading for the walls results

Table 23. Calibration of optical inspection techniques.

Microballoon	Diameter, μm		Wall thickness, μm			Scanning electron microscope
	Talystep	Image Splitter	Refractive method	Interference method	Talystep	
1C	74.25	74.71	0.75	0.5 - 0.6	0.69 0.64	-
2C	70.25	70.18	0.50	1.0 - 1.2	1.27, 1.19 1.27	0.62
3C	70.25	70.18	-	-	-	-
4C	-	73.77	-	-	0.72	-
5C	74.50	75.09	0.5 - 0.8	0.7 - 0.8 <0.4	1.05 1.12	0.81 - 0.85 0.92 - 1.13
6C	73.75	74.71	0.6	1.2 - 0.6	-	-
7C	72.75	74.34	1.4	0.9 - 1.0	1.12, 1.10 1.26, 1.32	-

Fig. 29. Appearance of a microballoon when shearing eyepiece is used.

Fig. 31. Appearance of a microballoon when focus is below the waist.

Fig. 30. Appearance of a microballoon when focus is above the waist.

Fig. 32. Appearance of a microballoon when focus is at the waist.

from the difficulty of finding a perfectly spherical shell. This lack of concentricity between the inside and outside surface makes

it difficult to correlate all the readings. Additional data are now being taken to improve the reliability of the optical methods.

VII. Assembly of the Laser Targets

INTRODUCTION

Assembling laser targets entails selecting microballoons and gluing them to 5- μ m glass fibers. Dust, static electricity, and surface tension are all major problems in this process. Two manipulators, a vacuum pump, microvacuum chucks, and a microscope comprise the basic "gluing station" where almost all targets are assembled. Vacuum chucks are hollow glass capillary tubes (2-mm o.d.) that are heated and pulled to various diameters on a pipette puller.

ASSEMBLY TECHNIQUES⁷¹

All targets are mounted on a hollow glass stalk at 100 μ m from the tip. The tip diameter is 3 to 5 μ m and the stalk diameter is 15 to 20 μ m. This satisfies the specification that no mass greater than 30 ng be close to the target.

The basic assembly technique is the same for all the targets, varying only in the type of the glue used. The following discussion lists the three different types of bonding agents presently in use together with their advantages and disadvantages:

- Shell Epon 828 70/30 wt%.
 - Advantages - The set-up time can be varied from 2 to 12 h by building up heat in the epon mixture before applying it to the target. The long set-up time allows the target to be manipulated after applying the glue. The glue is also strong and viscous.
 - Disadvantages - It takes too long (20 to 30 min) to cure the glue. The problem is that the amount of glue used is so small that less heat is generated than in a larger batch. Thus, a longer curing time is necessary. It is also inconvenient to have the epon and catalyst come in gallon cans.
- Hardman "Double Bubble" epoxy.
 - Advantages - The glue comes in a one-job package, has a quick set-up time (15 to 45 min), good strength, and good viscosity. It is the most commonly used glue and is good for any type of target. It is predictable and controllable.
 - Disadvantages - Because of the extremely short work time (about 3 min), this epoxy requires quick work under the microscope with no mistakes, and proper preparation.
- Eastman 910 with and without surface activator.
 - Advantages - It is suitable for the mass production of target bonds because it is almost instantaneous. Without the surface activator, it is a one-part glue.
 - Disadvantages - Low viscosity causes 910 to have a coating action, although the action can be controlled, to a certain extent, upon application. Using 910 with a surface activator helps to create an instant bond and control the coating; however, this two-step process forces us

to apply the activator before the 910. The glue will set in a small volume, i.e., it will harden inside the 3- μ m tip before it can be extruded out if we do not keep it moving.

The basic gluing technique is to inject the glue into the rear of a hollow glass stalk using a hypodermic needle. Pressure is applied to the glue using a regu-

lated air supply or a duster cannister. The amount of pressure will depend on the viscosity of the glue and the diameter of the tip. Pressurizing the glue will extrude it out of the tip and onto the target, which is also being held by vacuum chuck. After the operation is completed, the vacuum side is opened up to air. After the glue sets, the assembly is removed from the micromanipulator.

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