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THE UPGRADING OF GLASS MICROBALLOONS

CONTRACT NO. NAS 8-33101

Authors: Stanley A. Dunn, PhD. and Steven Gunter

FINAL REPORT

PREPARED FOR

GEORGE C. MARSHALL SPACE FLIGHT CENTER
MARSHALL SPACE FLIGHT CENTER
ALABAMA 35812

BY

BJORKSTEN RESEARCH LABORATORIES, INC.
P.O. BOX 9444
MADISON, WISCONSIN 53715

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OBJECTIVE

To extensively study, examine and perturb the processes and mechanisms involved in producing glass microballoons of acceptable quality for laser fusion by gas jet levitation and manipulation.

SUMMARY AND CONCLUSIONS

(1) The temperature capability of the microlevitating furnace was extended beyond that of stainless steel prototypes. Temperatures up to 1450°C were achieved using platinum/rhodium (90/10) components and platinum/gold (95/5) solder. New techniques had to be found for fabricating the collimated hole structure (CHS) and other parts of the microlevitating furnace.

(2) Variants of the weighted check valve were examined as means of maintaining a constant pressure differential across the CHS during manipulations of chamber pressure and temperature. Inherent difficulties with this type of control indicate that positive electronic sensing and control may be necessary to achieve stable levitation during changes in furnace operating conditions.

(3) It was established that nearly complete loss of sodium and serious loss of other volatile constituents of glass can occur within minutes at temperatures well below the liquidus, causing the latter, in general, to rise. Thus, phase separation and corresponding microinhomogeneities can occur when the initial liquidus is below the operating temperature, but then rises above it as a result of such compositional losses. Single component glasses, e.g. silica, and elimination of the more volatile glass additives are ways around this difficulty.

(4) Glass microballoons (GMBs) levitated at temperatures below, as well as above, the liquidus appear to diffuse sulfur dioxide, a polar molecule with a moderately large diameter, and hydrogen, a much smaller molecule at comparable rates. Rates on the order of tens of atmospheres per hour (constant volume) per atmosphere of partial pressure differential have been observed at temperatures around the liquidus. Relatively rapid and convenient filling of molten GMBs by levitation in deuterium and tritium appears to be a possibility.

(5) Levitation in oxygen, as compared with nitrogen, was found to foster devitrification during heat treatments of GMBs of three different glass compositions at temperatures within several hundred degrees C of the respective liquidus temperatures. Similar levitated heat treatment of one of the GMBs in hydrogen showed no devitrification. These observations accord with others elsewhere that devitrification of silica is stimulated by oxidizing as opposed to reducing atmospheres.

There were some borderline significant observations that diffusion rates were higher with oxygen as the levitating gas as compared to nitrogen. Conceivably, such a phenomenon could be associated with the greater degree of devitrification and with other reports in the literature that bubble formation is fostered along the devitrification interfaces. Such localization could create shortened diffusion paths, thus accounting for the higher rates.

For levitation heat treatments below the liquidus temperature, it appears that inert and particularly reducing atmospheres, are preferred to oxidative. In turn, this means that in furnace construction for still higher temperatures, the cost and melting point limitations of the noble metals need not be restricting. Refractory metals, such as molybdenum and wolfram can be used.

RECOMMENDATIONS

It is recommended that the present effort be continued, namely the study, examination and perturbation of the processes and mechanisms involved in producing glass microballoons (GMBs) of acceptable quality for laser fusion by gas jet levitation and manipulation. The following specific proposals are suggested to materially assist in these aims:

(1) provide positive coordination among chamber pressure and temperature and levitating gas flow through microprocessor control of appropriate sensing and transducing devices. With this facility, then explore the coordinated manipulation of temperature and pressure to equalize GMB wall thickness;

(2) extend the temperature capability of the microlevitating furnace above 2000°C through use of refractory metals such as molybdenum and tungsten, using inert and reducing levitating gases;

(3) search for a way to positively control the orientation of the mass axis, as well as the speed of rotation of the levitated GMB. Implicit in this degree of control is the ability to stop all rotation. Using this capability and others above, centrifuge molten GMBs about multiple axes to achieve uniform wall thickness;

(4) explore the formation of GMBs from sections of levitated capillary sealed at both ends. Seal in gases of various polarities and molecular diameters;

(5) study the diffusion of gases in and out of heated levitated GMBs as a function of polarity and molecular diameter.

INTRODUCTION

Glass microballoons (GMBs) are currently used in the fabrication of targets for laser fusion studies and conceivably might also play a similar role in the ultimate laser fusion process. Although not all requirements of the GMBs may be known at the present time, certainly it has been recognized from the beginning that a high degree of geometric symmetry is a sine qua non.

The processes for producing GMBs commercially, and to some degree those dedicated to target manufacture have in them elements which tend to produce a random assortment of degrees of geometric symmetry. Consequently, an elaborate, time consuming selection process is necessary.

The present contractual effort and its predecessors was undertaken in the interest and with the hope of being able to treat GMBs in such a way as to remove any or all asymmetrical elements at will.

The cornerstone of this concept is and has been from the beginning the capability simultaneously of levitating, remelting and suitably manipulating the GMB. In work prior to the present contract, the goals of simultaneous levitation and melting had been achieved to a considerable degree with the development of the microlevitating furnace. At the same time, some of the necessary elements of manipulation had also been attained.

Specifically, the collimated hole structure (CHS) microlevitating furnace has several desirable control features implicit in its operation. Levitation is achieved through transfer of momentum to the GMB from vertically directed parallel jets of air issuing from the orifices of the CHS, operating in opposition to an inertial field such as that of gravity. A high degree of stability in the vertical direction is inherent in the spacing between jets. The momentum of the field of flow decreases with height due to the necessary lateral expansion of each jet. Hence, the required momentum transfer for levitation of a given GMB is a sensitive function of height above the CHS. Thus, the height of levitation can be controlled by adjusting the flow rate.

Lateral translational stability is inherent in the periodic grid work of high and low gas flows corresponding to the patterns of jets in the CHS. Momentum wells alternating with maxima represent well defined locations of lateral stability. This lateral stability can be further enhanced by creating a depression or dimple in the CHS surface encompassing an area which includes a number of jets. In this way, a potential well of larger scope is superimposed on the smaller scale periodic wells inherent in the pattern of the CHS itself. Lateral translational control is achieved by inclining the direction of the jets from the vertical with the aid of a gimbal mount.

GMB rotation rates up to 35 hertz have been obtained by exercising separate flow control over one of the centrally located jets. Referring to this separately controlled jet as "the jet" and the remaining ones as "the field", the rate of rotation has been shown to be controllable by adjustment of the difference in flow velocities of the field and the jet. The two different flow velocities impose a force couple, of course, upon any body situated in the boundary surface between them, the axis of the corresponding rotation tending to be at right angles to the velocities and in the plane of their common boundary.

Rotation tends to occur about a horizontal axis at high rates and about a more nearly vertical one at low rates of spin. It was learned from general observations that in the shifting of rotation axis the rotation inertial momenta of GMBs are markedly subservient to the viscous effects of the levitating gas. Beyond this, little effort has been made to achieve axis control in space and almost no effort on axis control in the mass of the GMB. The latter, while essential to inertial refinement of GMB geometry, has been given less attention in deference to other considerations.

It has been recognized that the volatilization of some glass constituents, e.g. Na_2O, could result in alterations in composition, possibly nonuniform, in glass composition of microballoons heated to melting for an appreciable length of time. Accordingly, one of the objectives of the present work has been to explore ways to retain glass homogeneity. The effects of different levitating gases and vapors were to be studied.

Heretofore, CHSs were made of stainless steel which, of course, limited the temperature attainable in the microlevitating furnace to about 1000°C. While this temperature is above the working point of many glasses, it nevertheless limits the fluidity which can be achieved, and thereby the speed with which centrifugal concentering can be realized. In switching to higher temperature metals and alloys, new techniques for fabricating the CHS are required.

When a GMB is cooled down in the furnace, it is essential to the preservation or improvement of geometric symmetry that a small positive internal pressure be maintained relative to the exterior. Since the interior absolute pressure is decreasing in proportion to absolute temperature, this means that a housing for the microlevitating furnace, call it the furnace housing, is required and the pressure within this housing must be reduced slightly more than enough to keep pace with reduction in the internal pressure. The coordination of housing pressure with temperature is, of course, more critical with the quench cooling designed to achieve equalization of wall thicknesses.

The reduction of furnace temperature also entails alterations in flow of the levitating gas. The velocity of the levitating gas jets decreases with the first power and the viscosity of the levitating gas approximately with the half power of the absolute temperature, hence, mass flow rate must be adjusted in inverse proportion to absolute temperature, to about the 3/2 power. The necessary coordinated control of temperature, flow rate and housing pressure is difficult to carry out manually. Automatic adjustment between at least two of these parameters would seem to be essential.

A conceptually simple alternative to the above adjustments to mass flow involves maintenance of a constant pressure drop across the CHS. Under this circumstance, corrections for thermal expansion and the effects of temperature on the viscosity of the levitating gas become unnecessary.

The primary concern of the present contract was to extend the temperature capabilities of the microlevitating microfurnace and its chemical compatibility with various levitating gases. Another objective was the development of a means of holding the pressure differential across the CHS constant. Studies then, of the effects of high temperature treatment of GMBs in various levitation gas environments were to follow.

EXPERIMENTAL

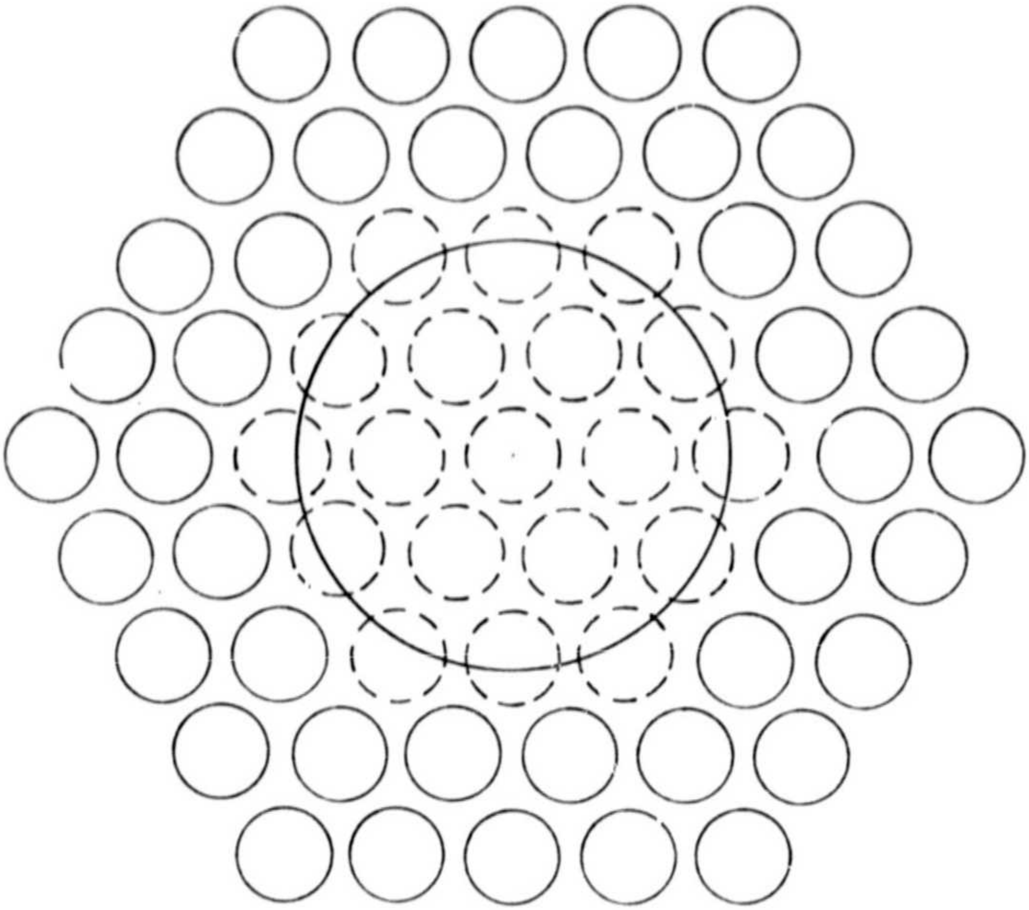
The desire to operate at temperatures in excess of 1000°C necessitated constructing the microlevitating furnace using metals more refractory than stainless steel. The further requirement of chemical inertness led to the platinum group metals. The platinum/rhodium (90/10) alloy (melting point 1830°C) was selected.

The method of fabrication was a difficult question. All of the previous levitation studies had been performed using stainless steel collimated hole structures (CHSs). The CHSs were manufactured by a drawing process. Stainless steel tubing filled with a lower melting ductile metal was swaged into parallel close-packed hexagonal bundles and drawn repeatedly through dies. The resulting parallel axial structure was sectioned and the ductile filler metal removed. Only a large scale production of CHSs makes this technique economically feasible. Since only a few platinum/rhodium CHSs were needed, the cost of the above procedure was prohibitive. Alternate methods were sought, including laser drilling and electron discharge machining (EDM), both future possibilities. They were abandoned, however, in favor of the more straightforward method of mechanical drilling.

The platinum/rhodium CHSs contain a hexagonal array of 0.127 mm diameter holes upon 0.152 mm centers (Figure 1). The drilling of these holes is a delicate and time consuming procedure. Holes drilled deeper than two or three diameters encourage drill breakage. Therefore, two thicknesses, 0.254 mm and 0.508 mm less than 1/4 and 1/2 respectively the thickness of the stainless steel CHS and two arrays, 19-hole and 61-hole, were studied. In the interests of expediency a 19-hole CHS was drilled and shipped first with the three more difficult 61-hole arrays to follow as they were completed.

Upon arrival, the drilled CHS was immersed in liquid nitrogen immediately before undergoing further machining. The cryogenic temperature served to embrittle the platinum, thus minimizing the danger of smearing the holes. The center 19 holes of the array were then dished with a 0.813 mm radius ball end mill to a depth of 0.127 mm. The resulting craterlike dimple assists in lateral translational stability during levitation, as mentioned above.

The use of platinum/rhodium for the construction of the levitating furnace presented slight design problems not encountered with the stainless steel prototype. Soldering, for example, required precise temperature control. The difference between the melting points of the platinum/10% rhodium alloy and the platinum/5% gold solder (melting point 1650°C) is only 180°C; furthermore, there appeared to be some fluctuation in this difference. Therefore, soldering, employed so extensively in the stainless steel furnace, was kept to a minimum. Close tolerance machining was emphasized.



Scale: 500:1

Figure 1. The Hexagonal Array of a Platinum/Rhodium CHS.

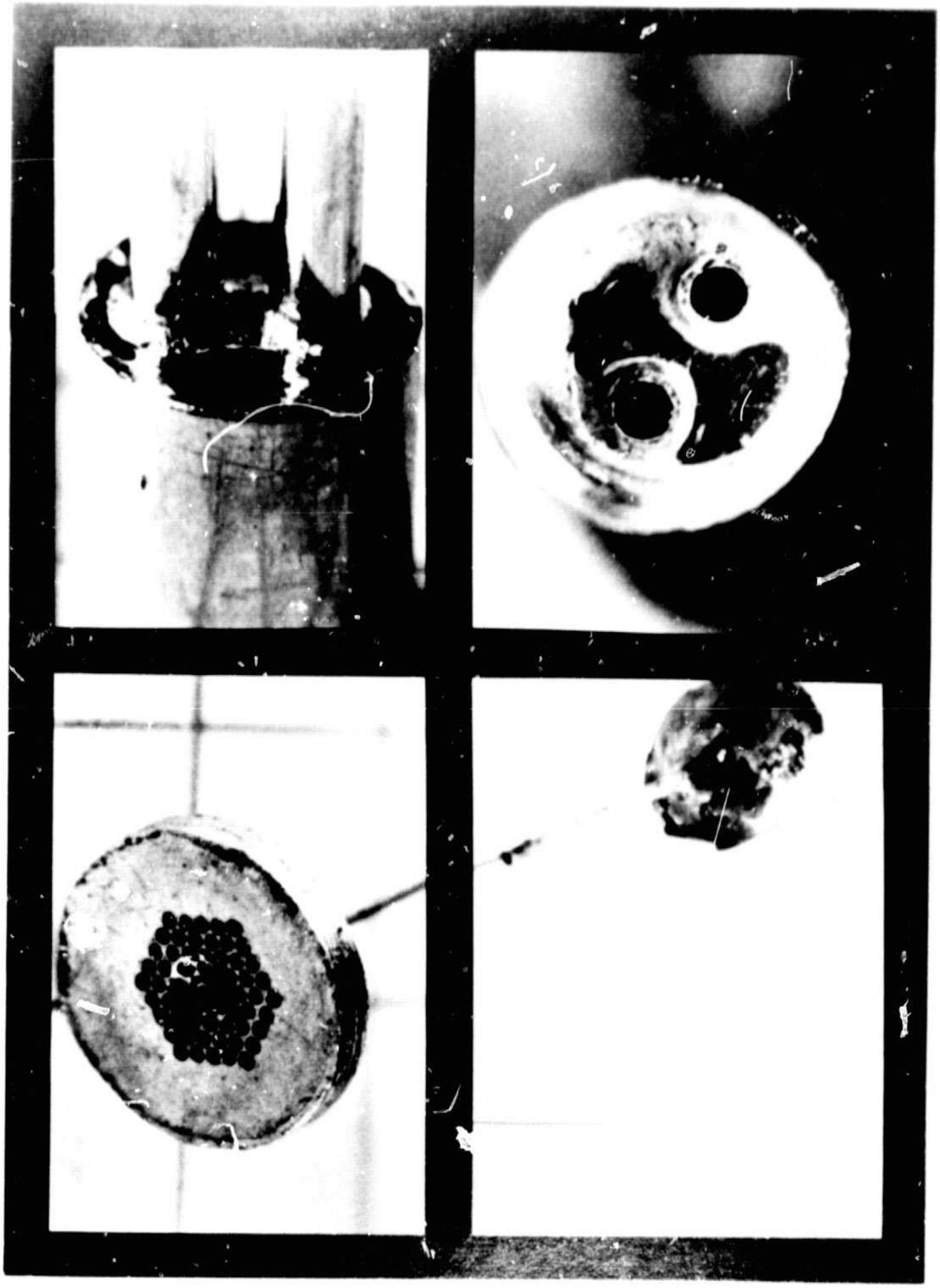
* 19-hole CHS array is in broken lines. The large circle is the approximate location of the dimple.

The installation of the jet, a platinum/rhodium tube of 0.127 mm outer diameter (0.102 mm inner diameter), also required adept engineering. The jet tube was press fit into the center hole of the dimpled CHS array (Figure 2c). The CHS disk was then press fit into a counterbored 3.175 mm outer diameter platinum/rhodium tube. The edge of the tube was rolled onto the disk to anchor its position. At this point, a partition was placed within the body creating two plena (Figure 3a). The lower plenum supplies gas to the jet and the upper supplies gas to the field. Platinum/gold solder forms were inserted around the jet tube and along the outer wall to seal any leaks. The assembly was then slowly heated in an induction heater until the solder began to flow. When the same procedure was used to install the bottom disk, which enclosed the lower plenum, the jet tube -- no longer visible for temperature monitoring -- apparently became too hot and melted.

The subsequent design eliminated the partition and with it the problem of internal temperature detection (Figure 3b). The bottom disk was press fit into the body and soldered. Two platinum/rhodium supply tubes were inserted through the predrilled holes in the bottom disk and also soldered (Figures 2a and 2b). The jet was threaded down one of the platinum/rhodium supply tubes and sealed with silver solder (melting point 600°C) (Figure 2d). After a period of high temperature testing the jet was examined and found to be functional.

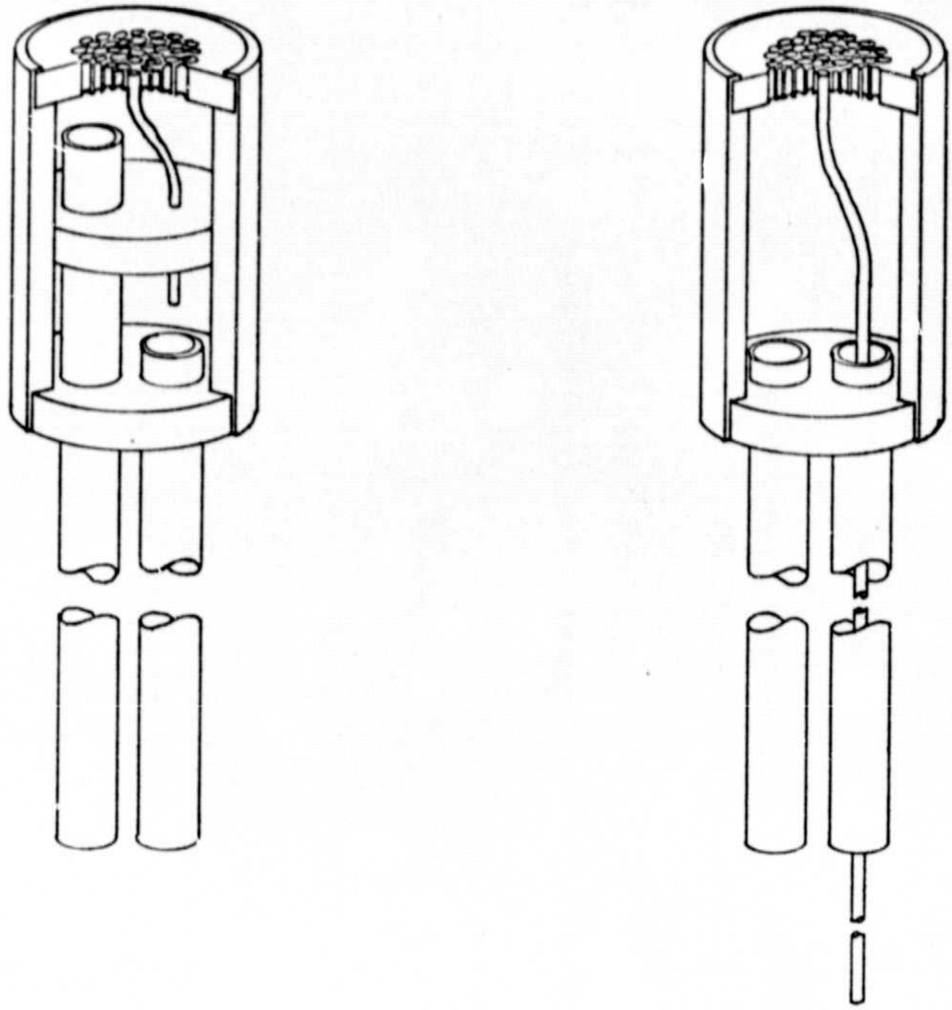
The platinum/rhodium levitating gas supply tubes serve the added function of electrical heaters. Together with the microlevitating furnace which they feed, they form a series electrical heating circuit, power connections being made to their tubular brassy extensions below the furnace housing. Initially, this was the only source of furnace heating, just as in the previous stainless steel CHS prototypes.

Whereas this arrangement had brought the CHS to within a few degrees of the supply tubes in the stainless steel versions, it proved inadequate with the platinum/rhodium apparatus. The tubes were brought to a temperature of 1555°C (measured by optical pyrometer). Without a flow of levitating gas the CHS dimple read a temperature of 800°C. A flow of levitating gas improved heat transfer yielding a temperature of 925°C. In recognition that the total mass flow of levitating gas was smaller in the present CHS than its stainless steel predecessors by virtue of the much smaller number of holes the gas flow was increased to compensate, but with an improvement of only a few tens of degrees C. A further distinction from the prior work with stainless steel is the increasing importance of radiation losses at the higher temperatures.



a b c d

FIGURE 2. CHS, JET TUBE AND GAS SUPPLY TUBE SOLDER JOINTS WITH BOTTOM OF CHS HOUSING



A B

Figure 3. CHS Body Designs for Jet Installation

The levitation region above the CHS dimple was checked for temperature distribution (Figure 4). A normal levitating flow of nitrogen was administered, $3.8 \cdot 10^{-8}$ m^3/s. The dimple attained a temperature of 925°C. Readings of temperature were taken on a two dimensional grid above and to either side of the vertical axis of the CHS. Readings were taken by platinum-platinum/10% rhodium thermocouple (130 micron diameter wire with a 400 micron bead). The area directly above the dimple is shown to have a temperature gradient of approximately 0.05°C/micron. A 200 micron diameter GMB could have as much as a 10°C temperature differential top to bottom if stationary, less of course, if rotating.

The widths of the temperature profile peaks are comparable to, but more or less within the field of levitation orifices. The pattern suggests that attenuation of jet temperature is brought about largely by radially inwardly entrained injections of colder surrounding gas. If so, then the thermal gradient might be reduced further by increasing the area of the levitation field or by establishing a more isothermal environment.

A coil of platinum/rhodium wire, 0.913 mm in diameter was placed around the microlevitating furnace to serve as an additional heat source, as well as to block radiation losses in that direction (Figure 5). Under otherwise similar conditions, the dimple could now be brought to a temperature of 1100°C. To further combat radiation losses, double walled cylindrical boron nitride (BN) heat shields were installed. With this addition, a dimple temperature of 1450°C was attained.

In order to generate more heat within the body of the microfurnace and CHS, the levitating gas supply tubes were transplanted from the bottom to the opposite sides, thus lengthening the electrical path through the microfurnace body (Figure 6). While better direct electrical heating through the microfurnace was achieved, the radiant contribution from the surrounding coil was reduced. The reduction resulted from the necessity of expanding the coil to make room for the laterally entering levitating gas tubes. There were operational disadvantages and little temperature improvement and the gas supply tubes were returned to their original position.

Conceptually, the simplest way to maintain stable levitation during changes of microfurnace temperature and pressure is to maintain the pressure differential across the CHS constant. Under this condition, the effect upon GMB levitation, of a thermally induced change in viscosity will be compensated by a suitable adjustment in levitating flow through the CHS capillaries. Similarly, temperature produced changes in gas density are also compensated. In addition, by definition as it were, the levitation flow remains constant throughout fluctuations in furnace pressure.

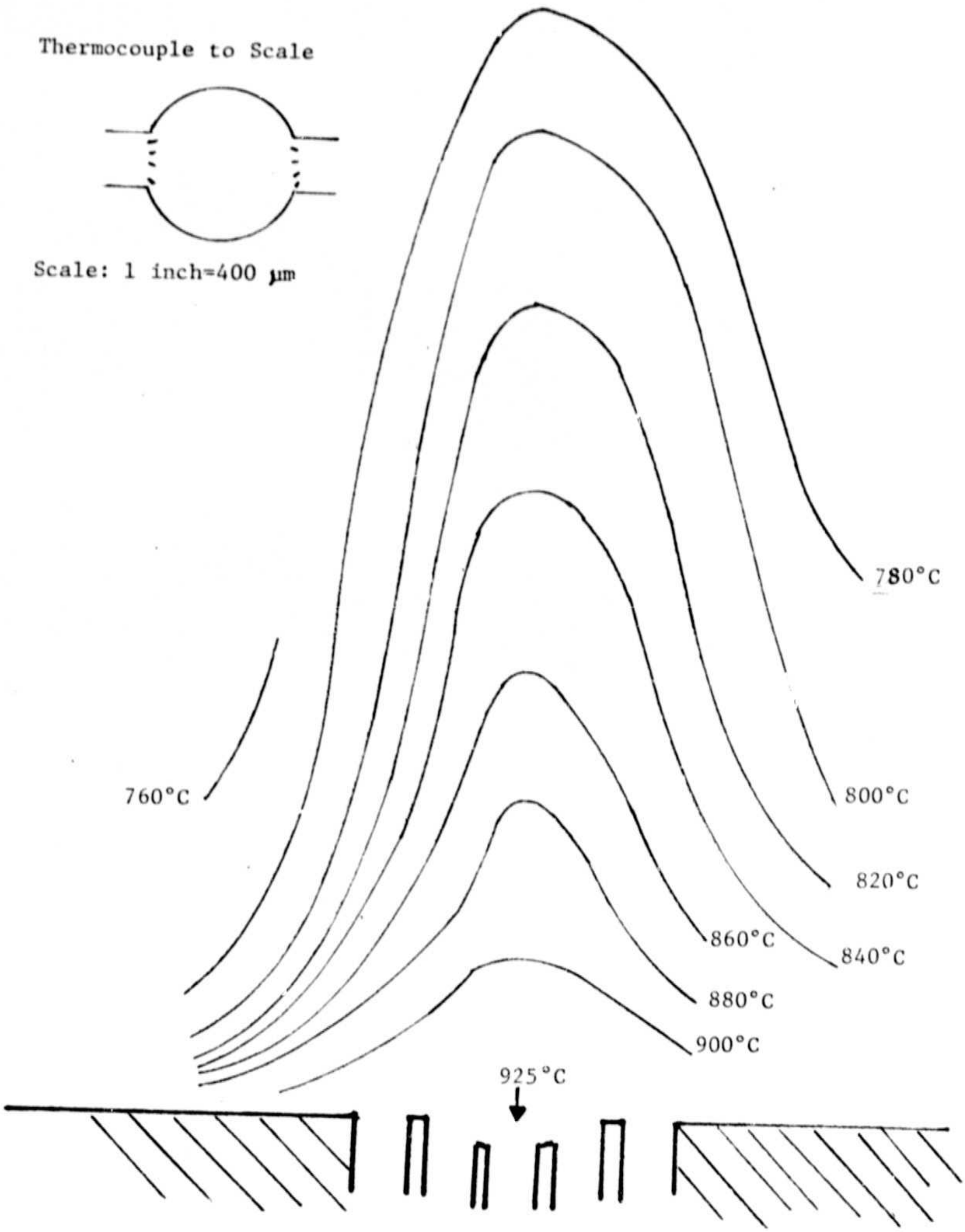


Figure 4. Isothermal Profile of Levitation Region Above CHS Dimple

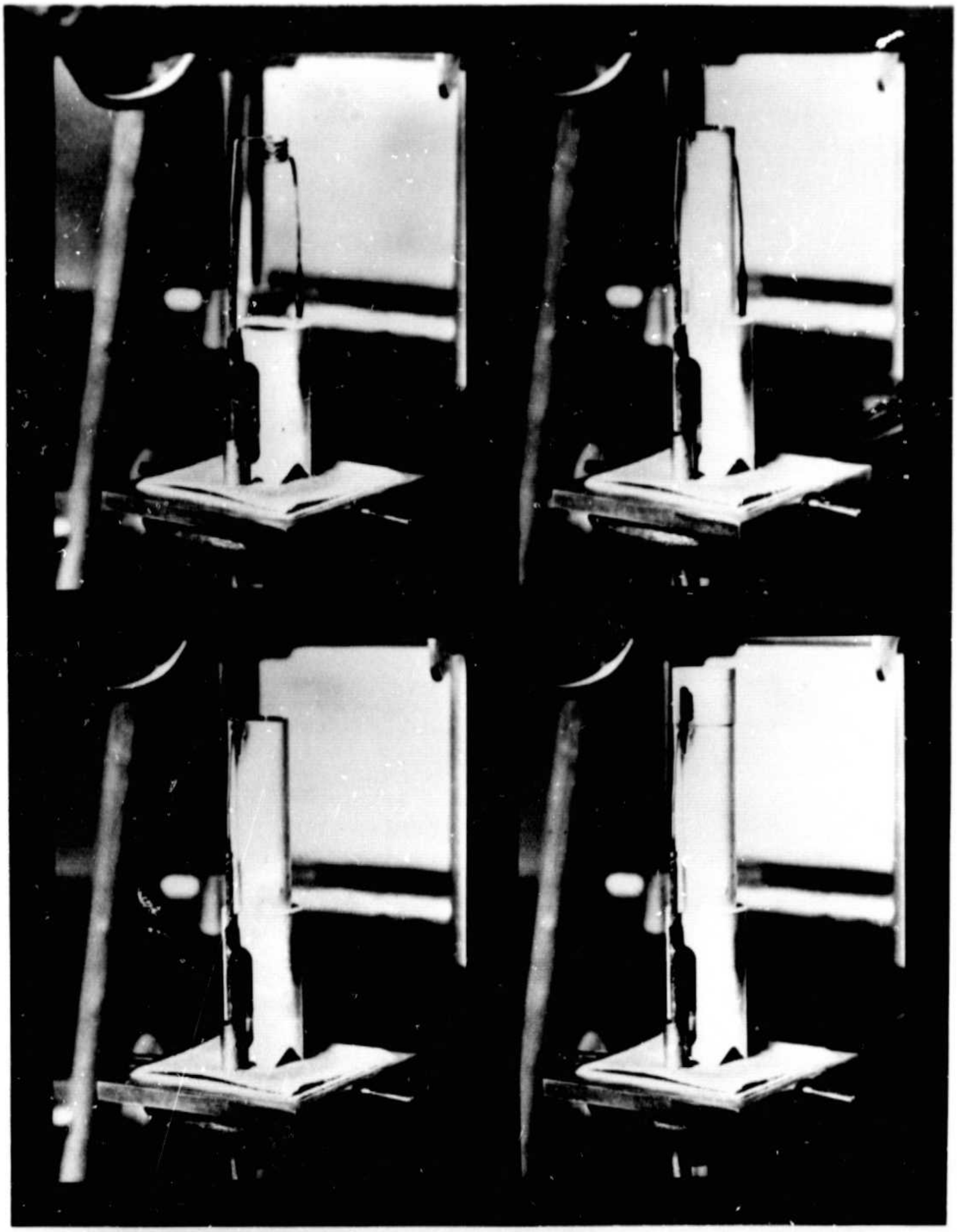


FIGURE 5 HEATING COIL AND BORON NITRIDE HEAT SHIELDS FOR LEVITATION FURNACE
(CHS AND SUPPLY TUBES NOT IN PLACE)

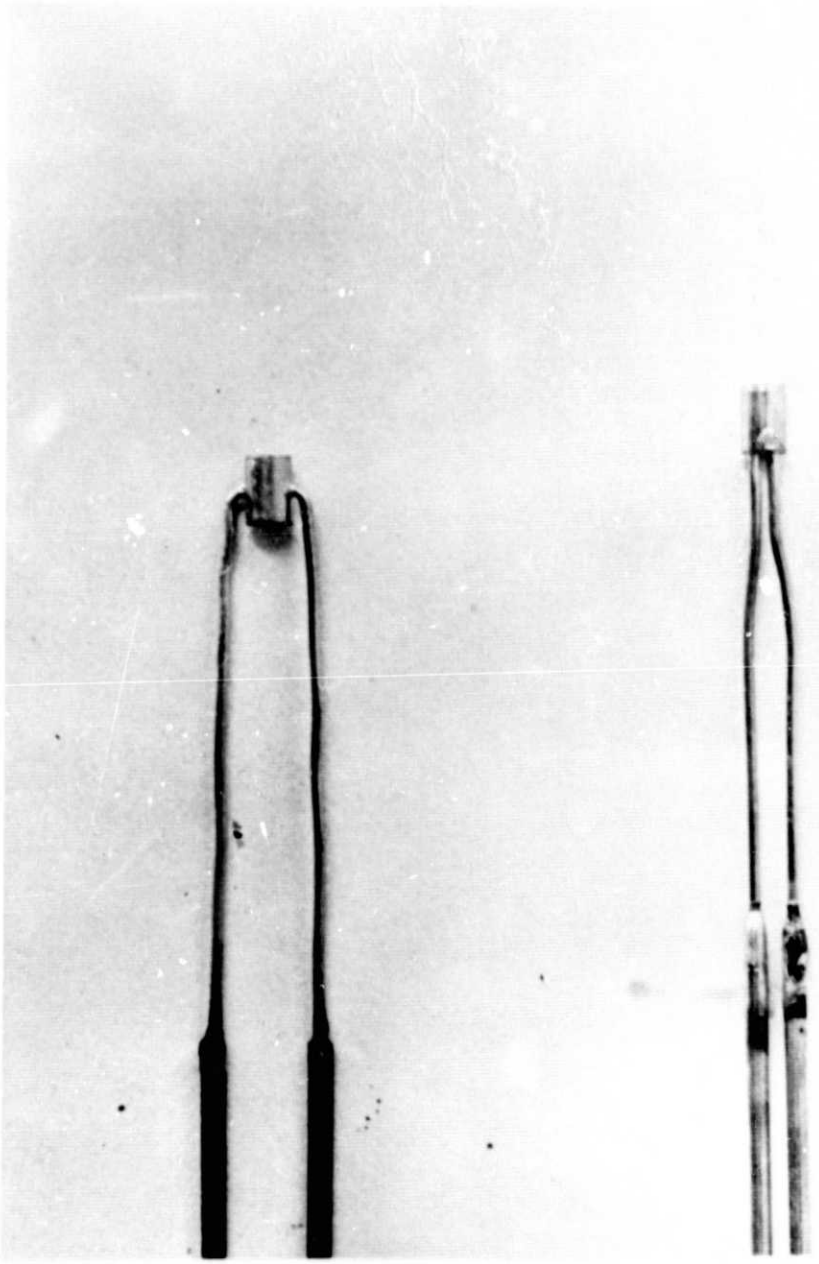


FIGURE 6. LATERAL AND BOTTOM ENTERING GAS SUPPLY TUBE CONFIGURATIONS

The difficulty in putting this concept into practice lies in part in the minuteness of the pressure differential which must be measured and, or at least, held constant, of the order of tenths of a Torr. The device used to attempt this control was a precision bore piston and cylinder situated within the furnace housing on a vertical axis (Figure 7). The cylinder was connected to the levitating gas feeding the CHS. The differential pressure across the CHS thus, ideally at least, cannot exceed the weight of the piston divided by its cross-sectional area. The differential pressure could be controlled by altering the weight of the piston with lead shot.

To prevent the piston from being blown out of the cylinder, horizontal slots were cut in the piston skirt below the head to allow escape of excess levitating gas. It was intended that the piston weight be adjusted so that during high temperature levitation, the top of the cuts in the skirt would ride just above the top of the cylinder wall, allowing the escape of some levitating gas in parallel with that flowing through the CHS. When the pressure in the furnace housing was reduced, the piston would tend to hold the pressure differential constant. In this way, the same reduction in pressure which was occasioned in the furnace housing would be passed on to the levitating gas supply. The increase in the supply of levitating gas called forth in this way would be mainly that vented through the piston skirt slots as already described.

A prototype of this device was constructed and tested. While it did function as intended there was, however, lag in movement and an attendant pressure differential spike, more pronounced the more rapid the housing pressure reduction. In addition, even after the spike had subsided, the pressure differential did not return all the way to the original value. This residual slight increase in differential pressure may be viewed as being due to the increased velocity of flow through the piston slot and the attendant locallized Bernoulli reduction in pressure in the vicinity of the slots. The net area upon which the piston's weight must be supported by the static pressure of the levitating gas is correspondingly reduced and the gas static pressure accordingly increased. Although this effect is inherent in the concept, it can be minimized by design.

The graphite piston and glass cylinder are precisely mated and offer very little friction to relative motion. Nevertheless, there is some friction and this undoubtedly contributes to the lag and the spike. This friction could be virtually eliminated by replacing the piston with a weighted cap, resting on and closely mated with the top of the cylinder, and hinged to one side. Such a cap was tried out. The spike was reduced somewhat, but not eliminated.

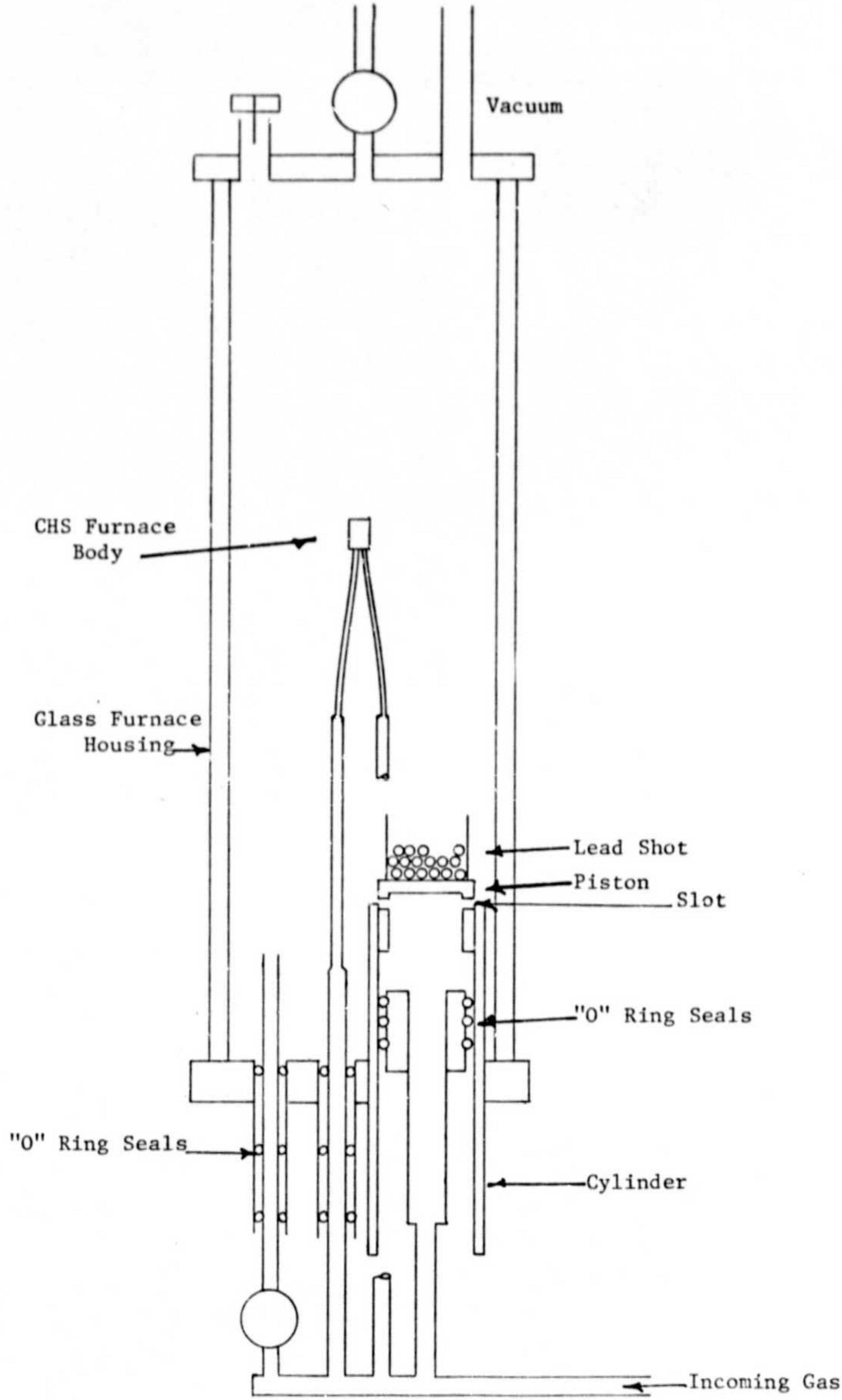


Figure 7. Mechanical Differential Pı..ssure

A more serious contributor to the spike may be the inertia of the piston or cap resisting motion, in response to the reduction of furnace housing pressure. The effect of this inertia can be reduced by increasing the cross-sectional area of the cylinder so that less movement is required to accomodate a given increase in flow rate.

Finally, there is the problem of levitation gas holdup in the supply lines. The increasing pressure drop across the CHS cannot be relieved any faster than the gas molecules in the supply lines can respond to each other and convey the pressure reduction achieved by the piston. In addition to that delay, there is a further short interval of time while the gas in the line between the CHS and the piston impeded by viscous drag and inertia respond to the new pressure. This delay is a function of the distance betweem CHS and piston. There is accordingly, a lower limit to the size of this delay, of the order of half a millisecond because of the length of piping necessary to connect the CHS and the cylinder.

This system was not developed beyond the first prototype in part because of the press of other work. It now appears that microprocessor control through electronic sensors and transducers may be the more reliable way to achieve the positively coordinated pressure, flow and temperature regimes necessary for cooldown of heat treated GMBs and for wall equalization manipulations.

The levitating characteristics of the 19-hole and the 61-hole CHSs were compared. The 61-hole array produced a very stable levitation; the response of a GMB to flow adjustment was prompt and predictable. The transition from stable to unstable levitation was slow and easily correctible. The 19-hole CHS, being 1/2 as thick (0.254 mm versus 0.508 mm) and with less than 1/3 the number of holes, is highly sensitive to flow fluctuations. Accordingly, its stable levitation range is quite small. One other drawback is the greater degree of interference from electrostatic effects. There is a large open area surrounding the array where a GMB may become attached and defy attempts to dislodge it.

The extent to which a GMB is affected by static charge, grease, air currents, etc. is inversely related to its diameter. Four hundred micron GMBs were generally easy to handle. In fact, these microballoons were the first to be levitated upon the 19-hole CHS, probably due to their indifference to electrostatic charge. As the GMB diameter approaches 230 microns, its susceptibility heightens. Grease and oil contamination also make levitation increasingly difficult with the smaller GMBs.

It is important that the flow of the levitating gas above the CHS be laminar. Presumably, turbulent vortices which approach the diameter of the GMB in size would foster erratic behavior. In order to evaluate slip stream behavior, smoke was injected into the gas stream and its profile upon emerging from the CHS (19-hole array) was examined (Figure 8). The photograph is verification that the flow is indeed highly laminar and that turbulence within the levitating stream should present no foreseeable difficulties.

A factor not mentioned in the Introduction and which plays a role in GMB rotation in addition to that of the jet is the inclination of the levitation flow axes from the vertical. The horizontal component of the jet flow causes the GMB to move off center with respect to the jet in the direction of inclination. The displacement increases with the inclination from the vertical. The aerodynamic lift of the jet opposes this displacement increasingly with the magnitude of the latter and within limits of around 10° inclination strikes a dynamic equilibrium with it. An associated effect of the displacement of the GMB from the axis of the jet is to cause the GMB to rotate at a rate which increases with the degree of displacement.

A gimbal mount was provided to permit inclination of the microlevitating furnace and housing about two mutually perpendicular axes (Figure 9). Lugs supporting the furnace housing from the gimbal were originally made of plastic. These softened, however, with furnace heat and were replaced with glass. The gimbal was constructed so that the CHS dimple could be located at the intersection of the two axes, thus simplifying viewing during angular adjustment of the furnace.

The pressure differential gauge* shown in Figure 7 connected across the CHS and its feed tubes (no jet, both tubes feeding the field) had a full scale reading of two inches of water ($5.1 \cdot 10^{-7}$ kg/m^2) whereas only the lowest 10% of the scale was used. Reading accuracy was correspondingly poor. Inasmuch as the pressure differential levelling device had been abandoned, the corresponding differential pressure gauge was

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* Magnahelic Differential Pressure Gauge
Model 2002C
Dwyer Instruments, Inc.
P.O. Box 373
Michigan City, Indiana 46360

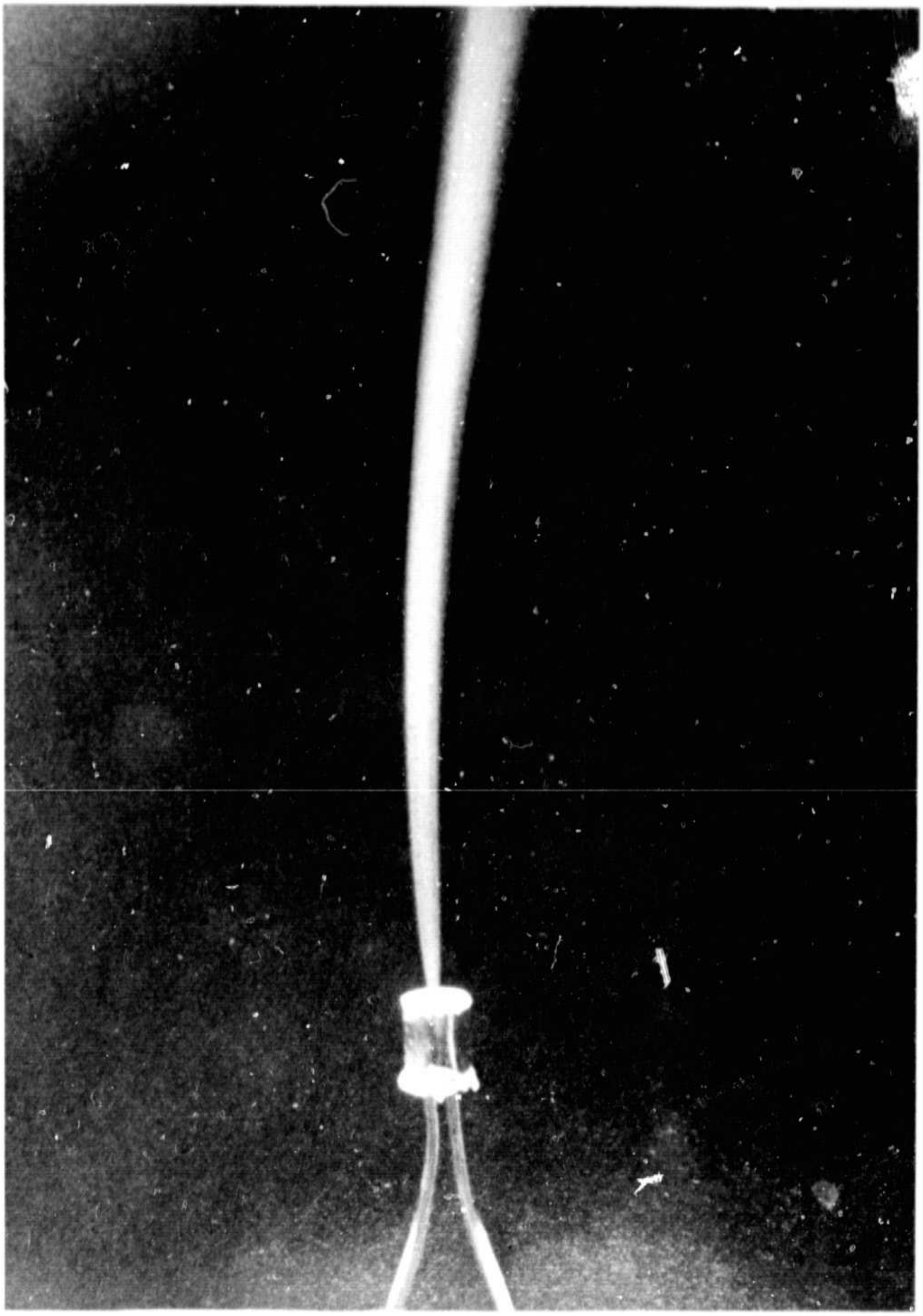


FIGURE 8. SLIPSTREAM OF THE LEVITATING GAS

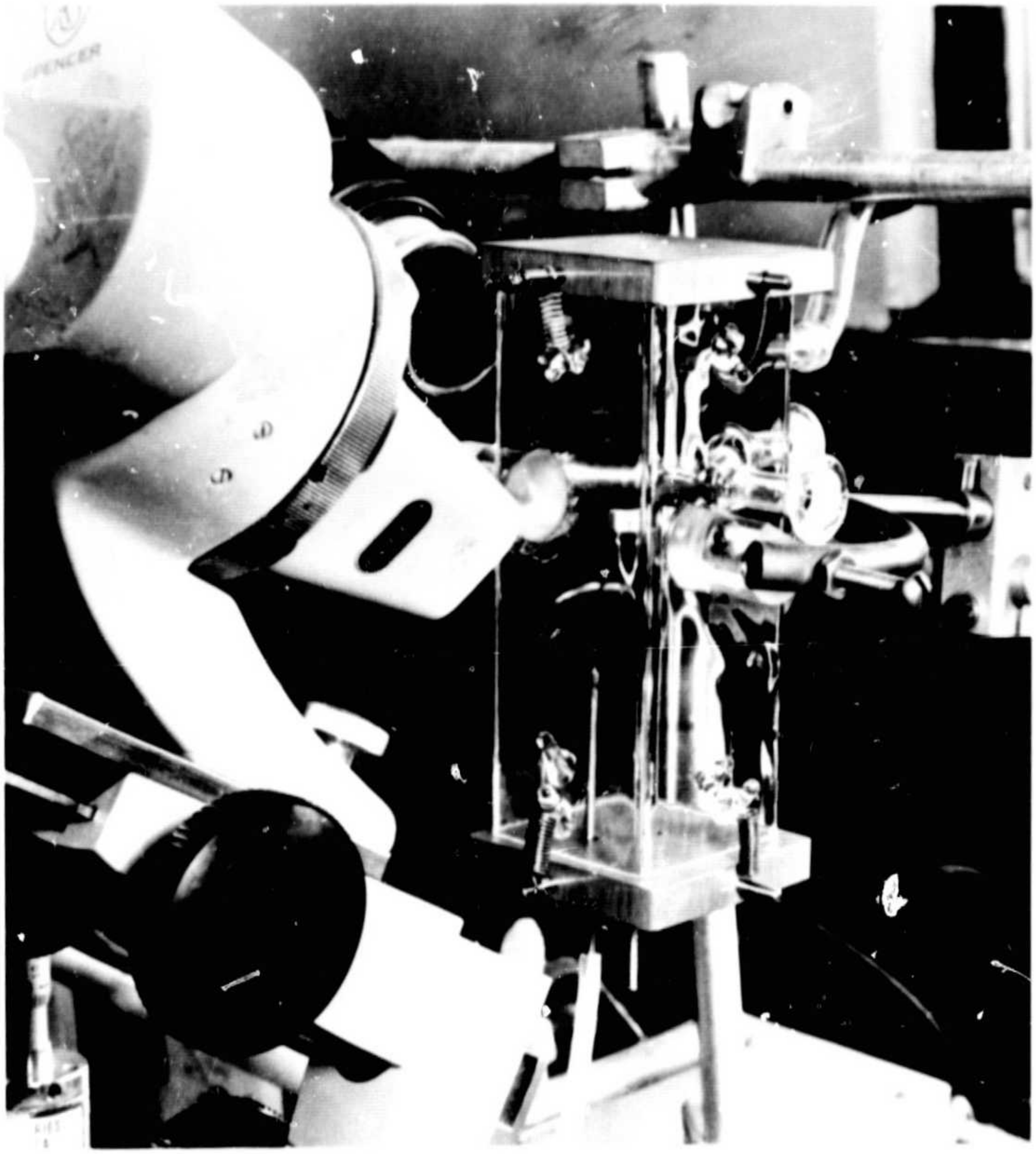


FIGURE 9 . GLASS HOUSING FOR MICROLEVITATING FURNACE SHOWING GIMBAL MOUNTING

replaced with a mass flow meter** one of whose virtues lay in more precise readings near midscale. Full scale was ten standard cubic centimeters per minute (sccm); typical room temperature readings were four to five sccm. Readings with the furnace at 1400°C fell below one sccm due to the expansion and viscosity effects of temperature, as already discussed.

Microfurnaces with jets were constructed, though seldom used because of delays in construction and the fact that the nature of most of the work did not require them. CHSs with a field and no jet differed only in the deletion of the capillary tube extending from the central CHS orifice down the jet supply tube. With a jet, separate flow controls and lines are required. With the field only, the two supply tubes are connected through a "Y" tube to a common source of levitating gas.

Levitating gas flow is controlled by a pressure regulator and a fine adjustment metering valve***. The same pressure regulator can be used for both metering valves with furnaces having a jet (Figure 10). The CHS/feed tubes and the coil are heated electrically by separate AC circuits. Both circuits are low resistance, ca. 0.17 ohms. For operation at a dimple temperature of 1400°C the CHS/feed tube circuit typically will draw about 25 amperes at 4.2 volts, the outer coil, 30 amperes at 6 volts. A safe red line temperature for any part of the heating circuits would appear to be 1500°C.

** Mass Flowmeter
Model ALL10,4-10M
Teledyne Corporation
Hampton, Virginia

*** Precision Gas Metering Valve
Model N. MV-25-ST-SWGB
Vacuum Accessories Corporation of America
390 Central Avenue
Bohemia, New York

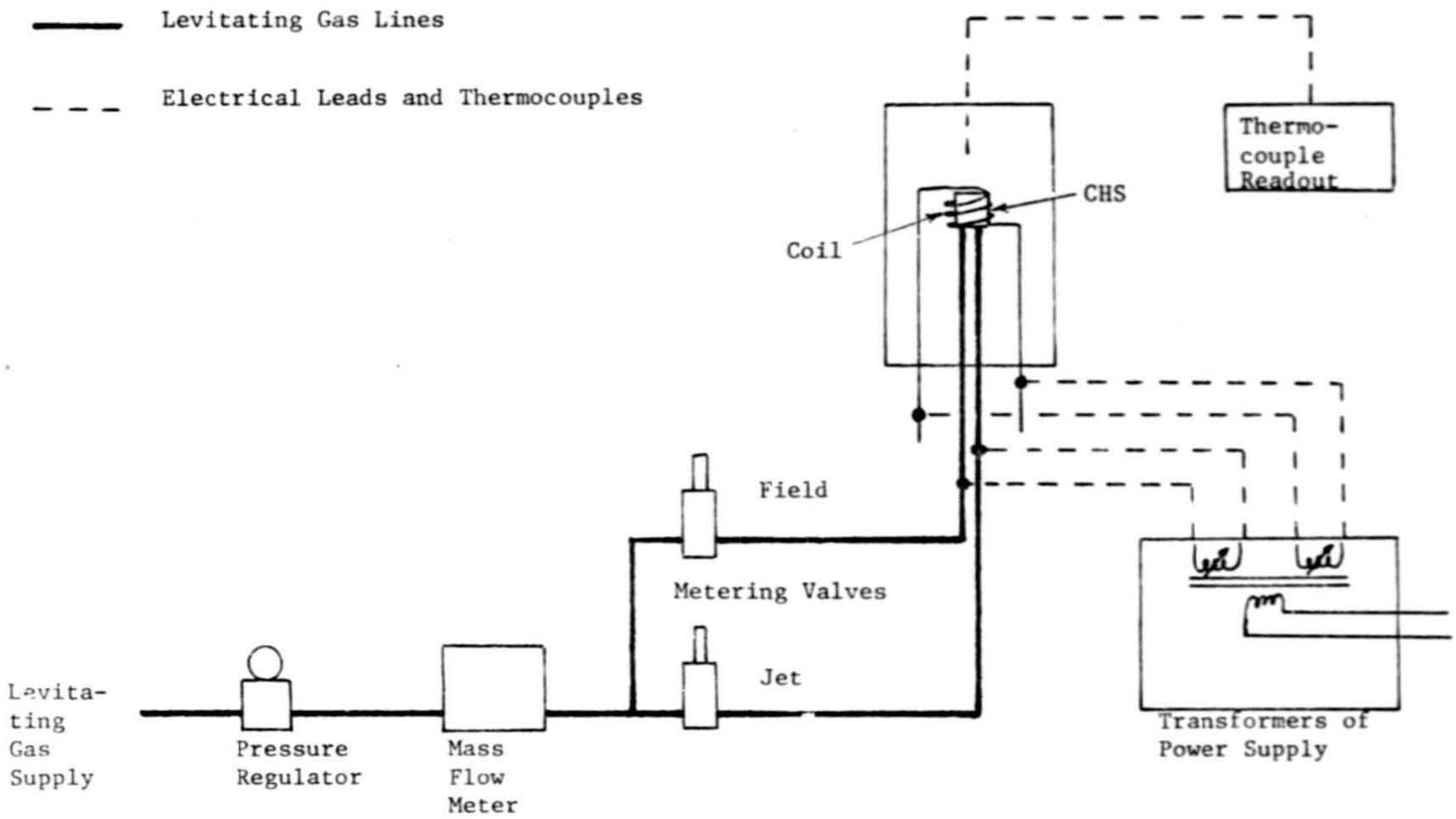


Figure 10. Schematic of Levitating Gas Flow and Electrical Wiring.

RESULTS AND DISCUSSION

As the temperature capability of the noble metal microlevitating furnace progressed, GMBs were subjected to various levitation treatments at appropriate temperatures. The behavior of GMBs during treatment and alterations in appearance as a result of it were noted. Only GMBs appearing to be good spheres with uniform wall thicknesses were treated. Irregularities resulting from the treatments were looked for: both macro-irregularities, deviations of the same order of magnitude as the GMB diameter, such as asphericity, and micro-irregularities, blemishes of the same order of magnitude or smaller than the wall thickness of the GMB such as microcrystals formed by devitrification.

Rotation about a horizontal axis could have been stimulated deliberately and, to some extent controlled through use of the jet with or without the gimbal, as indicated previously. Neither the jet nor the gimbal alignment capability were used, however, nor were the GMBs marked to facilitate observing rotation. Nevertheless, due probably to inhomogeneities in the field interacting with GMB irregularities, some rotation of various descriptions and degrees was encountered, observations of spin rate and axis orientation being possible in some cases using dust particles or other surface imperfections to sight on.

In general, rotation rates whatever they were at the beginning, decreased appreciably or stopped entirely upon heating, sometimes resuming some or all of the original rotation upon cooling down again. Initial rates ranged from 4 to approximately 300 rpm. In several instances the axis of rotation was noted to have shifted during heating, taking up a more vertical orientation. The increase of viscosity with temperature would increase coupling among adjacent stream lines and thus, perhaps reduce the strength of drag force couples operating on GMBs about axes having a horizontal component. Drag force couples about the vertical axes, due presumably to slight misalignment of stream lines from the vertical, would be less directly affected by increased viscosity engendered coupling among streamlines. Vertical axis spinning might then be expected to persist at higher temperature relative to rotation components about horizontal axes.

The successful levitation of a GMB depends upon a balance between gravitational and aerodynamic forces. During the heating of a levitating GMB this balance is a dynamic one. While the temperature is increasing, the mass flow of levitating gas must be reduced to compensate for gas expansion and a rise in viscosity (Figure 11). In one instance, the flow was reduced more than 77%, from $7.5 \cdot 10^{-8}$ m^3/s to below $1.7 \cdot 10^{-8}$ m^3/s.

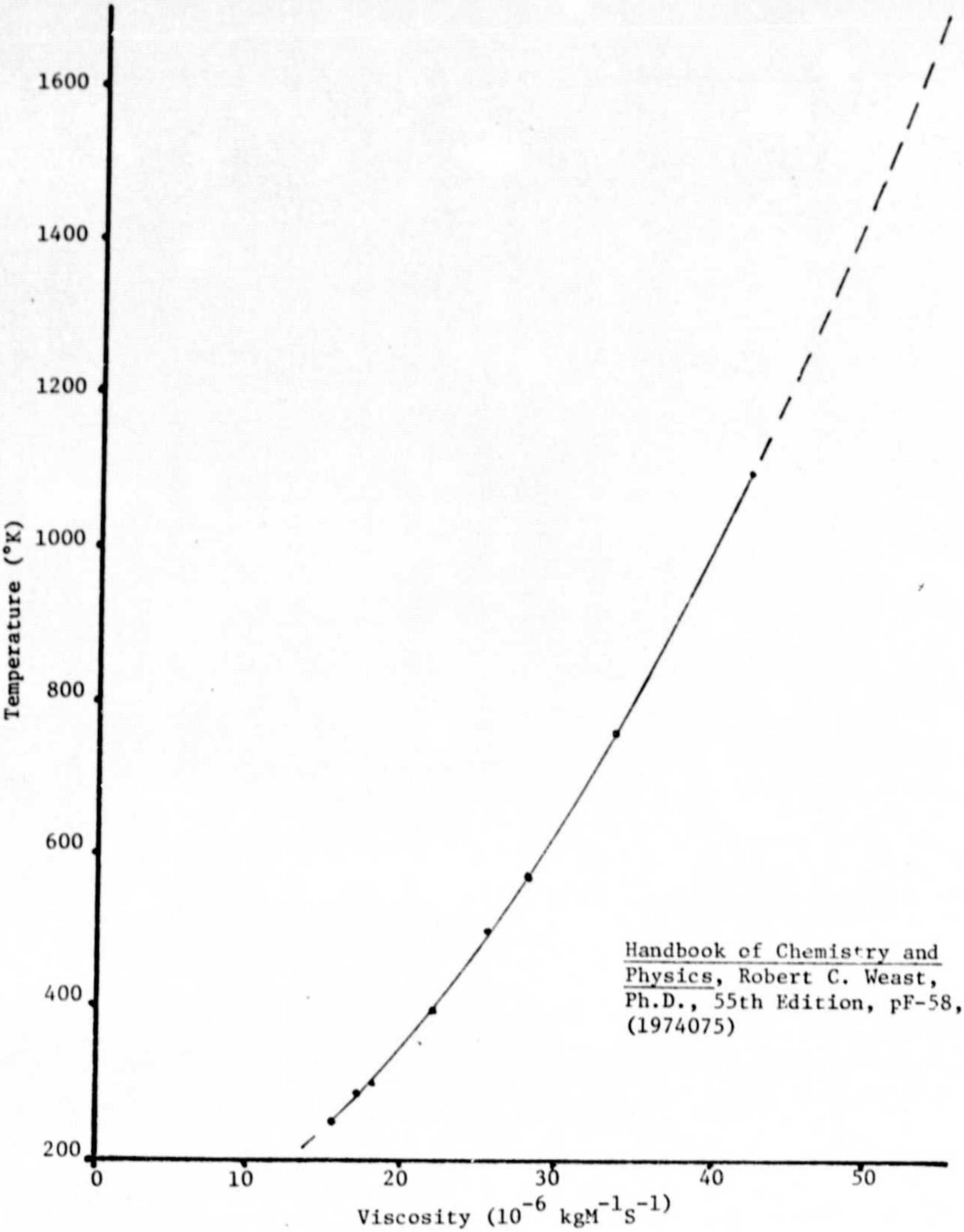


Figure 11. Viscosity of Nitrogen as a Function of Temperature.

As already discussed, pressure coordination with temperature has not been satisfactorily worked out at this time, hence macro distortions, puckering and wrinkling due to low internal pressures during final cool-down were anticipated and observed.

The first series of levitating heat treatments was carried out when the temperature capability of the furnace had been brought to a little above 1200°C. This, of course, is considerably above the temperatures achieved in any of the previous work with stainless steel CHSs. It is not, however, above the liquidus of either of the GMBs to be treated: designation T2R85 and T2R88, having estimated liquidus temperatures of 1480°C and 1550°C respectively (Figures 12 and 13).

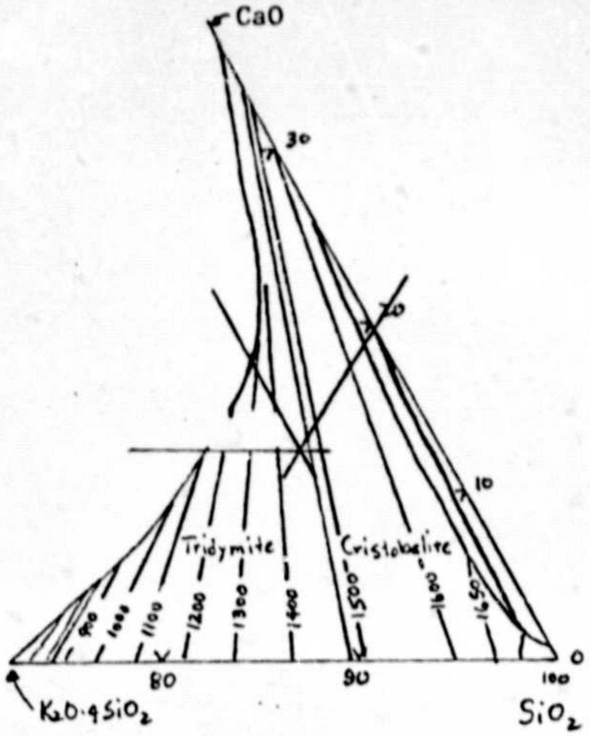
The heat treating of levitated GMBs was studied by factorial plan with respect to four variables at two levels each: levitating atmosphere (O_2 and N_2), glass type (T2R85 and T2R88), temperature (900°C and 1200°C), and exposure time (5 minutes and 10 minutes)(Figure 14).

Sixteen GMBs were treated according to the condition combinations of the plan, then recovered, mounted and photographed at approximately 200X (Figures 15 through 18). The original photomicrographs were reduced somewhat for this report. All GMBs were around 400 um diameter and of KMS Fusion, Inc. origin.

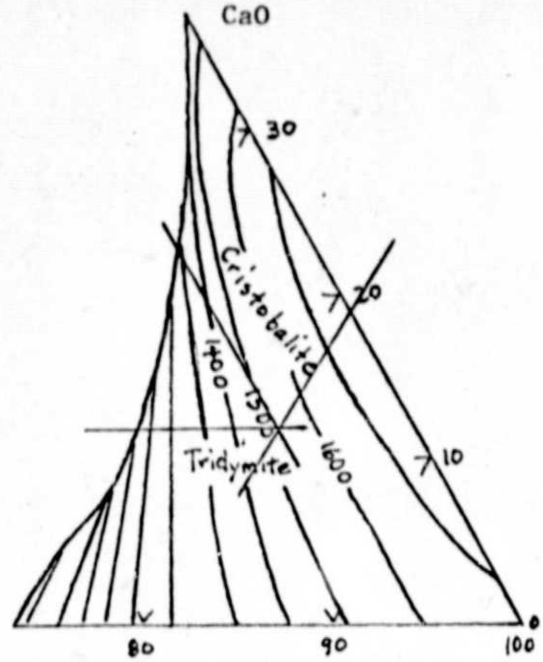
Unfortunately, three of the sixteen GMBs were lost during handling after the heat treatment and several others were broken. However, some useful conclusions still were possible through microscopic observation. To some degree, these observations are reflected in the photomicrographs.

It was clear that for both glasses the high temperature produced more devitrification. The higher viscosity at the lower temperature more than offsets the greater thermodynamic tendency to crystallize. Although the liquidus temperature of the two glasses differ by about 100°C there is little distinction between them regarding devitrification. The spheres i and j show the expected effect of time upon devitrification. The oxygen environment appears to foster devitrification relative to nitrogen, as seen most clearly comparing i with the remaining shards of k and m with o (some mounting cement is spread over parts of the surface of m).

Some information concerning the working points of the two glasses is to be found in the 900°C tests. Three of the higher silica GMBs (T2R88) sollapsed after sixty seconds at temperature. Of the lower silica GMBs (T2R85) three were wrinkled but uncollapsed and one, e, was unaffected. The effect of time of exposure can be seen in the fact that the unaffected e was one of the GMBs subjected to the shorter five minute exposure, while the most distorted GMB, h, was one of those given the longer treatment.



1)



2)

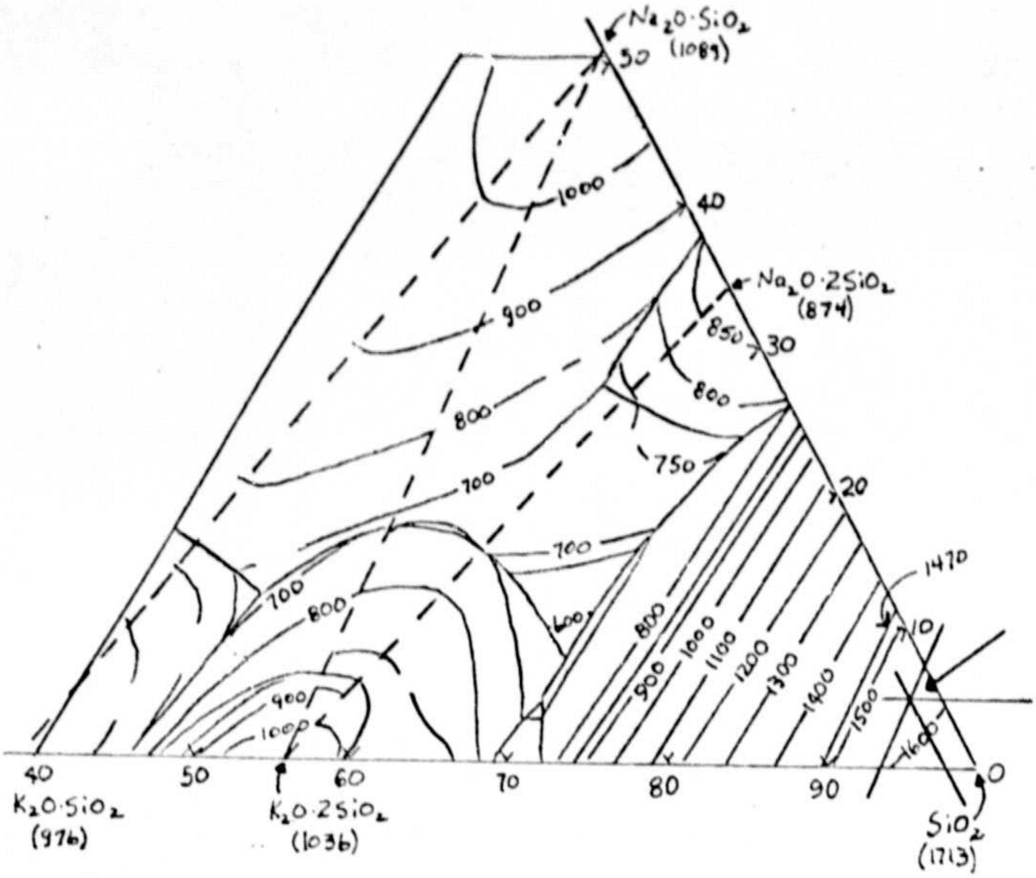
Component	Proportion (wt.%)	(mol.%)
Na_2O	5	4.8
CaO	12	12.8
K_2O	2	1.3
B_2O_3	.03	.03
SiO_2	81	81

NOTE: The B_2O_3 content is ignored and the liquidus determined on each diagram assuming all of the alkali oxide content is of the one alkali oxide appropriate to the diagram. A temperature 10°C below the average is taken as the liquidus of the glass.

Figure 12. Composition of GMB T2R85 and Phase Diagrams from Which Liquidus May Be Estimated.

1) G.W. Morey, F.C. Kracek and N.L. Bowen, J. Soc. Glass Technol., 14, 158 (1930).

2) G.W. Morey and N.L. Bowen, J. Soc. Glass Technol. 9, pp232,233 (1925).



3)

Component	Proportion (wt.%)	Proportion (mol.%)
Na_2O	5	4.9
K_2O	2	1.3
SiO_2	93	93.8

Figure 13. Composition of T2R88 and Phase Diagram From Which Liquidus May Be Determined.

3) System SiO_2-$K_2O\cdot SiO_2$-$Na_2O\cdot SiO_2$. F.C. Kracek, J. Phys. Chem. 36, 2538 (1932).

Temperature (°C)	Levitating Gas	T2R88		T2R85	
	Heating Time (Minutes)	5	10	5	10
900	N_2	A	B	E	F
	O_2	C	D	G	H
1200	N_2	I	J	M	N
	O_2	K	L	O	P

Figure 14. Factorial Plan of GMB Heat Treatment Conditions.

NOTE: Photomicrographs appear in groups of four sequentially in Figures 15 through 18 (e.g., a,b,c and d are in Figure 15, etc.)

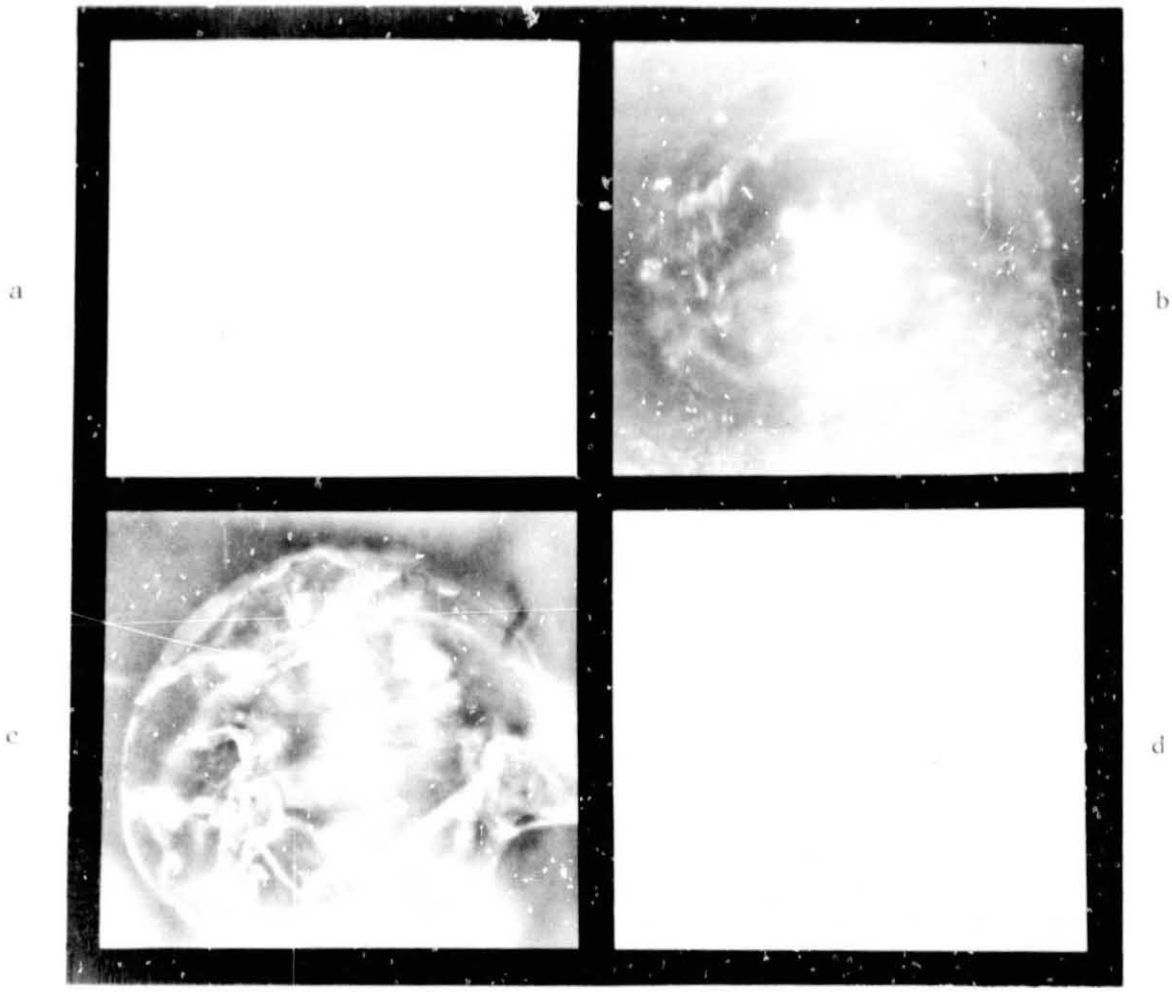
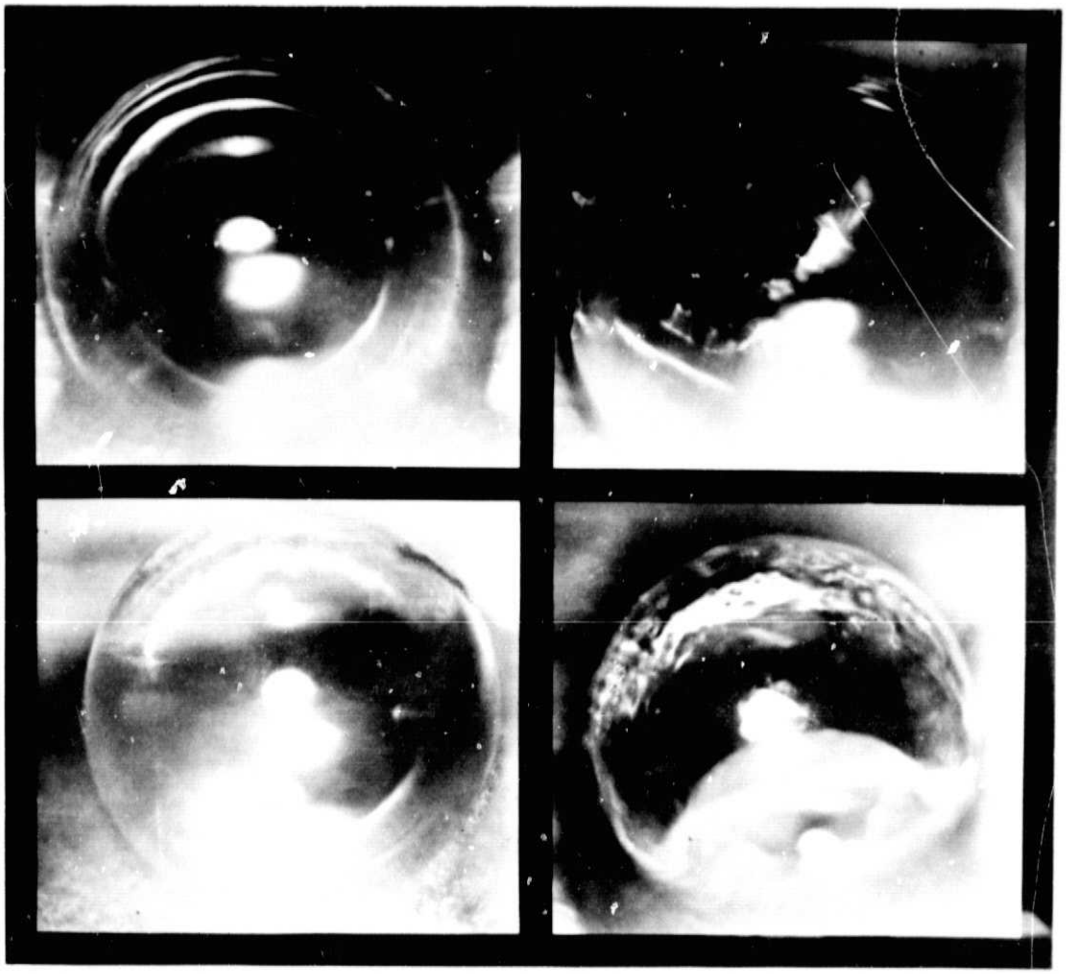


FIGURE 15. PHOTOMICROGRAPHS OF THE GMBS FOLLOWING LEVITATION AND HEAT TREATMENT (SEE FIGURE 14) (200X)



e f g h

FIGURE 16. PHOTOMICROGRAPHS OF THE GMBS FOLLOWING LEVITATION AND HEAT TREATMENT (SEE FIGURE 14) (200X)

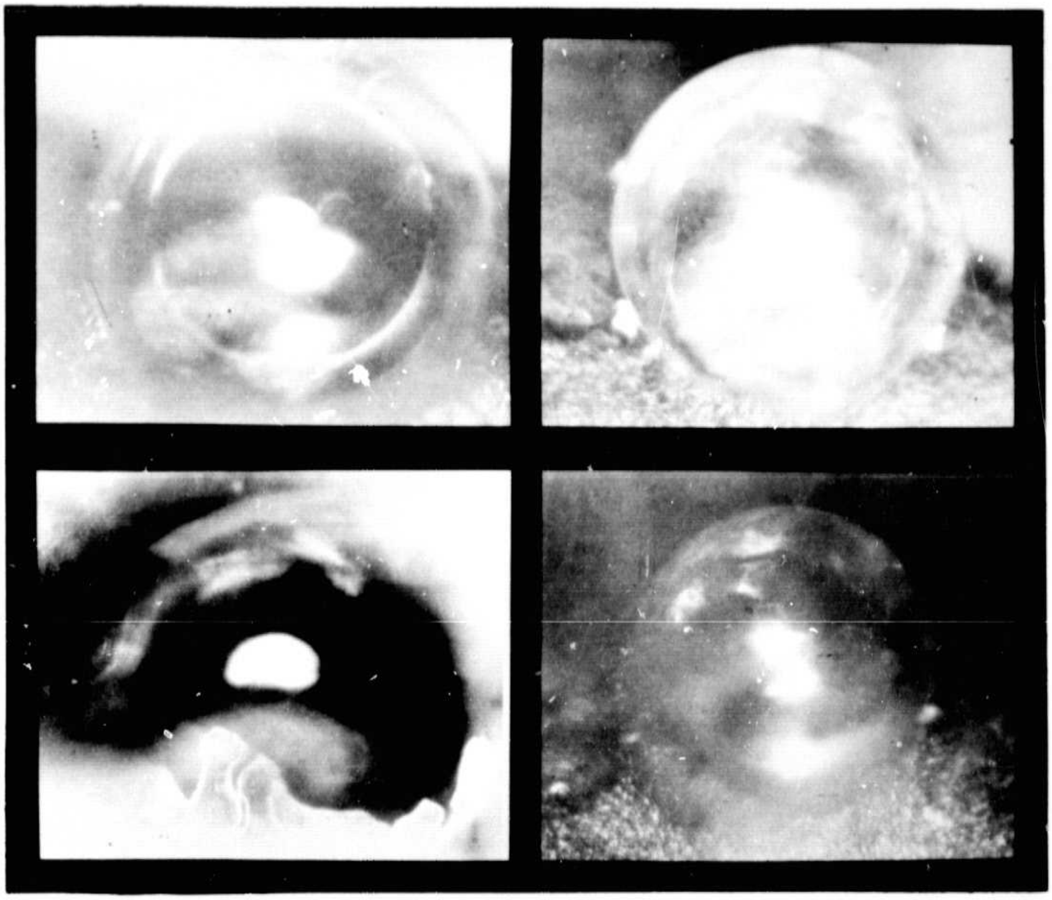


FIGURE 17. PHOTOMICROGRAPHS OF THE GMBS FOLLOWING LEVITATION AND HEAT TREATMENT (SEE FIGURE 14) (200X)

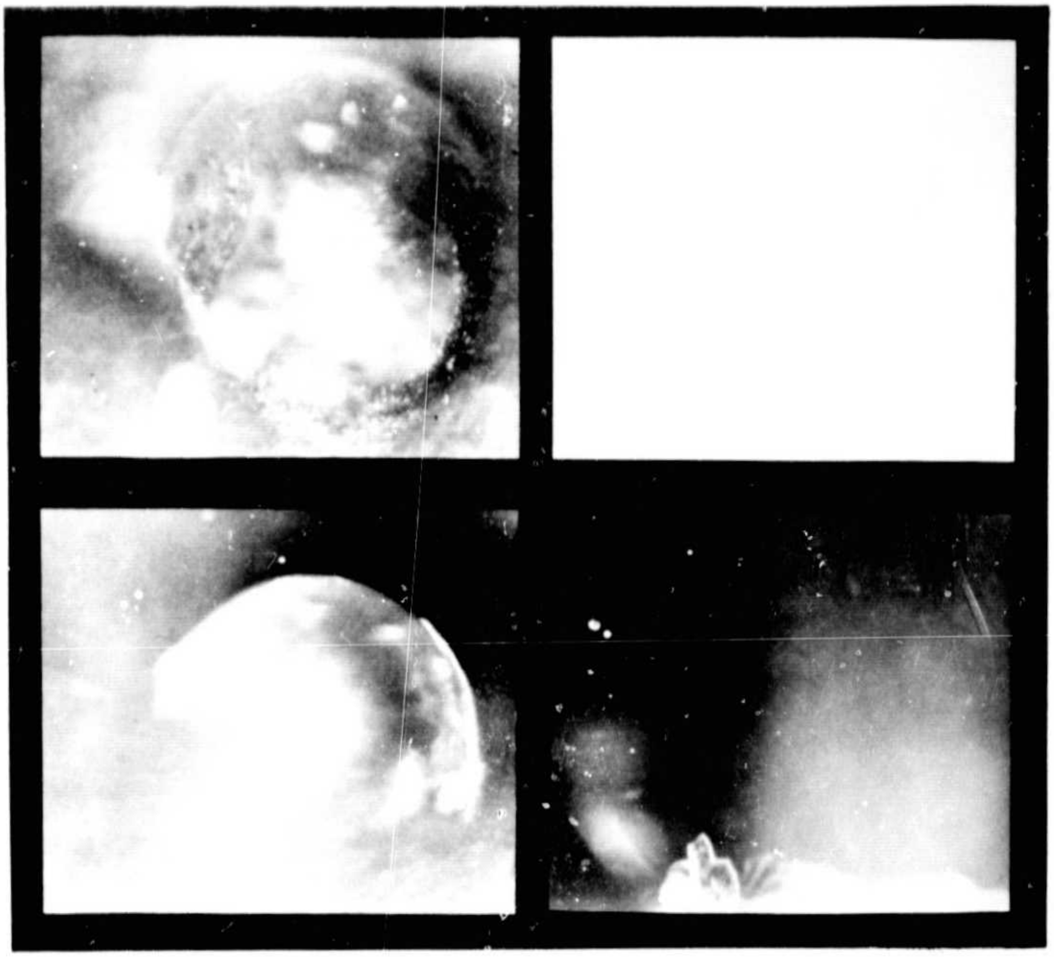


FIGURE 18. PHOTOMICROGRAPHS OF THE GMBS FOLLOWING LEVITATION AND HEAT TREATMENT (SEE FIGURE 14) (200X)

The puckering and/or collapse noted reflects a temperature of formation of the GMBs somewhat higher than that of either of the heat treatments. The degree of contraction is greater with the 900°C GMBs as would be expected.

Because of the difficulties in extending operating temperature above 1450°C GMBs of lower melting glass composition were sought for the next series of tests. GMBs provided by Los Alamos Scientific Laboratory designated BXX9 were selected. They were manufactured by 3M Company with a liquidus of 1288°C. Although details of the composition are proprietary, it was learned that the glass is primarily a sodium silicate containing 78% silica. The diameter of the BXX9 spheres is 230 ± 20 μm, appreciably smaller than the GMBs of the preceding series.

A 2^3 factorial series was designed to study the effects of levitating gas, time and temperature upon microsurface features of GMBs (Figure 19). Macrofeatures, such as wrinkles were to be ignored since as pointed out above, proper external pressure compensation had not been worked out for the reduction in internal pressure accompanying final cooldown. The plan called for temperatures above and below the liquidus of the BXX9 glass, namely 1100°C and 1400°C, heat treating times of five and 20 minutes and the two levitating gases, oxygen and nitrogen. Due to difficulties in designing and fabricating a functional jet equipped CHS, all experiments were conducted on a CHS without a jet.

It was found that the temperature of these smaller microballoons could not be raised at a rate much above 10°C per second without risking fracture and/or blowout. In all cases, temperature was raised as expeditiously as possible within this limitation. In the cooling mode much higher rates were tolerable and therefore employed in the interest of minimizing any devitrification not caused by the heat treatments themselves. The first reduction of 350°C was accomplished in about five seconds, the next 150°C in five more seconds.

The possibility of blowing out the GMB by raising its temperature too rapidly indicates that thin and thick sections of wall can be made to heat up at appreciably different rates by changing the temperature of the environment swiftly. The implication is strong that a rapid cooling regime followed by a carefully coordinated external pressure reduction can indeed be used to reduce disparities in GMB wall thickness.

Exposure (Minutes)	5		20	
Levitating Gas	O_2	N_2	O_2	N_2
Temperature (°C)				
1100	R	Q	S	V
1400	T	U	X	W

Z

Letter Designation of GMB

Figure 19. Factorial Plan of Levitating Conditions to be Studied Using BXX9 GMBs.

After the treatment temperature, 1100°C or 1400°C, had been attained it then became necessary generally to increase the flow rate again. The increase appeared to follow a shrinkage which was noted in most of the levitated GMBs. The shrinkage proceded most rapidly over the first three or four minutes of heating and at a much slower rate thereafter. While the aerodynamic lift varies with the square of diameter, the density factor in the Stoke's settling equation goes inversely with the cube, the net effect being that shrinkage without loss of mass requires an increase of levitating gas velocity inversely proportional to the first power of the GMB diameter. This proportionality, of course, would be altered by any accompanying change of mass as, for example, by volatilization of one or more components of the glass.

In general, the GMBs developed bubbles covering 10% to 30% of their surface area. During the heat treatment some of the bubbles burst, but even after twenty minutes of heat treating the craters of many of the bubbles remained behind. Photomicrographs afterward gave the appearance of a moonscape or a geodesic shell (Figures 20 and 21). In a few instances, bubbles were large enough to distort the generally spherical shape (Figures 20T and 21W). Even more distortion was caused when one or more of these large bubbles would blow out or burst (Figures 20R and 21S).

The ubiquity of the bubbles suggests that the BXX9 microballoons were formed in the first place with the aid of a gas dissolved in the glass and that the gas was by no means entirely removed during manufacture.

The persistence of the crater following the rupture of the bubble suggests a glass with a working point higher than that (ca. 700°C) of the BXX9 glass being used (see also Figure 16b). Sodium oxide (Na_2O) the second most concentrated component of the glass, has an appreciable vapor pressure (sublimination point 1275°C), at the two treating temperatures. It is possible, therefore, for the original liquidus temperature to rise as a result of loss of sodium oxide. The initial liquidus is above the lower of the two treatment temperatures, but a process such as this might raise it above the upper one as well. Thus, with either heat treatment, silica may precipitate. Such precipitation, of course, would provide a satisfactory explanation for the persistence of features on the molten GMB surface.

Other evidence was present to suggest phase separation at both treatment temperatures. There are several rosettes with hexagonal symmetry on one of the GMBs. And, nearly all of the GMBs exhibited under strong magnification, a fine wormy texture. The "worms" were of uniform

R Q

T U

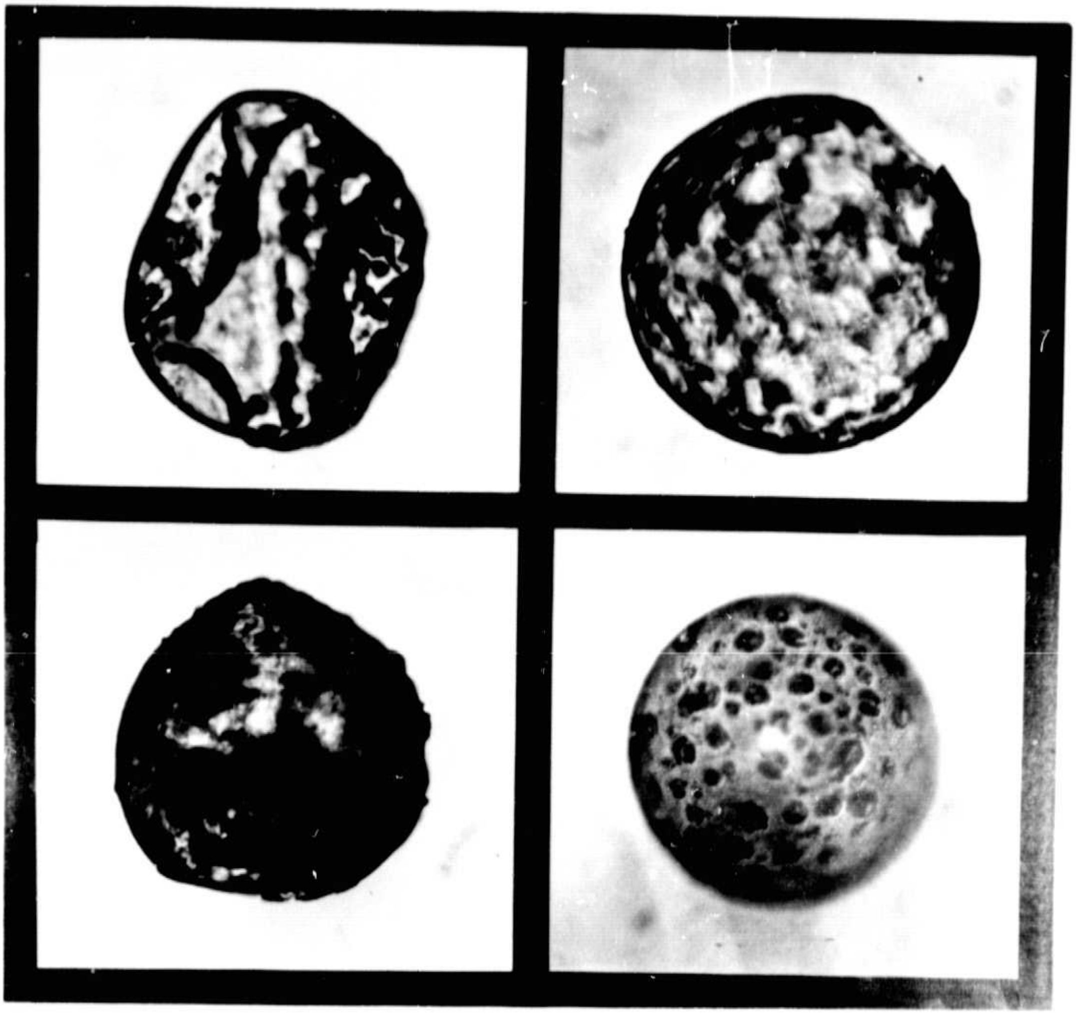
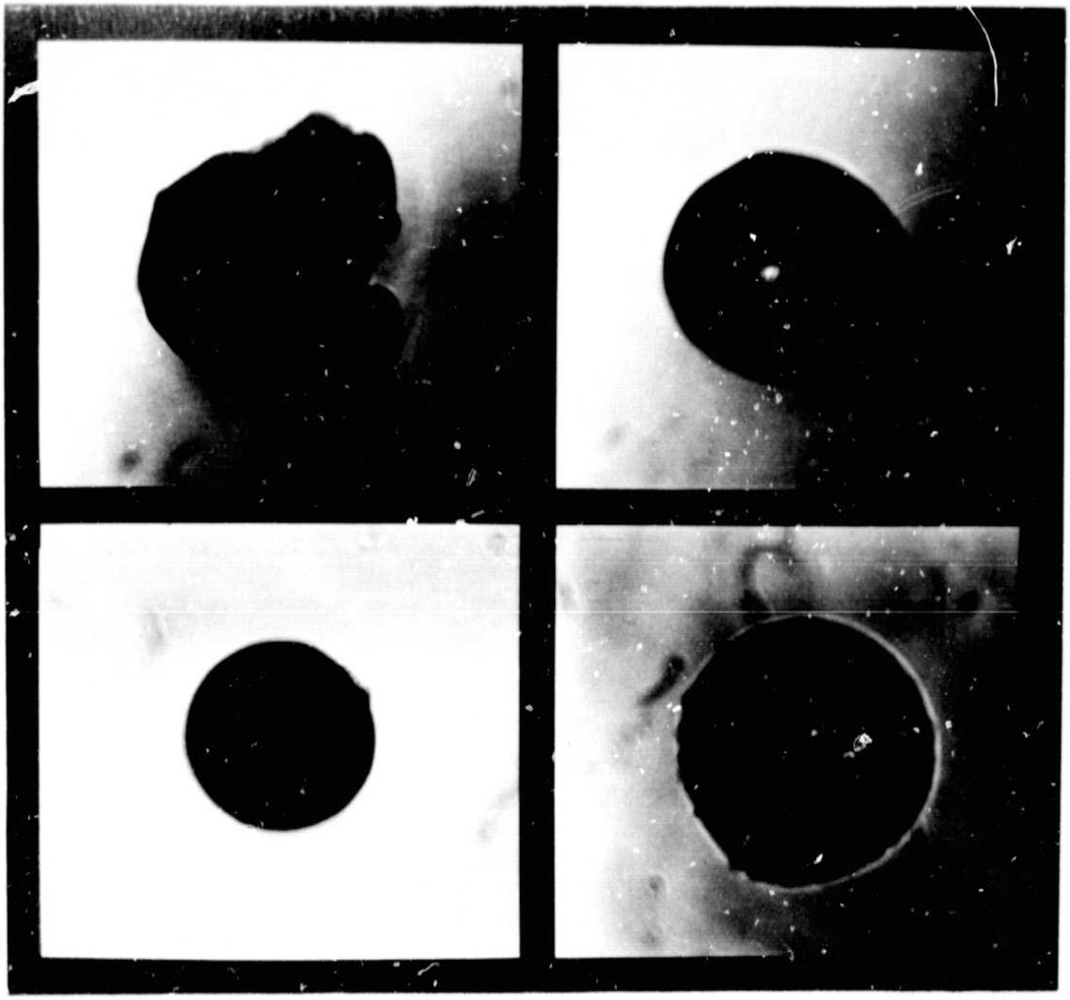


FIGURE 20. PHOTOMICROGRAPHS OF THE GMBS FOLLOWING LEVITATION AND HEAT TREATMENT

(SEE FIGURE 19) (200X)

S V



X W

FIGURE 21. PHOTOMICROGRAPHS OF THE GMBS FOLLOWING LEVITATION AND HEAT TREATMENT (SEE FIGURE 19) (200X)

width (ca. 5 µm) and spaced apart about an equal distance (Figure 22). Most of the features were rounded rather than angular suggesting that both phases were liquid rather than liquid and crystalline. The rosette fingers, however, were elongated and were oriented at 60° angles from one another, one of the dominant angles of crystalline silica.

Confirmation of the volatilization of the Na_2O came through the courtesy of Mr. Ray Downs of KMS Fusion. Mr. Downs analyzed the heat treated T2R85 samples of the previous test series by energy dispersive X-ray spectroscopy and found no sodium in GMBs treated at either treatment temperature. With potassium he obtained signals from the lower but not from the higher temperature treated GMBs.

The temperature and the treatment durations of the previous series of tests were both lower than those respectively in this latter series. These two factors would assure even higher loss rates of alkali metals in the present series of tests. This relatively greater alkali loss explains why other indications were more pronounced in the latter than in the former series.

To the eye aided by a microscope, the GMBs levitated in oxygen appeared to show more extensive frostiness, presumably devitrification, than did those levitated in nitrogen. The photomicrographs, unfortunately, fail to show this distinction.

The shrinkage mentioned earlier was assessed by measurements made on the photomicrographic images (Figure 23). The Grand Average final diameter was 179 µm, corresponding to a shrinkage of 51 µm from the original diameter of 230 ± 20 µm. This corresponds to over a 50 volume percent reduction, three to four times that attributable to thermal contraction. Diameters were not determined individually because of the many GMBs required in order to get eight of them clear through the test cycle. The initial population diameter, which was known to be fairly uniform, was assessed by randomly selecting and measuring several individuals.

Statistical analysis reveals one effect which is significant beyond the 95% confidence level, namely greater shrinkage occurs with the longer exposure time. Some gaseous diffusion constants are of the proper magnitude to account for such behavior through loss of gas by diffusing through the hot GMB wall.

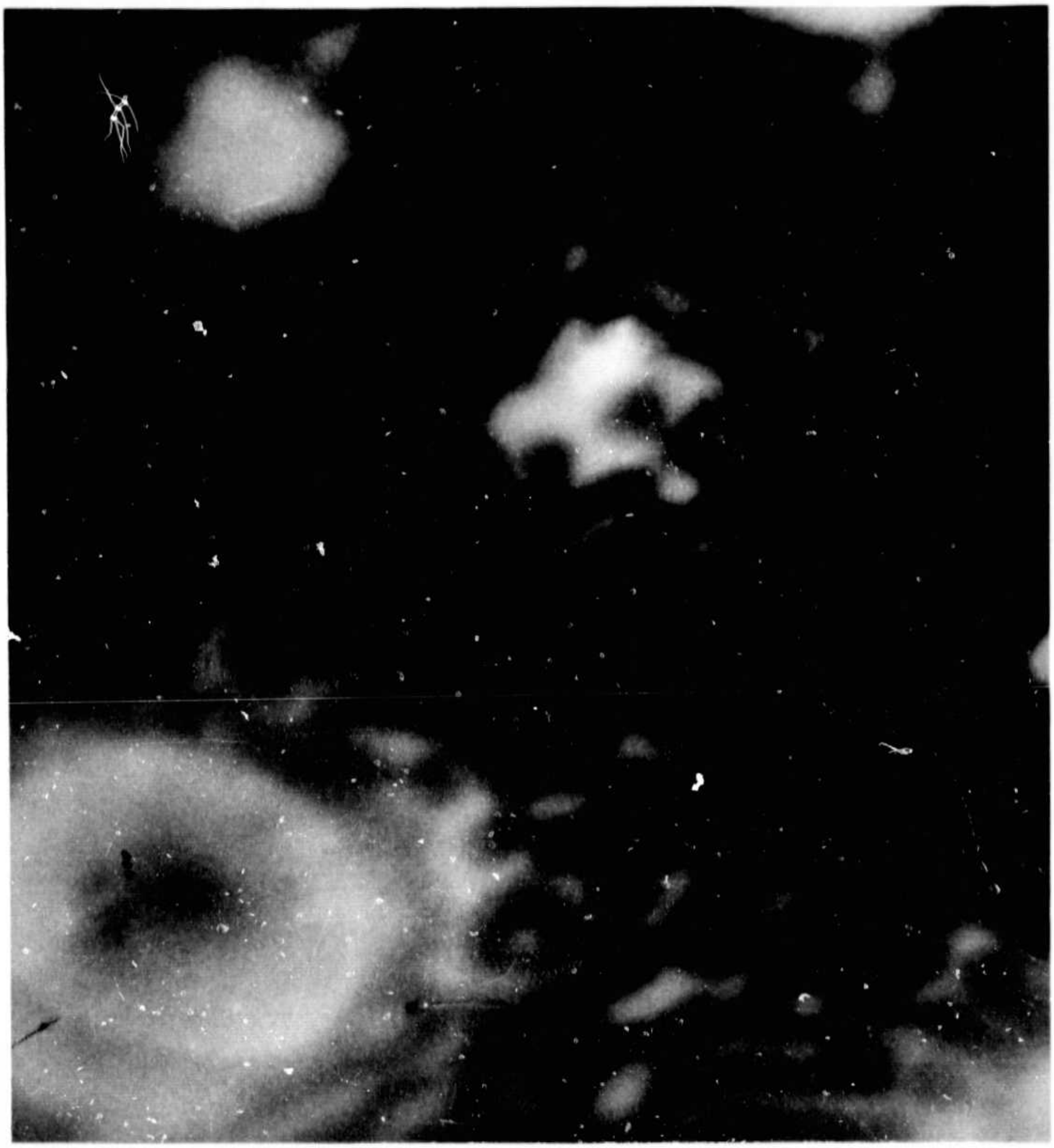


FIGURE 22. SEM PHOTOGRAPH (1000X) OF HEAT TREATED GMB SURFACE SHOWING "WORMY" TEXTURE (PHASE SEPARATION)

Duration (Minutes)	5		10	
Levitating Gas	O_2	N_2	C_2	N_2
Temperature (°C)				
1100	195	236	150	147
1400	197 .	204	111	195

XXX

GMB Diameter (10^{-6}m)

Figure 23. Effect of Levitating Conditions Upon GMB Shrinkage.

While no other effects attained the 95% level of confidence, that of levitating gas identity was significant between the 85% and 90% levels. The effect, such as it was, amounted to a greater shrinkage with oxygen than with nitrogen, as the levitating gas. Such an effect, if indeed it exists, may be related with the higher degree of devitrification associated with oxygen as the levitating gas. Oxidative atmospheres have been shown to stimulate devitrification relative to neutral and reducing ones [4]. It has also been demonstrated that bubble formation is fostered by the devitrification process and that the bubbles tend to accumulate at the solid-liquid (or sometimes liquid-liquid interface) [5]. The latter type process conceivably could shorten the effective diffusion path. In this way, oxygen by stimulating devitrification, together with its associated localized bubble formation, could account for the greater shrinkage rates observed.

It is reported that the gas content of the BXX9 GMBs is predominantly sulfur dioxide (SO_2) with much smaller amounts of oxygen and nitrogen. The volume shrinkage is of such magnitude as to require that the postulated diffusion be mainly of SO_2, though probably also including the oxygen and nitrogen.

A brief search failed to turn up any information on diffusion of SO_2 through glass. The proprietary nature of the BXX9 composition makes an extensive search for diffusion data of SO_2 futile. However, it can be inferred from size and bond type information that SO_2 might diffuse at a rate at least comparable to that of nitrogen. It is of comparable size but it should be more soluble in glasses in general because of its polarity.

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4) Ainslie, N.G., Morelock, C.R. and Turnbull, D., Devitrification Kinetics of Fused Silica, Symposium on Nucleation and Crystallization in Glasses and Melts, The American Ceramic Society, Inc., 97(1962).

5) Boffee, M., Percriaux, G, and Plumat, E., Formation of Bubbles During Devitrification and Remelting of Crystals in Glass, Symposium on Nucleation and Crystallization in Glasses and Melts, American Ceramic Society, Inc., 47(1962).

Primarily because of its much smaller size hydrogen (H_2) diffuses through most glasses more rapidly than nitrogen [6]. This might place the diffusivity of SO_2 somewhere between those of nitrogen and hydrogen. Accordingly, a BXX9 GMB was levitated in hydrogen. After ample time had been allowed to purge the furnace housing of oxygen, the GMB was heat treated for twenty minutes at 1200°C, 88°C below the initial liquidus. The diameter of the GMB was monitored through a 90X stereoscopic microscope having a calibrated reticle in one eyepiece. The initial diameter was 230 µm; measurement precision was ± 10 µm.

Two observations separate this experiment from any of its heat treatment predecessors: (1) the GMB remained clear and free of any indications of devitrification and (2) no indication of shrinkage was noted throughout the twenty minute heat treatment.

Bearing in mind that the treatment was sufficient to remove virtually all of the sodium and perhaps most of the potassium, the liquidus undoubtedly rose a number of scores of degrees from its initial value of 1288°C, thereby thrusting the glass deeper into the devitrification region. The absence, nevertheless, of visible evidence of devitrification is readily attributable to the effect of the reducing environment already mentioned. The absence of bubble formation may be due indirectly to the same cause. That is as already mentioned, bubble formation in some instances is fostered by devitrification, while the latter in turn, is a function of the oxidative character of the environment.

The absence of a detectable change in GMB diameter is suggestive of opposite but approximately equal diffusions of SO_2 outward and H_2 inward. In both cases the partial pressure differentials would have started out at or near one atmosphere and, if carried far enough, would have asymptotically approached zero. If the SO_2 and H_2 diffusion constants differed by less than an order of magnitude, the imbalance of diffusion might escape detection within the limit of measuring accuracy. Further, the loss of alkali might also tend to obscure an imbalance through its effect on increasing the stiffness of the GMB as the treatment and diffusion procede.

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6) Stanworth, J.E., Physical Properties of Glass, Oxford at the Clarendon Press, pp 119-123 (1950).