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IMPROVED QUALITY GSC-4 SEALING GLASS

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ABSTRACT

A glass commonly used to make graded seals between fused silica and higher expansion glasses, General Electric Company GSC-4, was remelted to obtain higher quality glass than is available commercially. Remelting the commercially available glass cane in a platinum crucible at 1700°C for periods of 40 to 60 hours produced a homogeneous glass free of crystalline inclusions and bubbles. During this melting, water was evolved and some constituents were lost from the surface layer. The bulk composition was not substantially changed and the remelted glass had approximately the same thermal expansion coefficient and viscosity as the original glass.

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Introduction

To form glass seals between fused silica and other glasses or ceramics, a graded seal must be used to distribute the stress which results from the difference in thermal expansion between the fused silica and the other members. Such graded seals may use General Electric Company GSC-4 glass to join to the fused silica. This glass consists essentially of SiO_2 and B_2O_3 . Owing to its large viscosity at high temperatures, it is very difficult to melt this glass and attain a homogeneous glass free of bubbles and residual crystals.

The glass is only available from the General Electric Company as cane approximately 1/8 inch in diameter. To form tubing the cane must be wrapped around a mandrel and flame worked to form a tube. Since the rod is generally of poor quality with regard to bubbles and inclusions, the glass blower must select the best portions of the cane and discard the rest.

The purpose of this work was to obtain higher quality GSC-4 glass which was free of bubbles and inclusions and had approximately the same thermal expansion coefficient as original GSC-4. An additional objective was to obtain this higher quality glass in a form which could more easily be shaped into tubing than the rod.

Experimental Procedure

Lengths of GSC-4 cane were broken into ~ 2 inch segments and placed in a platinum crucible 3.5 inch x 4.5 inch tall. The glass was melted in an electric furnace* at 1700°C in air for 40-60 hours to remove the

*DT31 High Temperature Laboratory Furnace, Deltech, Inc., Denver, Colorado.

bubbles. The crucible was covered with a platinum sheet.

Since the glass was very viscous, and also because it was desirable to keep the surface layer isolated from the bulk of the glass, no attempt was made to cast the glass. It was cooled in the melting furnace to $\sim 600^{\circ}\text{C}$, at which time the crucible was transferred to an annealing oven. The glass was held at the annealing point for 3 to 4 hours then cooled at $50^{\circ}\text{C}/\text{hour}$ to 300°C , at which time the oven was turned off.

Rods of glass were removed from the crucible by diamond core drilling the glass to within $1/8$ inch of the bottom, then tapping the crucible with a mallet to break the cores free. Cores ranging from $1/4$ inch to 2 inches in diameter with lengths of up to 2 inches were obtained.

To determine if there was a significant change in composition during remelting, portions of the glass from the bottom of a core and the top 0.030 inch of a core were analyzed and compared to the original glass.

To ascertain how much water was being lost during the remelting process, the IR transmittance of a piece of remelted glass was compared to a specimen of the as received material which had been heated and flattened to form a sample suitable for the measurement.

Thermal expansion of a remelted sample was compared to the original glass by making a pull sample (P.R. Farina, 7121). In addition the thermal expansion of each material was measured with a dilatometer.

Since the loss of water and/or a change in composition can affect the viscosity of a glass, the viscosity of the remelted GSC-4 was measured and compared with the as received materials using a beam bending viscosity apparatus, as previously described by Shelby.[‡]

Results and Discussion

An analysis of GSC-4 (performed in 1967) is shown in Table I along with B_2O_3 and Na_2O analyses which were done to compare the remelted material to the as received GSC-4.

There appears to be some difference between the GSC-4 of 1967 and the material currently being used. This difference in composition is not inconsistent with differences from batch to batch found in industrial glass melts. The analyses of the remelted material and the as received material showed no significant loss of the volatile Na_2O and B_2O_3 occurred in the bulk glass.

Residual stress present in the core drilled slugs near the surface, apparently due to differential thermal expansion, suggested that the surface layer was of slightly different composition. Chemical analysis was performed on the top 0.030 inches of the glass. The layer of different composition was apparently a very small portion of this sample, therefore no significant change in composition was detected.

[‡]J. E. Shelby and R. L. Bertolotti, "Annealing of MC2649 Glasses", SCL-RR-710346.

TABLE I
Analysis of GSC-4 Glass

1967 ANALYSIS*		AS RECEIVED [±]	REMELTED TOP [±]	REMELTED BOTTOM [±]
	wt%			
SiO ₂	83(By difference)	---	---	---
B ₂ O ₃	15.5±1	18.0±1	19.1±1	20.5±1
Al ₂ O ₃	0.84±.08	---	---	---
Na ₂ O	0.8±0.1	0.61±0.1	0.55±0.1	0.63±0.1

*D. E. Wanner & B. T. Kenna

[±]D. Anderson, 5521

The concentration of water in glass may be determined from IR transmission spectrum using the Beer-Lambert Law (Equation 1).

$$C = \frac{1}{Ed} \log \frac{1}{T} \quad (\text{Eq 1})$$

C - concentration of water

E - extinction coefficient

(70 l mole⁻¹ cm⁻¹)

d - thickness of piece (cm)

T - transmittance

This calculation showed the concentration of water was reduced from 0.020 wt% to 0.013 wt% by remelting the glass. The water present in the glass initially probably came from boric acid (H₃BO₃) used as a raw material to form the glass melt. Incomplete melting of the glass, as evidenced by the presence of many gas bubbles and some crystal fragments, could account for the higher concentration of water in the as received glass.

The thermal expansions of the original and remelted glass are listed in Table II and shown in Figure 1. As suggested from the pull test, the expansion of the glass did not change significantly after remelting.

The viscosity of GSC-4 rods as received and rods made from remelted glass are shown in Figure 2. The data listed in Table III show the relation of specific viscosities to temperature. The raw data are summarized in the Appendix.

TABLE II

Thermal expansion of GSC-4 before and after 60 hour remelt.

Sample	Average Thermal Expansion Coefficient ($\times 10^6 \text{ } ^\circ\text{C}^{-1}$)		T_g ($^\circ\text{C}$)
	(25-300 $^\circ\text{C}$)	(25- T_g $^\circ\text{C}$)	
As received, clear	2.27	1.58	538
As received, grey	2.26	1.58	540
Remelt, sample #1	2.17	1.37	538
Remelt, sample #2	2.20	1.45	541

TABLE III

Viscosity of GSC-4 before and after 60 hour remelt.

Sample	Viscosity Temperature Relationship				E_a <u>kcal</u> mole
	10^{10} poise	10^{11} poise	10^{12} poise	10^{13} poise	
As received, (clear)	693 $^\circ\text{C}$	643	595	551	75
As received (gray)	700	647	600	558	79
Remelt (#1)	696	636	594	551	80
Remelt (#2)	690	638	591	547	75

Figure 1 Thermal Expansion of GSC-4 Glasses.

Figure 2 Viscosity of GSC-4 Glasses.

The change in concentration of water did not appear to change the thermal expansion or viscosity of the GSC-4. It was anticipated that the loss of water during remelting would increase the viscosity of the glass. Apparently when dealing with such low concentrations of water, the effect of changing the concentration on viscosity is negligible.

Samples of the remelted glass submitted to the Scientific Glass Laboratory (Sandia, Albuquerque) were found to soften and work the same as commercial GSC-4, except no bubbles were generated. It was also found that good quality tubing could be formed by drawing from a thick walled tube produced by drilling cores from the bulk glass. (R. D. Snidow and P. R. Farina, 7121-4).

Conclusions

Remelting of General Electric GSC-4 in an electric furnace for 40-60 hours at 1700°C produced bubble free glass with properties similar to commercial GSC-4. The glass was essentially unchanged, except for the loss of the gas which caused the bubbles. The remelting procedure described here can be used to prepare high quality GSC-4 glass for forming graded seals.

APPENDIX

TABLE I. VISCOSITY OF GSC-4 GLASS AS RECEIVED*

Clear Rod		Dark Rod	
Temperature (°C)	Viscosity (poise)	Temperature °C	Viscosity (poise)
500	6.69×10^{13}	503.5	1.26×10^{14}
518	3.77×10^{13}	526	5.54×10^{13}
532	2.57×10^{13}	543.5	2.64×10^{13}
545.5	1.34×10^{13}	557.5	1.07×10^{13}
556	7.56×10^{12}	572	4.56×10^{12}
566	4.60×10^{12}	586	2.33×10^{12}
576.5	2.88×10^{12}	599.5	1.09×10^{12}
586	1.75×10^{12}	612.5	5.75×10^{11}
594.5	1.04×10^{12}	612.5	5.92×10^{11}
603	6.44×10^{11}	621	3.55×10^{11}
603	6.41×10^{11}	634.5	1.89×10^{11}
612.5	4.26×10^{11}	634.5	1.96×10^{11}
622	2.66×10^{11}	647.5	9.57×10^{10}
632.5	1.61×10^{11}	661.5	5.09×10^{10}
641.5	1.04×10^{11}		
651.5	6.50×10^{10}		
661.5	4.17×10^{10}		
672	2.62×10^{10}		
682	1.68×10^{10}		

*Measurements made by W. L. Chrisman, 8334.

TABLE II. VISCOSITY OF GSC-4 GLASS REMELTED 60 HOUR

Sample No. 1		Sample No. 2	
Temperature (°C)	Viscosity (poise)	Temperature (°C)	Viscosity (poise)
501	6.75×10^{13}	511.5	4.37×10^{13}
509.5	5.54×10^{13}	521.5	3.96×10^{13}
520.5	3.80×10^{13}	532	2.45×10^{13}
534	2.13×10^{13}	542.5	1.38×10^{13}
544	1.37×10^{13}	553	7.62×10^{12}
548.5	1.13×10^{13}	562	4.67×10^{12}
554.5	8.68×10^{12}	572	2.81×10^{12}
564.5	4.78×10^{12}	582.5	1.53×10^{12}
575	3.09×10^{12}	593.5	8.63×10^{11}
584	1.94×10^{12}	602.5	6.26×10^{11}
595	1.10×10^{12}	602.5	5.31×10^{11}
603.5	6.39×10^{11}	613	3.37×10^{11}
612	3.87×10^{11}	623	2.07×10^{11}
623.5	2.07×10^{11}	633.5	1.24×10^{11}
624	2.09×10^{11}	632.5	1.36×10^{11}
634	1.172×10^{11}	641.5	8.61×10^{10}
644.5	7.02×10^{10}	652	5.11×10^{10}
644.5	9.10×10^{10}	662	3.24×10^{10}
654.5	6.06×10^{10}	673	1.99×10^{10}
664.5	3.40×10^{10}	683.5	1.30×10^{10}
673.5	2.39×10^{10}	694	8.16×10^9
687	1.41×10^{10}		

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