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MACOR™
Machinable
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Technical Paper

Vacuum Compatibility of Machinable Glass Ceramics

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Abstract

The thermal outgassing and helium permeation characteristics of Macor™ machinable glass-ceramic are discussed. Up to 600°C it is shown that this material can be treated like glass vacuum system components. The quantities of outgassing constituents under vacuum conditions are given and the need for vacuum baking freshly machined material is demonstrated.

Although the material can be used up to 1000°C, between 600°C and 1000°C some fluorine evolution from the material takes place and could present a corrosion problem to some systems. Helium permeability of this material is an order of magnitude lower than for Code 7740 glass.

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Introduction

The degree of vacuum attainable in any vacuum system depends on a balance between the speed of the vacuum pumping system employed and the leakage, either real or virtual, into the system. Real leaks can be closed, while virtual leaks, such as permeation through the material or outgassing from the material, must be eliminated by choosing the proper materials to be used in the vacuum system.

The machinability of Code 9658 Machinable Glass-Ceramic (MGC)^a makes it ideal for various uses within high vacuum systems provided its virtual leakage is low enough. In addition to machinability, this material is non-magnetic, has a thermal expansion compatible with most metals, is chemically durable, and provides excellent electrical insulation.

The properties of MGC as well as its mica-like structure have been discussed by Beall¹. The use of MGC at cryogenic temperatures has also been investigated by Lawless². Although this material is being used in many vacuum applications, nothing has been published on its vacuum compatibility. This paper presents the helium permeability and thermal outgassing characteristics of MGC. The effect of ceramming the green glass as well as the need for outgassing freshly machined MGC is discussed in such a way as to give the potential user some idea of the quantities of gas he can expect to be evolved with and without thermal treatments.

(a) Code 9658 MGC is sold under the trade name of MACORTM by Corning Glass Works. Use of the trade name is essential since other mica-glass-structured materials do not have the same outgassing characteristics.

Thermo Outgassing

It is well known that in order to achieve high vacuum conditions or to maintain reasonable vacuum without continuous pumping, it is generally necessary to first 'bake-out' the system or the materials to be used in the system. Glass or glassy materials are no exception to this general rule.

Todd³ has shown that for ordinary glasses, the gas evolved due to thermal bake-out is primarily water and that the water evolution can be described as a diffusion process. Todd also determined that several hours of vacuum baking at 500°C will effectively remove water from the first 10 to 20 microns from the outer surface.

The method⁴ used to determine the gases evolved thermally involves using a mass spectrometer (MS) as a selective flow meter. The bakeout chamber is a 1½ inch diameter fused silica tube which is connected directly to the source of a CEC-620 cycloidal MS (no limiting conductance). The outgassing rate from the samples actually becomes the controlling leak to the MS.

With the MS calibrated in terms of flow rate for each of the gases monitored, the sample is heated in steps up to 1000°C and the resulting flow curves recorded. These curves are then integrated over time to obtain the total quantities of each gas.

The MS data for the water evolution from a freshly machined surface of MGC is plotted in Fig. 1. At each successive temperature step the water flow rate increases rapidly and then decreases exponentially. Each step is approximately 40 minutes in duration. The dashed lines indicate the expected decay to system background if the temperature were not raised.

Figure 1
Water flow curves for a freshly machined surface (FMS). Flow Sensitivity = 9.3×10^{-6} Torr-cm³/s-div.

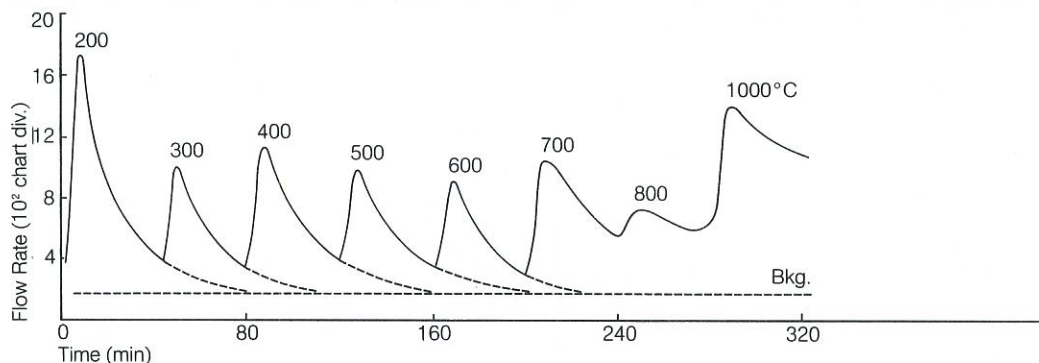


Table I

Gases Evolved From Code 9658 Machinable Glass-Ceramic^(a)

T(°C)	Freshly Machined Surface ^(b)					As-Cerammed Surface ^(b)		
	H ₂ O	CO/N ₂	CO ₂	HF	BF ₃	H ₂ O	CO/N ₂	HF
200	21.9	0.20	0.09			0.4	0.05	
300	31.9	0.95	0.45			1.6	0.19	
400	43.3	2.5	1.1			3.1	0.44	
500	53.8	3.4	1.3			4.9	0.58	
600	65.1	3.9	1.5	Trace		6.6	0.70	
700	77.7	4.6	1.8	1.2				
800	89.6	7.1	2.0	3.7	4.8	7.8	1.6	
1000	113. (c)	21.9	3.3	26.1 ^(c)	21.5	12.7 ^(c)	4.6	4.8 ^(c)
						No NF ₃ observed		

(a) All quantities are cumulative totals in units of Torr-cm³ at 25°C.

(b) Samples were 1.4 mm thick with a surface area of 26.5 cm².

(c) Quantity of HF and H₂O at 1000°C integrated for first 40 minutes only (see Fig. 2).

Table I lists the cumulative total quantities of each gas evolved at each temperature step for a sample with a freshly machined surface (FMS) as well as for one with an 'as-cerammed' surface (ACS). The CO/N₂ column is essentially all CO up to 800°C. At 1000°C, the mass 28 peak changes so rapidly that one can not differentiate between N₂ and CO. Minor quantities of CO₂ were observed for the 'as-cerammed' sample but are not listed in Table I.

It is rare that materials used in high vacuum environments are required to be used or even baked out at temperatures above 500°C. Therefore, let us divide the use of MGC into two different categories; normal usage below 600°C and high temperature usage above 600°C.

Normal Vacuum Bake-outs (<600°C) As can be seen from the regular, rapidly decaying water flow curves below 600°C of Fig. 1, Code 9658 MGC behaves similarly to glasses when heated in vacuum and water is removed effectively. One would then expect that for use at room temperature, a short bake-out at 200°C or 300°C should be quite adequate to remove surface water and reduce the rate of outgassing to a negligible amount at use temperature.

Table II

Water Evolved after 1 hour bake-outs

T(°C)	Quantity of Water in ½ hour (Torr-cm ³)	
	After 300°C Bake	After 500°C Bake
100	Nil	Nil
200	0.8	Nil
300	—	0.5

Table II shows some outgassing data for the same size sample as used in Table I after baking for 1 hour at 300° and 500°C. After the 300° bake-out, no measurable water is observed at room temperature or 100°, and only 0.8 Torr-cm³ was measured in ½ hour at 200°C. Similarly, after a 1 hour bake at 500°C, there is only 0.5 Torr-cm³ water in the first ½ hour evolved at 300°C. Longer bake-outs would obviously reduce these figures further.

Comparison of Table II with the as-cerammed surface data in Table I would indicate that, although the ceramming schedule which bakes the material to >1000°C is an efficient outgassing mechanism, it is not as efficient for removing water from near the surface as is a vacuum bake at 500°C. The reason for this is that no special precautions are taken to assure a dry atmosphere during ceramming. The degree of water loss from the sample is very dependent on the partial pressure of water next to the surface.

High Temperature Bake-out (>600°C) From 700° to 1000°C (Fig. 1) we see that there is no longer the rapid decay in the water evolution curves. This is not completely understood, but it is believed that simple diffusion from the first few microns depth is no longer the only process taking place. From 600° to 700°C we also begin to see some fluorine evolution from the sample.

Code 9658 MGC is basically a crystallized fluorophlogopite mica phase within an aluminoboro-silicate glassy matrix! At these higher temperatures, we believe sufficient energy is available to free fluorine from the crystalline phase and this fluorine then diffuses out through the glass as the ion F^- . Upon reaching the sample surface (or the surface of the vacuum system) sufficient water is always present to react with F^- to form HF gas. It is the HF that we measure in the mass spectrometer.

The quantities of HF become more significant above 800°C as shown in Fig. 2 for both the 'freshly machined surface' and the 'as-cerammed surface'; the latter data again reflecting the outgassing which already resulted due to ceramming.

Figure 2
Fluorine evolution and its effect above 800°C. FMS—Freshly machined surface, ACS—As-cerammed surface.

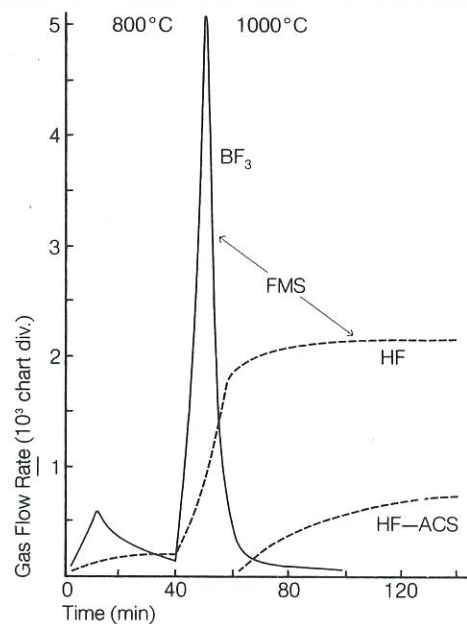
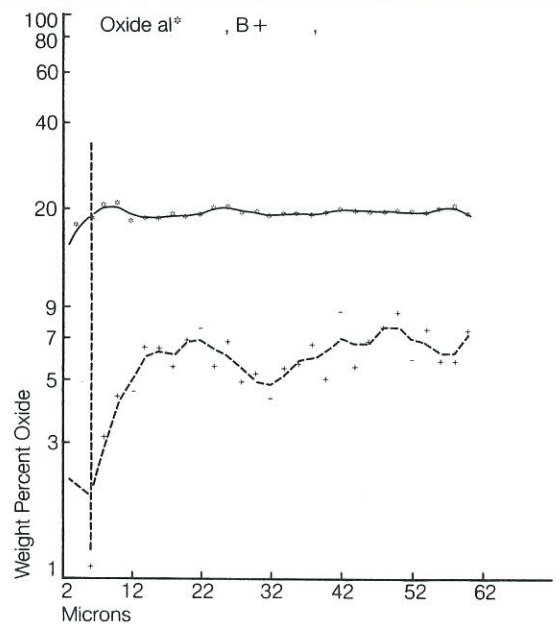


Figure 3
Electron microprobe profile for boron and aluminum oxides after 1000°C. bake of freshly machined surface. (Vertical dashed line is best estimate of sample edge.)



Wherever HF is present along with a boron-containing material, in this case the sample itself, it is not surprising to find BF_3 gas. Of special interest is the very rapid rise and drop-off of the BF_3 flow rate at 1000°. The fact that the BF_3 decreases to practically zero while the HF evolution increases to a steady level indicates that the boron source is being depleted. Therefore, if, as we believe, the boron is merely etched from the surface of the MGC by the HF, then there should be a definite depletion of boron from the surface.

To check this, a piece of the FMS sample, after the outgassing shown in Fig. 2, was cross-sectioned and several boron profiles were measured with an electron microprobe⁵. Fig. 3 shows a typical profile for B_2O_3 and Al_2O_3 . The oxide of Al was profiled to help determine the exact location of the sample edge (shown by the dashed vertical lines). The boron profile clearly indicates a depletion of boron to a depth of approximately 10 microns. The removal of boron from the surface at 1000°C also explains why no BF_3 was observed during outgassing of the sample with the 'as-cerammed surface'.

The outgassing data discussed thus far involves only those gases that are non-condensable. The outgassing apparatus from bake-out furnace to MS detector never exceeds 200°C; therefore, if species that condense above this temperature were present they would go undetected. To determine if condensable species were present, a 10 cm² sample of FMS material was placed in our Knudsen-cell type high temperature mass spectrometer and studied up to 1000°C⁶.

In addition to water and HF already discussed, only very small amounts of potassium vapors were observed from 650° to 1000°C. These results are shown in Table III. At 650°C, for instance, the potassium evolution was calculated to be 0.8 picograms per second. To put this in perspective, 1 Torr-cm³ of water is equivalent to 1 microgram. So at 650°C, the ratio of water to potassium evolved in a half hour assuming no depletion of potassium would be equal to 5×10^4 .

Table III

Potassium Evolution from MGC (10 cm² sample area)

T (°C)	P _K (Torr)*	Max. Flow Rate** (grams/s)
650	1.2 x 10 ⁻⁷	0.8 x 10 ⁻¹²
1000	2.0 x 10 ⁵	104 x 10 ⁻¹²

*P_K is partial pressure of K in Knudsen cell.

**Flow rate calculated from conductance of Knudsen cell effusion hole.

Helium Permeability of MGC

The helium permeability measurements were made on a gas diffusion system attached to a CEC-21-104 MS. The typical procedures used for this type measurement have been described elsewhere⁷. Thin-walled cylinders were made by drilling the center hole and machining off the outside from a piece of one-half inch stock. The active thin section was 91 mm long with inside and outside diameters of 6.4 and 7.7 mm respectively, so that the average wall thickness was 0.65 mm. The half-inch thick walled end section was then attached to the vacuum system via standard Swagelok® connectors using Teflon® bushings.

A steady state solution of the diffusion equation for a cylinder is given by⁸:

$$P = \frac{q}{t\Delta p} \frac{\ln b/a}{2\pi l}$$

where q/(tΔp) is the flow rate per unit pressure gradient, b and a are outside and inside diameters respectively, and l is length of the cylinder.

Steady state helium flow measurements were made at eight different temperatures from 150°C to 450°C. 450°C was about the upper temperature limit for the Teflon® bushings used in the Swagelok® connectors. Table IV lists the temperature, flow rate to pressure ratios, and permeation constants in conventionally accepted units. A least squares fit of the data in Table IV yields the following equation for P:

$$P = 5.4 \times 10^{-8} \exp\left(\frac{-7240 \text{ cal/mole}}{RT}\right)$$

A typical Arrhenius plot of the permeation data for Code 9658 MGC is shown in Fig. 4 along with similar plots for some well known glasses⁷. The very hard and tight structured alumino-silicate glass (1723) and the softer soda-lime glass (0080) are less permeable than is MGC. Code 9606 is a glass-ceramic while Code 7740 glass is the most commonly used boro-silicate glass for vacuum applications. Code 9658 MGC is at least one order of magnitude less permeable to helium than is Code 7740 glass throughout the temperature range studied.

Figure 4
Helium Permeability of Code 9658 MGC compared to some common glasses

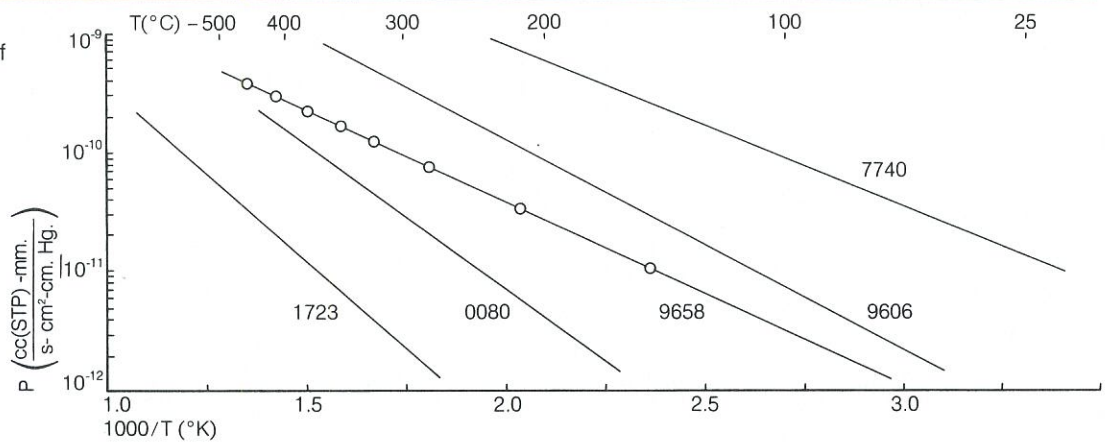


Table IV

Helium Permeation Constants—Code 9658 MGC

T (°C)	$\frac{1000}{T(^{\circ}\text{K})}$	$\left(\frac{q}{t\Delta p} \frac{\text{Torr-cm}^3}{\text{s-Torr}}\right)$	P $\left(\frac{\text{cm}^3(\text{STP})\text{-mm}}{\text{s-cm}^2\text{-cm. Hg.}}\right)$
154	2.34	2.52×10^{-8}	1.05×10^{-11}
218	2.04	8.10	3.37
277	1.82	1.59×10^{-7}	6.62
320	1.69	2.90	1.20×10^{-10}
355	1.59	3.75	1.56
388	1.51	5.12	2.13
427	1.43	6.80	2.83
450	1.38	9.11	3.80

Conclusions

In the normal vacuum use temperature range (25°C to 600°C), the outgassing and diffusion characteristics of Code 9658 machinable glass-ceramic are essentially the same as for glasses used in vacuum system construction. Its helium permeability is about one order of magnitude lower than that of Code 7740 glass in this same range. There should be no problems encountered in using Code 9658 MGC in high or ultra-high vacuum systems, even as the vacuum container material, so long as it receives a reasonable vacuum bake-out at a slightly higher than its intended use temperature.

The above is probably also true above 600°C, but a word of caution must be added. Although the material can be taken as high as 1000°C, at these high temperatures some fluorine diffusion from the material will take place and, even though these quantities are extremely small, they could be corrosive to certain systems.

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References

- ¹ G. H. Beall, *Advances in Nucleation and Crystallization of Glasses* (L. L. Hench and S. W. Freiman, eds.) Amer. Cer. Soc. Spec. Publ. No. 5 (Freiman, Columbus, 1971) p 251.
- ² W. N. Lawless, *Cryogenics*, May 1975, p 273-277.
- ³ B. J. Todd, *J. Appl. Phys.* V26, No. 10, 1238-1243, Oct. 1955.
- ⁴ This method has been briefly described in an earlier paper by J. P. Williams, et al, *Amer. Cer. Soc. Bull.*, V55, No. 5, May 1976.
- ⁵ T. W. Bierwiler and W. R. Kane of this laboratory, private communication.
- ⁶ The High Temperature Mass Spectrometer is a Nuclide Model 12-90-HT.
- ⁷ V. O. Altemose, *J. Appl. Phys.*, V32, No. 7, 1309-1319, July 1961.
- ⁸ R. W. Barrer, *Diffusion In and Through Solids*, Cambridge Press, New York, 1941.