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FIFTH PROJECT REPORT

to

Sandia Corporation

Contract 57-1967 (dated 2/21/67)

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M. E. Nordberg, collaborating
with Mr. T. H. Elmer, Mr. V. O. Altemose, Dr. C. B. King
Mr. R. G. Foster & Mr. L. A. Pauls

Corning Glass Works

[redacted]

Classified By R G Hogan

Date 10/27/67

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This report covers work on Contract 57-1967 with Sandia Corporation, Albuquerque, New Mexico, that was carried on in August and the first three weeks of September, 1967.

During this period, the new CEC, type 21-104 mass spectrometer was received, installed and calibrated to a point where significant measurements could be made at flow rates down to about 10^{-7} cc (STP) per second.

Measurements were made on a variety of oxide films on porous glass, and on fully impregnated and fired porous glass drawn into capillaries. Corning brand fused silica, Code 7940, was also measured. It gave surprisingly low He/H_2 flow ratio of only about 200. Capillaries of Amersil fused silica were obtained from Sandia for flow rate and ratio measurements.

Most encouraging data are those on a sample (No. VA-32 in Mr. Altemose's section) of porous glass coated by Mr. Elmer with alumina from a solution spray. A helium flow rate of 2.4 cc/sec./atm. was obtained on a sample with an area of 11.2 sq. centimeters. The He/H_2 flow ratio is reported in the range 400 - 670, the wide range resulting from uncertainties in the H_2 flow extrapolation to low temperatures.

Pin holes in the films present a problem. Exposing samples to water vapor at 1000°C/hr. has been reported helpful in sealing these holes. Impregnating the porous glass at the pin hole by dipping the filmed tube in an alkali-borate solution and then firing has also produced leak-free samples.

A new technique for depositing oxide films is under development. Solutions containing compounds of the elements desired in the film are introduced into the furnace holding the porous glass sample by means of a fine spray.

Sealing tests along the lines discussed at Sandia in July (see Fourth Project Report) were started. Wetting of tungsten with solder glass (Code 7574 cement) was not good in the preliminary tests. This difficulty could undoubtedly be solved, but further developments along this line have been stopped in the laboratory, at least until the development of a reliable film-type filter and a process for producing it.

Mr. Pauls reports that the "thimble"-forming system, and the glass melting unit were 80% complete. However, all work was stopped early in September pending release of Government platinum. The unit can be in operation three weeks after receipt of platinum at the Corning Glass Works Platinum Shop.

Martin E. Nordberg
(Martin E. Nordberg)

Date: October 26, 1967

MEN:lh

Methods of Producing Impervious Layers on Porous Glass

- T. H. Elmer

1. Treatment of Porous Glass

Presintered porous glass tubes were coated with du Pont's BAYMAL by immersing the porous section in sols containing from 1 to 4 wt. % BAYMAL. They were rinsed in distilled water to remove excess BAYMAL, oven dried at 160°C, and then subjected to potassium borate and boric oxide vapors to produce impervious glassy skins for gas permeation studies.

A sample which had been treated in the above manner was found to have a separation factor of about 470. Microprobe analysis of the skin (28.6 thick) indicated that it contained appreciable amounts of potassia and, furthermore, gave evidence that the silica adjacent to the skin had reacted to form a silicate glass with the alumina and potassium borates.

The procedure used in preparing the above sample was as follows: The sample, which had been coated with colloidal alumina, was heated to 800°C and exposed to potassium borate vapors for 10 minutes. The potassium borate, which was supported on 6 to 8 mesh chrome refractory granules, was vaporized by heating to about 1010°C. Air partially saturated with water vapor was used as carrier gas for the potassium borate vapors. After this treatment, the sample was subjected to boric oxide vapors at 800°C for 10 minutes and finally fired in steam at 1025°C for 20 minutes.

2. Elimination of Pin Holes

Although it has been possible to produce glassy films on porous glass substrates, it has been difficult to do so without producing some pin holes. To date, these pin holes have been the main source of leaks. In the previous report,

it was pointed out that exposing the surface of the sample to water vapor at 1000°C results in leak-tight samples.

It has been found possible to also produce leak-tight samples by immersing them in alkali-borate solutions, drying and refiring at 1000°C. The salts enter the defects and on firing close the porous glass around them. By dipping the samples in both alkali borate and aluminum nitrate solutions, it has been possible to produce alkali-boro-aluminosilicate glasses around the defects.

3. Reconstructed Glasses

In order to determine whether the embedded layer approach will produce samples with proper separation factors, we totally impregnated porous glass tubing in alkali-borate solutions containing mole ratios of alkali (Li, Na, K or Rb) to boron atoms of 1/3, 1/2, 1/4 and 1/5.

The impregnated glasses were dried and fired at 900°C (1/2 hr.) to produce reconstructed glasses containing the various alkali metals. An additional series of glasses was prepared which contained both alkali metals and some alumina. The latter was introduced in the porous glass as aluminum nitrate. The potassia-containing series has been evaluated by Mr. V. O. Altemose. The results were not very encouraging. However, glasses containing only alumina indicated that separation increases markedly with alumina content. The glasses were all drawn into capillaries, approximately 1mm O.D., prior to mounting on the mass spectrometer.

4. Alumina Skin Samples

A Code 7913 glass tube was coated with colloidal alumina and treated with the gas oxygen flame to form an alumina-rich silica skin. The composite glass was then drawn into a capillary for gas permeation studies. The separation was substantially doubled over that for untreated 96% SiO_2 glass.

Porous glass tubes which were coated with an amorphous layer of alumina by vapor deposition techniques also showed promise for the intended application.

5. Impervious Layers Inside Porous Glass

Mr. Charles Zippiroli has continued working on the problem of producing thin impervious layers of alkali borate-rich silicate glasses by impregnation techniques. He has been able to incorporate alumina in addition to alkali borate, but has not been able to produce leak-tight thin layers.

6. Apparatus for Coating Work

Some effort was directed toward improving the apparatus used in coating studies. Zircon refractory has been substituted for the C-104 refractory granules (magnesia-chrome) to avoid chrome contamination of the glassy skins produced by vaporizing alkali borates from the borate loaded refractory granules. A suitable apparatus for rotating the samples during the coating cycles has been installed. It eliminates nonuniform skin thickness which was encountered from time to time when coating stationary samples.

A new apparatus for applying oxide coatings by vapor deposition techniques has been built and is presently being assembled. It will make it possible to deposit thin films by decomposing fine mists of various metal-organic compounds as they come in contact with the hot porous glass.

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Glass-Metal Seals

- C. B. King and F. Martin

Some work has been done along the line of making a butt seal directly between the impregnated VYCOR brand graded seal and tungsten in the form of 1/16 inch thick sheet. Code 7574 cement was used to effect the joint at a temperature of 750°C. Difficulty has been encountered in getting wetting between the cement and the tungsten. This will evidently require a closer control of the surface oxidation and furnace atmosphere than had at first been anticipated. Preglazing of the tungsten is another approach.

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Gas Permeation Studies
(July 18 - Sept. 22, 1967)

- V. O. Altemose

During the above period, 68 samples were examined. These were primarily of two types; namely, films over porous glass substrates and impregnated 96% silica-type capillaries. Also, one sample of Code 7940 fused silica (disc-type) was measured.

Twenty-two (22) of these samples were outright leakers and, of the rest, complete helium and hydrogen permeation curves were obtained for 27 samples.

The new CEC-type 21-104 mass spectrometer was received, installed, and calibrated. A vacuum system for diffusion measurements was also built and attached to the mass spectrometer. This new equipment has been in use for permeation measurements for about three weeks.

1. Potassium-Borate Films

Eight (8) samples which were made by depositing $K_2B_4O_7$ and B_2O_3 on porous glass tubes were obtained for diffusion measurement. Of these, 5 were leakers and 2 checked. The remaining 1 (VA-43) was measured for both helium and hydrogen gases. Four (4) of the leakers were then given a steam treatment by T. H. Elmer and all became vacuum tight ("healed").

Permeation results for VA-42 (steam-treated) were such that this sample seems to have been completely consolidated. The substrate tube is no longer porous. VA-43 had a surface area of 11.9 cm^2 and a film thickness of 54 microns. The He/H_2 flow ratio was about 100, with a total flow of helium at 25°C of 1.6×10^{-6} cc/sec./atm.

2. Other Oxide Films

Samples from this group included the following:

VA-14	SnO_2 from $SnCl_4$ and O_2
-20	TiO_2 from $TiCl_4$ and O_2
-22	$FeO-Fe_2O_3$ from $FeCl_3$ and O_2
-28	A-4 (SnO_2 + [low] Sb_2O_3)
-30	A-60 (SnO_2 + [high] Sb_2O_3
-31 & 32	Amorphous Al_2O_3 (from a spray)
-72 & 73	Amorphous Al_2O_3 (from a spray) + B_2O_3 (vapor)
-74 & 75	Amorphous Al_2O_3 (from a spray) + B_2O_3 (vapor)
-49 & 50	Colloidal Al_2O_3 (BAYMAL) + $K_2B_4O_7$ (vapor) + B_2O_3 (vapor)
-70	Colloidal Al_2O_3 (BAYMAL) on consolidated glass and fire polished

Results were as follows:

Sample	Area (cm^2)	Film Thickness (u)	K-He (25°C)	R (He/H_2)	$\dot{Q}$ (cc/sec/atm
VA-14	15.8	33	4.8×10^{-10}	12-140*	1.8×10^{-5}
20	11.6	41	2.5×10^{-10}	270	5.3×10^{-6}
22	15.2	43	6.5×10^{-11}	85+	1.7×10^{-6}
28	15.4	25	5.9×10^{-11}	170	2.8×10^{-6}
30	15.2	56	1.6×10^{-10}	380	3.3×10^{-6}
31	15.6	43	4.0×10^{-11}	440	1.1×10^{-6}
32	11.2	41	1.1×10^{-10}	400-670*	2.4×10^{-6}
72	8.9	38	7.2×10^{-12}	250	1.3×10^{-7}
73	9.4	28	7.2×10^{-12}	380	1.8×10^{-7}
49	11.2	29	3.2×10^{-12}	470+	9.4×10^{-8}
50	11.2	36	3.0×10^{-12}	160	7.0×10^{-8}
70	--	--	6.2×10^{-11}	600	--

Units of K are the usual $\frac{cc(STP) - mm.}{sec-cm^2-cm.Hg.}$

R is ratio of helium to hydrogen flow at 25°C.

$\dot{Q}$ is helium flow in cc/sec/atm for entire sample

* Range of values is given due to uncertainty in slope of curves.

The high value of R for VA-31 and 32 is encouraging. Four attempts were made to repeat these two samples. VA-74 and 75 were both leakers while VA-72 and 73 appeared to be somewhat tighter and had lower separation ratios.

Except for VA-49 and 50, the films were produced by a spraying technique. These two, were made by dipping the substrate tubes in colloidal BAYMAL solutions then heating in vapors of $K_2B_4O_7$ followed by B_2O_3. VA-49 showed a good separation, but the helium flow was considerably lower than for the other type films. For some unknown reason, separation by VA-50 did not duplicate VA-49 results.

3. Impregnated Capillaries

This group of glasses was produced by impregnation of the porous glass tubes before consolidation and then pulled into capillary form. The following table gives the sample number, the impregnation solution, permeation rate for helium at 25°C, and the separation ratio.

Sample	Solution	K (He @ 25°C)	R
VA-51	30 % $Al(NO_3)_3$ in H_2O	--	400
52	50 % " " "	not run	--
53	70 % " " "	5.9×10^{-11}	>500
54	0 % " " "	9.9	375
VA-55	Li/B ratio = 1/5	5.5	160
56	Na/B " "	Sample Broke	--
57	K/B " "	2.2	175
58	Rb/B " "	2.2	190-270
VA-63	Al_2O_3 + K/B = 1/2	7.0×10^{-12}	130
64	" + 2 coats (K/B = 1/2)	5.7	70
65	" + K/B = 1/3	2.6×10^{-11}	180
69	" + 2 coats (K/B = 1/5)	4.0	170

Of the above samples, VA-54 with no Al_2O_3, agrees quite well with ordinary Code 7900 glass. As the alumina concentration increased, so did the ratio R. For VA-70, the BAYMAL coated Code 7900 capillary, the coating reduced the helium permeation rate by a factor of two, but increased the separation ratio to 600.

4. Code 7940 Glass

Hydrogen and helium permeation curves were determined for Code 7940 glass (fused silica). The enclosed curves give a comparison of the permeation rates for Code 7940 and the other silica samples run previously. The great spread in the helium curves among the Code 7940, 7943 and 7971 glasses is surprising, and no explanation is offered at this time. The difference in the slopes of the helium curves accounts for most of the difference in separation ratios which are:

	Approx. Ratio
Code 7900	380
7971	325
7940	200
7943	270

Conclusion

In all the thin films checked to date, separation ratios of about 500 or greater seem to be primarily due to the presence of Al_2O_3. The effects of other materials on this ratio in the skins produced so far are indefinite.

* This was erroniously numbered 7945 in previous reports.

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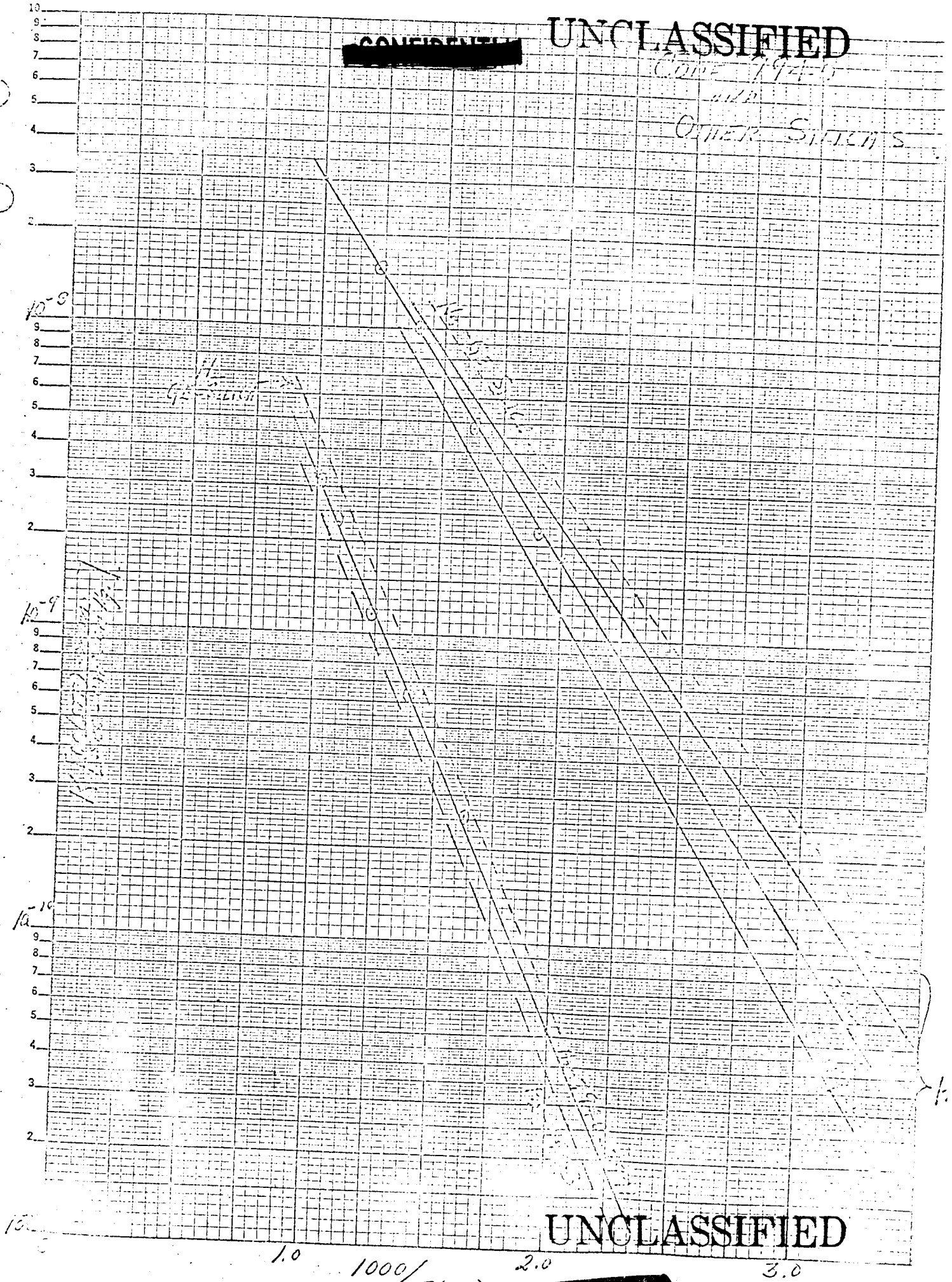

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