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AEC RESEARCH AND
DEVELOPMENT REPORT

GA-8574
C-93b, Advanced
Concepts for Future
Application -
Conversion Devices
M-3679 (56th Ed.)

CESIUM SORPTION IN MATERIALS FOR THERMIONIC CONVERTERS

by

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Prepared under
Contract AT(04-3)-167
Project Agreement No. 14
for the
San Francisco Operations Office
U. S. Atomic Energy Commission

April 8, 1968

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ABSTRACT

This report covers work done from October 1966 - January 1968 under AEC Contract No. AT(04-3)-167 on cesium sorption in materials which could serve as integral reservoirs in thermionic converters.

Samples of integral reservoir materials were received and characterized as to their purity, BET surface area, and pore spectrum. Five samples from the carbon, graphite, porous tungsten, and porous alumina groups considered were selected and loaded with cesium over a range of 600-1000°C sample temperature, 0.1-30 torr cesium vapor pressure, and 0-1000 mg Cs/gram sample cesium loading. In addition, the cesium loadings of five porous tungsten samples were measured at 800°C and 10 torr cesium vapor pressure.

The conclusions of these tests were that the cesium sorption in the Al_2O_3 , tungsten and carbon samples tested depended primarily on adsorption. Cesium loadings at 800°C and 10 torr were 0.4 mg Cs/g Al_2O_3 , 0.06 mg Cs/g W, and 500 mg Cs/g carbon. The cesium loadings in these materials were in general agreement with their BET surface areas.

The cesium loading in a W-10 W/o Ta sample was 2.1 mg Cs/gm at 800°C and 10 torr. This loading was approximately 100 times that expected from surface area considerations, but these results were shown to be at least partly due to cesium sorption in the tantalum.

The cesium sorption in the graphite samples tested depended primarily upon compound formation and where in general agreement with earlier work. At 800°C and 10 torr, cesium loadings of 400 mg Cs/gm were formed.

No significant changes in the cesium loading characteristics of any of the materials tested were observed over the duration of the tests, which lasted from 100-1200 hours. However, at the conclusion of the testing it was discovered that the carbon sample had crumbled and that both graphite samples had delaminated. The maximum loadings achieved in these three samples were approximately 1g Cs/g C.

INTRODUCTION

Cesium thermionic converters used in research work employ liquid cesium reservoirs because they present the simplest and most accurate method of providing a known cesium pressure within a converter. In a thermionic reactor core, however, the minimum temperatures are generally around 600-700°C so that liquid reservoirs would either have to be located externally or special coolant loops brought into the core since liquid cesium equilibrium vapor pressure at temperatures around 600°C greatly exceeds the pressures of 1-10 torr required for optimum operation. An attractive solution to the problem is the use of a sorption type reservoir integral within each converter, where cesium adsorbed onto a surface or absorbed into a lattice has an equilibrium vapor pressure in the required range. Since the integral reservoir will be located within the converter, its temperature must reside at a level somewhere between the emitter and collector temperatures. Emitter temperatures are on the order of 1600-1800°C. Collector temperatures range between 600-800°C. Therefore, the reservoir temperatures and cesium vapor pressures of interest lie in the range of 600-1800°C and 1-10 torr respectively.

Accordingly, a program was initiated to investigate materials which could serve as integral reservoirs. Earlier work⁽¹⁾ with high surface area tungsten and molybdenum substrates has shown that they may be capable of satisfying the requirements listed above. High surface area carbons and charcoals^(2,3) are also attractive candidate cesium sorption materials. Cesium has been found to form lamellar compounds with graphite⁽⁴⁻⁹⁾ and the equilibrium temperatures of these compounds fall in the ranges of interest. Finally, porous alumina was investigated, primarily because certain types are known to be compatible with cesium and the refractory metals normally found in thermionic diodes.⁽¹⁰⁾

The first part of the program was aimed at compiling lists of as many possible sources of the above materials as possible and obtaining suitable samples. Next, the samples were characterized as to their purity, surface area, pore spectrum and sintering stability. Finally, five samples were

chosen and cesium pressure, sample temperatures, and cesium loading were monitored on isotherms from 600-1000°C and 0.1-30 torr. At the conclusion of this first series of tests, the cesium loadings of five porous tungsten samples were measured at 800°C and 10 torr.

SAMPLE SELECTION

The sample materials which were tested, listed in Table 1, were chosen from each type of material on the basis of purity, surface area, sintering stability, sample size and/or structural characteristics. Details of the materials sources and characterization data for all samples are given in Appendix A.

The tungsten sample which was tested from 600-1000°C and 0.1 to 30 torr was chosen mainly on the basis of stability since there was little variation in surface area or purity among the samples. Stability data on porous tungsten developed in the ionizer program⁽¹¹⁾ has shown that tungsten 2% boron and tungsten 10% tantalum have better sintering stability than normal tungsten. The W-10 Ta sample was chosen over the one containing boron because the high thermal neutron capture cross section of boron could lead to problems in a reactor due to the helium production from the boron (n, α) reaction. The five tungsten samples which were tested at 800°C and 10 torr represented all the other types of porous tungsten which had been procured.

Purity and surface area were chosen as the criteria for selection of the carbon sample. Both the Witco Carbon #337 and the Pure Carbon FC-50 possess high surface area, 874m²/g and 347m²/g respectively, and high purity. The Pure Carbon sample was chosen because it was a bonded slab of carbon where the Witco Carbon was in a granular form.

Since all of the graphites had high purity, one criterion used for selection (after excluding yarns and fragile pieces) was minimum surface area, since in graphite the primary interest was in the formation of the lamellar compounds and not in surface adsorption. In addition, both isotropic and anisotropic graphite samples were selected in order to determine whether differences in cesium loading characteristics might be observed. The

Material	Sample No.	Source	Source Designation	Density gm/cm ³	BET Surface Area		Test Piece Parameters	
					m ² /gm	m ² /cm ³	Weight(gms)	Dimensions (mm)
Alumina	141	American Lava Corporation	ALSIMAG 548	2.49	0.2 ± 0.05	0.5 ± 0.15	1.226	25.5 x 3.18 x 5.99
							1.295	25.2 x 3.25 x 6.02
Carbon	251	Pure Carbon Co.	FC-50	0.85	347	295	0.431	25.1 x 6.28 x 3.28
							0.485	25.6 x 6.24 x 3.28
Graphite --Isotropic	332	Carborundum Co.	CARB-I-TEX 700	1.44	0.39 ± 0.02	0.56 ± 0.03	0.594	24.9 x 7.24 x 2.42
							0.641	24.8 x 7.21 x 2.64
--Anisotropic	355	Gulf General Atomic	Pyrolytic Graphite	2.08	.8	1.7	.550	13.3 x 6.60 x 2.90
Tungsten	526	EOS NAS3-6269	W-10 ^W /o Ta	15.10	0.023 ± 0.005	0.34 ± 0.07	5.333	13.1 x 6.53 x 4.28
	513	TRW	Pure W	14.6	.04	.51	2.375	8.61 x 5.87 x 3.12
	527	EOS NAS3-5253	Pure W	15.2	<.3	.25 Calculated	3.031	7.95 x 7.90 x 3.15
	530	Astromet Assoc.	Astromet 105	13.0	.04	.54	4.580	Irregular
	533	EOS	Misc. Piece	14.2	<.02	<.28	4.233	Irregular
	538	Phillips Metalonics	Pure W	12.8	.05	.64	2.180	8.59 x 6.35 x 2.92

TABLE 1
SAMPLES SELECTED FOR PRESSURE-TEMPERATURE LOADING EXPERIMENT

samples selected were Carborundum CARB-I-TEX #700 (isotropic) which is a graphitized cloth and a Gulf General Atomic sample of anisotropic graphite.

Of the alumina samples, the one having the best purity and the highest surface area of the samples received, American Lava ALSIMAG 548 was chosen.

EXPERIMENTAL APPARATUS AND PROCEDURE

The apparatus for measuring the pressure-temperature loading characteristics consisted of an isothermal sample oven, a liquid cesium reservoir which provided the required cesium and established the cesium pressure over the sample, and a gamma ray counting system to monitor the cesium loading (Cs^{134}) in the sample. The counting system was calibrated with a cesium standard that was irradiated along with the cesium metal. Details of this apparatus are given in Appendix B.

Chemical cleaning was used to remove contaminants introduced during sample preparation, but high vacuum outgassing at temperatures around 1200°C was relied upon for the final preparation prior to cesium loading. Details of these procedures are given in Appendix C.

COMPARATIVE SUMMARY

Table 2 compares the cesium loadings of the samples tested at 800°C and 10 torr cesium pressure, a typical operating point. As shown, the cesium loadings per square meter of surface area of the carbon, alumina, and at least three of the six tungsten samples are between 1.1-2.0 mg Cs/m^2 . These quantities correspond roughly to $1\frac{1}{2}$ - $2\frac{1}{2}$ monolayers based on a cesium cross sectional area of $28\text{\AA}^2$. Therefore, the cesium sorption in these cases was primarily one of adsorption. However, the cesium loadings of the graphite, W-10 w/o Ta, and EOS W samples suggest another mechanism. The mechanism in graphite was assumed to be compound formation as discussed in References 4-9. The mechanism in the W-10 Ta sample was shown to be partly due to the presence of tantalum and is discussed more fully in the following pages. The reasons for the high loadings of the EOS W sample have not been determined. The test durations are also listed in Table 2. No significant changes in the

SAMPLE	DURATION OF TEST (hr)	PORE DIA μ	CESIUM LOADING @ 800°C, 10 Torr mg Cs/g	CESIUM LOADING @ 800°C, 10 Torr mg Cs/m ²
Pure Carbon FC-50	450	--	505.	1.75
Carborundum CARB-I-TEX 700 Graphite	1000	--	400.	1002.
Pyrolytic Graphite	500	--	420.	525.
EOS W-10 Ta	1200	2.79	2.1	91.
EOS W Misc. Pcs.		--	0.17	>9
EOS W 5253		3.44	0.12	>0.4
Phillips W angular powder	100	3N	0.062	1.2
Astromet, W 105		5N	0.054	1.3
TRW, W		2N	0.038	1.1
ALSIMAG 548, Al ₂ O ₃	250	--	0.4	2.0

TABLE 2
COMPARISON OF CESIUM LOADING ALL SAMPLES TESTED

cesium loading characteristics of any of the materials tested were observed over the duration of the tests which lasted from 100-1200 hours. However, the carbon and both of the graphite samples were broken up during testing. The maximum loadings achieved in these three samples were approximately 1g Cs/g.

Carbon Sample - Pure Carbon FC-50

Isotherms for the carbon sample are shown in Figure 1. Both sorption and desorption points were taken over the range of interest. On the initial loading at 700°C an irreversible effect was noted. The initial sorption curve and all subsequent points at 700°C are plotted in Figure 2. After this first loading, no significant hysteresis was observed. These first results were probably due to the replacement of sorbed gases by cesium on the high surface area carbon. Equilibrium times varied over a range extending from approximately 15 minutes at 10 torr to approximately 4 hours at 1/10 torr.

The Freundlich isotherm equation⁽¹²⁾ produced a satisfactory fit to the data.

$$v = k p^{1/n}$$

with v = quantity adsorbed

p = cesium vapor pressure

k = a constant which is a function of
temperature

for our data $n = 7.38$. No significant variations in n were observed.

Lines of constant loading (isosteres) versus $1/T$ are plotted in Figure 3. These curves approximate the pressure-temperature dependence which would exist in a small volume thermionic cell.

The isosteric heat of adsorption was calculated from the relationship:

$$q = -R \frac{\Delta (\ln p)}{\Delta (1/T)}$$

Figure 1--Pressure-Loading Isotherms for Pure Carbon FC-50

Figure 2--Irreversible Effect Observed on Initial Loading of Pure Carbon FC-50

Figure 3--Clausius-Clapeyron Plot for Cesium Carbon System

where R is the gas constant, 1.987 cal/deg mole
p is the pressure in torr
T is the sample temperature in degrees K

The variation of a q with respect to loading is shown in Figure 4. As shown, q was essentially constant at approximately -33 Kcal/mole until the loading exceeded approximately 500 mg Cs/g carbon and then decreased. This break in the curve is thought to occur near the formation of the first monolayer.

The data in the form of Clausius-Clapeyron Plots is compared to earlier data⁽²⁾ taken on Columbia Charcoal (surface area of 1540 m²/g) in Figure 5. For the purposes of comparison the loadings in mg/Cs g C have been divided by the surface areas of the samples. There is a discrepancy between the measured N₂ BET surface areas and the cesium loadings. The Pure Carbon Sample appears to have the capability of holding about three times as much cesium per square meter as does the Columbia Charcoal. This difference could be due to prior treatment of the material such as the cleaning and outgassing procedures used. The Pure Carbon Sample was outgassed at 1200°C in an ultimate vacuum of approximately 10⁻⁸ torr. The Columbia Charcoal Sample was outgassed at 1000°C⁽¹³⁾ in a 10⁻⁵ torr vacuum.

The sample was on test approximately 450 hours. Data was taken at 700°C and 10 torr at various times during the test and indicated that no significant changes in loading (<5%) occurred during this period. However, upon removal from the oven, it was discovered that the sample had crumbled. The breaking up of the carbon was probably due to the alternate loading and unloading which must have produced swelling in the sample. More data is needed to establish whether the crumbling can be avoided by lower loadings and/or fewer sorption/desorption steps.

Graphite Samples: CARB-I-TEX 700 and Annealed Pyrolytic Graphite

Isotherms for the graphite samples are shown in Figures 6 and 7. As in the carbon test, both sorption and desorption points were taken. Also plotted in the figures is the 700°C isotherm based on Salzano and Aronson's work on the cesium-graphite lamellar compounds.⁽⁷⁾ A typical cesium-graphite reaction

Figure 4--Isosteric Heat of Adsorption for Pure Carbon FC-50

Figure 5--Clausius-Clapeyron Plots for Pure Carbon FC-50 & Columbia Charcoal

Figure 6--Pressure-Loading Isotherms Carborundum CARB-I-TEX 700

Figure 7--Pressure Loading Isotherms GGA Pyrolytic Graphite

is:

A series of compounds exists from C_{60}Cs to C_8Cs , and a two-phase equilibrium exists at any specific loading (in the range of the compounds). The cesium vapor pressure over the graphite depends only on the sample temperature and compounds involved.

For the CARB-I-TEX sample, Figure 6, there was a knee in the curve on the 700° isotherm where the transition from CsC_{24} to CsC_{10} should occur. However, as the cesium vapor pressure was increased the loading did not increase to the expected CsC_{10} level but instead rose uniformly with the cesium pressure. In general, the measured loadings were always less than that expected from prior work on the lamellar compounds. The equilibrium times for this graphite sample varied from $\approx \frac{1}{2}$ hour at 30 torr to ≈ 10 hours at 1/10 torr. The sample was on test approximately 1000 hours. No significant changes in the sample's loading characteristics were observed during that period. The layers of graphite cloth which made up the sample were found to have delaminated when the sample was removed from its oven. As in the case of the Carbon Sample, further studies are indicated to determine the maximum loadings which this material can withstand without damage.

Isotherms for the pyrolytic graphite sample, Figure 7, show several well defined plateaus, particularly those corresponding to the transitions between C_{36}Cs -- C_{24}Cs and C_{24}Cs -- C_{10}Cs . Again, the loadings were somewhat less than those corresponding to the formation of a specific compound. The equilibrium times were similar to those of the CARB-I-TEX sample except that they tended to be faster in the areas where the loading was changing slowly and were slower when a plateau was being traversed. The sample was on test 500 hours, and some delamination was observed after the test.

The CARB-I-TEX sample was isotropic and the annealed pyrolytic graphite, anisotropic. Whether this difference or others, such as the degree of graphitization of the two samples, is responsible for the differences in the isotherms is not known but will be investigated in future experiments.

Figure 8 is a Clausius-Clapeyron Plot of all the graphite data. There is agreement, within experimental errors, between this experiment and the previous one, particularly in the higher loading compounds. Also, there was agreement between the two types of graphite.

W-10 Ta and Tungsten Samples

Isotherms at 600, 800, and 1000°C for the W-10 Ta sample are shown in Figure 9. The three isotherms show hysteresis effects and do not appear consistent. Equilibrium times were very long; complete equilibrium was rarely achieved in less than 24 hours. Because of the long stabilization times involved, no isotherm was retraced, but the point at 1000° and 10 torr was reproduced at the beginning and end of the test, which lasted for approximately 1200 hours.

The cesium loadings that were obtained were approximately 100 times higher than those expected from the measured BET surface area (with krypton). Also, the loading of 7 mg Cs/g W was never exceeded, even when the sample temperature was lowered to only 30°C hotter than the saturation temperature of cesium at 30 torr. Two possible explanations for the observed loading were considered. First, a chemical reaction could be involved, perhaps with the tantalum in the sample. After the test of the sample, microprobe analysis was done. At the end of the test approximately 1 mg Cs/g W-10 Ta was left in the sample. Microprobe scans were run on the sample to determine the location of the cesium. The results of these scans are shown in Figures 10 and 11. Figure 10 shows qualitative x-rays scans for tungsten, tantalum, and cesium over the same area of the sample. Areas of high cesium concentration correlate directly with areas of high tantalum concentration. Figure 11 shows several line scans taken in various areas of the sample. Again, areas of high cesium concentration correlate directly to areas of high tantalum concentration. In addition, presence of a fourth constituent in the areas of high cesium concentration is indicated since the fractional parts of W, Ta, and Cs add up to only approximately 75 atom percent of the total. Possible candidates for the missing 25% are oxygen or nitrogen.

Figure 8--Clausius-Clapeyron Plot for Graphite Samples

Figure 9--Pressure-Loading Isotherms for W-10 Ta Sample

TUNGSTEN

TANTALUM

CESIUM

◀ ————— ca. 45μ ————— ▶

ca. 1800X Figure 10--X-Ray Scanning Pictures of EOS
6269 w/o Ta After Test with Cesium

FIGURE . II
MICROPROBE SCANS
W-10 Ta SAMPLE

The possibility that capillary condensation had been occurring was also considered, particularly since a loading of 7 mg Cs/g W corresponded to enough cesium to fill 60% of the sample's pore volume.

In an attempt at reproducing the W-10 Ta result, five tungsten samples were selected, loaded into a niobium oven, attached to the apparatus and outgassed at 1100°C. The samples were then loaded with cesium at 800°C and 10 torr. Then points were taken at 30 torr at 600°, 1000°, and 600° in order to load and unload the samples. When the conditions of the first data point were repeated, no hysteresis was observed. Therefore, the oven was cooled down, retaining the cesium in the samples. The samples were then removed from their oven and counted separately. The cesium contents of these samples have been listed in Table 2.

The highest loading observed in mg Cs/g on the five samples was less than one tenth that of the W-10 Ta piece. Since the pore structures were roughly the same in all samples, it is improbable that the capillary condensation mechanism can be made to account for the high loadings. The last three samples all held about the same amount of cesium per square meter of surface area, an amount which is about equivalent to a monolayer coverage.

From the discussion it is clear that at least the cesium left at the end of the test in the W-10 Ta sample was associated with the tantalum. It is probable that the cesium loaded during the test was also sorbed in the tantalum.

Al₂O₃ Sample - American Lava ALSIMAG 548

Isotherms for the alumina sample are shown in Figure 12. The scatter in the data is primarily due to the fact that the count rate from the sample was only several times that of the background rate in the crystal (approximately 200 cpm). In addition, the equilibrium times were quite long (10-20 hours). Complete sorption and desorption curves were not done due to the long equilibrium times involved. The highest loading attained, approximately 1 mg Cs/g, corresponds to approximately 2.5 mg/cm³ of alumina.

Figure 12--Pressure Mounting Isotherms
for Alumina-American Lava ALSIMAG 548

Based on the measured BET surface area of $0.2 \text{ M}^2/\text{gram}$ and a cesium cross sectional area of $28(\text{\AA})^2$, one monolayer coverage amounts to approximately $0.2 \text{ mg Cs/g alumina}$. Actual loadings greater than five times this amount were achieved.

The sample was on test approximately 250 hours. The point taken at 600°C and 30 torr at the beginning and end of the test show that no significant changes occurred in the loading characteristics during this time. After removal from the oven, the sample appeared the same as it had prior to the test.

CONCLUSIONS

All of the materials actually tested in the cesium loading apparatus have shown the capability of maintaining cesium pressures in the range required for thermionic operation at temperatures greater than 600°C . In addition, no significant changes in cesium loading characteristics occurred over the duration of the tests, which lasted from 100-1200 hours. The cesium loading depended primarily upon surface area in the tungsten (except for the W-10 Ta and EOS W samples), alumina, and carbon samples and upon compound formation in the graphite samples.

Advantages and disadvantages exist for each of the materials tested. The low loading samples, alumina and tungsten, are compatible with the other materials in a thermionic cell and dimensionally stable. However, the stability of their surface area, upon which their cesium sorption capability depends, has yet to be demonstrated for times of interest for thermionic diodes (5000-10,000 hours).

The high loading carbons and graphites have yet to be proven to be compatible with thermionic cells and are not dimensionally stable at the loadings to which they were subjected in this study. In addition, the sintering stability of the high surface area carbons has to be demonstrated.

The choice of which material would make the best reservoir depends to a large extent upon what amount of cesium is expected to be lost during cell

operation. Work on this subject has been published⁽¹⁴⁾ and states in part, "the basic converter components, namely tungsten, molybdenum, tantalum, niobium and Al_2O_3 , are not important cesium sinks at their operating temperatures. Tantalum and niobium, which showed variable results among the three converters studied, may need rigid control of the concentrations of their interstitial impurities to minimize their cesium solubilities." Total cesium losses to the above materials in two of the three cells studied were less than 20 μg . These two cells were operated for 7558 and 10,406 hours. A 20 μg cesium loss corresponds to approximately 2% of the cesium reserve of a porous tungsten (Phillips or Astromet 105) reservoir of approximately 1 cm^3 volume. Therefore, on the basis of these low magnitude cesium losses, all of the materials tested appear attractive.

FUTURE WORK

Further work is planned on cesium losses in cells, carbon compatibility with thermionic diodes, and the long-term stability of all of the cesium-substrate systems. In addition, more samples will be tested in the pressure-temperature loading apparatus to determine their cesium loading characteristics.

REFERENCES

1. RCA, "The Development of an Adsorption Cesium Reservoir," Summary Technical Report, NYO-3642-4, December 1966.
2. C. E. Milstead, A. B. Riedinger, L. R. Zumwalt, "Cesium-Graphite Sorption Isotherms Determined by an Isopiestic Method," General Dynamics/General Atomic Division Report No. GA-6415 (Rev.), November 1965.
3. E. E. Anderson, G. L. Wessman, L. R. Zumwalt, "Fission Product Trapping--Sorption of Cesium by Activated Charcoal," Nuclear Science and Engineering, No. 12, April 1961, p106.
4. A. Herold, "Recherches sur les composés d'insertion du graphite," Bull.Chem.Soc., France, 1955, p999.
5. S. Aronson, F. J. Salzano, "Some Experimental Observations in the Caesium-Graphite System," Journal of Inorganic and Nuclear Chemistry, Volume 26, January 1964.
6. S. Aronson, F. J. Salzano, "Kinetic Study of the Decomposition of Cesium-Graphite Lamellar Compounds," J.Chem.Phys., Volume 42, No. 4, February 1965, p1323.
7. S. Aronson, F. J. Salzano, "Thermodynamics Properties of the Cesium-Graphite Lamellar Compounds," J.Chem.Phys., Volume 43, No. 1, July 1965, p149.
8. S. Aronson, F. J. Salzano, "On the Bonding Energy in Cesium-Graphite Compounds," J.Chem.Phys., Volume 44, No. 11, June 1966, p4320.
9. S. Aronson, F. J. Salzano, "Stability of Phases in the Cesium-Graphite System," J.Chem.Phys., Volume 45, September 1966, p2221.
10. L. N. Grossman, "Insulator Materials for Nuclear Thermionic Power Conversion," Thermionic Electrical Power Generation Conf., Proceedings, 1965 (London) Session 7b.
11. K. Butler, G. Kuskevics, M. LaChance, B. Thompson, H. Todd, "Development and Testing of Porous Ionizer Materials," NASA/CR-54707, EOS Report #6650 Summary, Part I, September 1966.
12. J. W. McBain, "The Sorption of Gases and Vapours by Solids," (London), 1932, p5.
13. C. Milstead, Gulf General Atomic, Private Communication.

14. G. Bizzelli, R. G. Hudson, L. Yang, "Post-Operation Determination of Cesium Contents in Life-Test Converter Components," Thermionic Conversion Specialist Conference, Proceedings, 1967, (Palo Alto), p271
15. A. Y. Cho, D. F. Hall, H. Shelton, "An Experimental Study of Porous Metal Ionizers," AIAA Fifth Electric Propulsion Conference, Proceedings, 1966, AIAA Paper #66-218.
16. V. D. Barth, H. O. McIntire, "Tungsten Powder Metallurgy," Technology Utilization Report, NASA SP-5035, November 1965.
17. J. M. Googin, L. R. Phillips, C. F. Piper, C. R. Schmitt, "Preparing and Sintering Tungsten Powder," AEC Research and Development Report, #Y-1476, March 1965.
18. R. Breitwieser, W. B. Nottingham, "Theoretical Background for Thermionic Conversion Including Space-Charge Theory, Schottky Theory and the Isothermal Diode Sheath Theory," NASA TN D-3324, March 1966.
19. J. Chin, Gulf General Atomic, Private Communication.

APPENDIX A
MATERIALS SOURCES AND CHARACTERIZATION DATA

MATERIALS SOURCES

A literature and vendor search was completed to establish the sources of possible materials. In addition to other sources, both the Defense Metals Information Center and the Ceramics and Graphite Center were contacted. The resultant list of manufacturers appears in Table 3. All samples which appeared interesting were procured. The types of samples requested were high purity ceramics, carbons, charcoals and graphites, as well as all types of porous tungsten. Other porous metals were not thoroughly investigated because 1) tungsten should be more stable with respect to sintering than the other metals readily available (porous molybdenum, nickel, etc.), and 2) there is a large volume of data on porous tungsten that was developed in the ion propulsion program.(11,15-17)

CHARACTERIZATION

Table 4 and the graphs and photos of Figures 13-36 summarize all data accumulated on the samples received. Manufacturers, description, and nominal purities are given. Also, density and percentage of theoretical density are noted. Surface areas were measured by the BET technique. Nitrogen was used on all materials except the porous tungsten samples where krypton was used. Impurities were measured by emission spectroscopy. Porosimetry data, where not furnished by manufacturers, were taken with a mercury porosimeter apparatus. The porosimetry data is presented as graphs, shown in Figures 13-21 of the cumulative pore volume (cc/gm or %) versus pore diameter. Microphotographs of selected samples appear in Figures 22-36.

TABLE 3
LIST OF MANUFACTURERS

	No Response	No Suitable Prod. Avail.	Sample Rec'd.
<u>ALUMINA</u>			
1. American Lava Corporation/Chattanooga, Tenn.			X
2. Brush Beryllium Company/Elmore, Ohio			X
3. Coors Porcelain Company/Golden, Colorado			X
4. Corning Glass Works/Corning, New York	X		
5. Du-Co Ceramics Company/Saxonberg, Penn.		X	
6. Frenchtown Porcelain Company/Frenchtown, New Jersey		X	
7. General Electric Company, Metallurgical and Ceramics Lab/Cleveland, Ohio		X	
8. McDaniel Refractory Porcelain Company/Beaver Falls, Penn.	X		
9. Silk City Industrial Ceramics/Hawthorne, New Jersey			X
10. Star Porcelain Company/Trenton, New Jersey	X		
11. Technical Ceramics & Lava Corporation/Caldwell Township, New Jersey			X
12. Thermokinetic Fibers, Inc./Nutley, New Jersey		X	
13. Western Gold and Platinum Company/Belmont, Calif.			X
<u>CARBON & GRAPHITE</u>			
14. Barneby-Cheney Company/Columbus, Ohio		X	
15. California Carbon Company/Torrance, Calif.			X
16. Carbonundum Company, Graphite Products Division/ Sanborne, New York			X
17. C. H. Dexter & Sons Company/Windsor Locks, Conn.		X	
18. General Electric/Detroit, Michigan			X
19. Great Lakes Carbon Corporation/Menlo Park, Calif.		X	
20. Gulf General Atomic/San Diego, Calif.			X
21. Pittsburgh Activated Carbon Company/Redwood City, Calif.			X
22. Pure Carbon Company/St. Marys, Penn.			X
23. Pyrogenics, Inc./Woodside, New York		X	
24. Smith Chemical & Color Company, Inc./Brooklyn, N.Y.	X		
25. Speer Carbon Company/St. Marys, Penn.			X
26. Tennessee Products & Chemical/Nashville, Tenn.	X		
27. Ultra Carbon Corporation/Bay City, Michigan		X	
28. Union Carbide, Carbon Products Division/New York, N.Y.		X	
29. Witco Chemical, Activated Carbon Dept./New York, N.Y.			X
<u>POROUS METALS</u>			
30. Astro Metallurgical Associates/Cincinnati, Ohio			X
31. Astro Metallurgical Corporation/Wooster, Ohio		X	
32. Electro-Optical Systems, Inc./Pasadena, Calif.			X
33. General Electric/Detroit, Michigan			X
34. Hughes Research Lab./Malibu, California		X	
35. Lewis Research Center/Cleveland, Ohio			X
36. Phillips Metalonics/Mt. Vernon, New York			X
37. TRW Systems/Redondo Beach, California			X
38. Wah Chang/New York, New York		X	

TABLE 4 - CHARACTERIZATION DATA

No.	DESCRIPTION OF MATERIAL	DENSITY g/cm ³	% OF THEOR.	SURFACE AREA		FIGURE # Pores/ Photo	IMPURITIES ppm							
				m ² /g	m ² /cm ³		Cr	Fe	Mg	Ca	Ti	Sr	Zr	Si
<u>Al₂O₃</u>														
101	Coors AD-995 (L32), pink solid			0.1±.05			4000	600	600					400
111	WESGO AL-300, white solid, 97.60% pure	3.67												
114	WESGO AL-1009, white solid, 99.85% pure	3.15	79.1	0.1±.05-0.3		22	400	80						400
123	Silk City SC-99P, white solid, 99.9+% pure	3.34	83.9	<.1			400	80			400			600
139	Technical Ceramics #1002, white solid	2.9	72.9	0.17-0.5			800	800	1000	200				>1%
141	American Lava ALSIMAG 548, white solid 99.8% pure	2.49	62.7	0.2±.05-0.5	13	23	200							100
<u>BeO</u>														
135	Brush 15-, white solid, 99% pure		82.	< 0.1			100	400						>1000
136	Brush 9-, white solid, 99% pure		80.	< 0.2			80	200		200				>1000
137	Brush 35-, white solid, 99% pure		61.	< 0.2			80	100		200				>1000
<u>CARBON AND CHARCOAL</u>							<u>Al</u>	<u>Fe</u>	<u>Mg</u>	<u>Ca</u>	<u>Na</u>	<u>Ni</u>	<u>Cu</u>	<u>Si</u>
208	Carborundum Carbon Felt, felt, 97.8% pure	0.07		0.8	0.050									
209	Carborundum Carbon Fiber, CY-2F, fiber, 99.5% pure													
215	General Atomic B-204, black solid	0.75	588				>1000	800		100				>1000
220	General Atomic #60, black solid	1.05	1.01	0.20-0.202	14	24	80	1000		80	100	80		80
243	Speer Carbon #37, black solid	1.33		0.32-0.43	15	25	200	200	40	100	400	80		80
246	Speer Carbon HP-5, black solid, crumbly	1.23		14.7-18.1	10		13	40	40		20			100
247	Speer Carbon HP-10, black solid, crumbly	1.26		1.30-1.84			8	40	10		2			80
250	Witco Carbon #337, granular, 99.5% pure	.45		874-585			< 1	200	<.5	<20	200			<10
							<u>Al</u>	<u>Fe</u>	<u>Mg</u>	<u>Ca</u>	<u>Na</u>	<u>Sr</u>	<u>Ba</u>	<u>Si</u>
434	California Carbon Activated Charcoal, granular						100	20	100	1%	800	100	20	80
440	Pittsburgh Activated Carbon, granular	.5		1050.N 525.			> 1%	> 1%	200	> 1%	800	400	100	> 1%
448	Pittsburgh Activated Carbon, granular	.5		1050.N 525.			> 1%	> 1%	100	> 1%	1000	600	100	> 1%
449	Pittsburgh Activated Carbon, granular	.5		1050.N 525.										
252	Pure Carbon FC-14, black solid, 99.9% pure	.90		6.8	6.		>1000	2	40	100	ND	2		8
251	Pure Carbon FC-50, black solid, 99.7% pure	.85		347	295.	20	80	200	20	80	ND	20		200
253	Pure Carbon FC-22, black solid, 95% pure			600.N			800	800	40	200	>1000	40	20	>1000
1.	0.41 after 1200°C Bakeout													
2.	0.78 after 1200°C Bakeout													
N.	Manufacturers Value													

TABLE 4 - CHARACTERIZATION DATA

No.	DESCRIPTION OF MATERIAL	DENSITY g/cm ³	% OF THEOR.	SURFACE AREA		FIGURE #		IMPURITIES ppm							
				m ² /g	m ² /cm ³	Pores/ Photo	Al	B	Mg	Fe	Ca	Cu	V	Si	
<u>GRAPHITE</u>															
307	General Electric, foamed pyrolytic fragile														
310	Union Carbide EGCR, black solid	1.633		.57	.93	17	27	20	2	1			20	40	
317	Speer 37G-L, black solid	1.376		.75	1.03	18	28	1		1	4	<20		<10	
318	Speer 3499S, black solid, 99.9% pure	1.617		2.28	3.69	19	29		1	1	1	<20	.5	20	
319	Speer 105G, black solid	1.447		2.23	3.23	20			2	1	<1	40	.5	40	
321	Carborundum Graphite Felt, 99.0% pure	7x10 ⁻²		.23	.016										
331	Carborundum GSGY2-30 Graphite Yarn, 99.97% pure														
332	Carborundum CARB-I-TEX 700, black solid	1.44		.39	.56	17	30	2	.5	1	8	40	.5	10	
345	Speer HPG-10, black solid, crumbly	1.12													
354	Graphite Flake, Pitch Binder			0.5					<.5						
355	Pyrolytic Graphite	2.08		0.8	1.62				<.5						
No.	DESCRIPTION OF MATERIAL	DENSITY g/cm	% OF THEOR.	SURFACE AREA		Pore/ Photo		PORE DENSITY	HOTTEST	SINTER	IMPURITIES ppm				
				m ² /g	m ² /cm ³	Dia.	Fig#	x10 ⁶ /cm ²	TIME	TEMP	Na	C	Fe	Mo	Rb
<u>POROUS TUNGSTEN</u>															
513	TRW Pure W	14.6	76	.035	.51*	2N	31		2 hr	1900 or 2000					
524	EOS F-7A, pure W														
525	EOS 7102, pure W	15.2	79	.018	.27*	3.02		2.	1 hr	2000°C			19	30	
526	EOS 6269, W-10 W/o Ta	15.1	78.5	.023	.34*	2.79	24	2.9	1 hr	2100°C			30	40	
527	EOS 5253, pure W	15.2	78.8	<.3	(.25)	3.44		2.2	1 hr	2000°C			3	20	
528	EOS 7103, W-2 W/o B ang. pwdr.	12.2	63.5		(.80)	1.92		3.9	5 hr	1800°C			91	200	200
529	ASTROMET 210-7, pure W, fragile														
530	ASTROMET 105, pure W, ang. pwdr.	12.96	67.5	.042	.54*	5N		32&33							
533	EOS Miscellaneous pieces	14.20		.01±.01	.14			34							
538	Phillips, pure W ang. pwdr.	12.82	67.0	.05	.64N			21/35							
					(.45)	3N									
* = Krypton () = Calculated N = Nominal															

* = Krypton
() = Calculated
N = Nominal

Figure 13 - Sample No. 141 American Leno 45000 100 Airline

100

Figure 14 - Sample No. 200 General Atomic 60 Carbon

100

Figure 15 - Sample No. 203 Super 37 Carbon

100

Figure 16 - Sample No. 240 Super HP 5 Carbon

100

Figure 17 - Sample 1 - 21 U to Carbon 600 (step 1) - Sample No. 1 - Carbon 600 - 1000 100 Airline

Figure 22-114 Al_2O_3 WESGO AL-1009

Figure 23--141 Al_2O_3 American
Lava ALSIMAG 548

Figure 24--220 Carbon General Atomic
#60

Figure 25--243 Carbon Speer
Carbon #37

100 μ

All photos at 250X

Figure 26--251 Carbon Pure Carbon
FC-50

Figure 27--Graphite Union Carbide
EGCR

Figure 28--317 Graphite Speer 37G-L

Figure 29--318 Graphite Speer 3499S

100μ

All photos at 250X

Figure 30--332 Graphite Carborundum
CARB-I-TEX 700

Figure 31--513 Porous Tungsten TRW
Pure W Etched

Figure 32--530 Porous Tungsten
ASTROMET 105 Pure W Etched

Figure 33--Porous Tungsten
ASTROMET 105 Pure W Etched

100μ

100μ

Figure 34--533 Porous Tungsten EOS
Misc.Pieces Copper Infiltrated

Figure 35--538 Porous Tungsten
Phillips Pure W Etched

All photos at 250X

10μ 2000 X

Figure 36--526 EOS .6269 W-10 Ta (Copper Infiltrated)
from NAS 3-6269

APPENDIX B EXPERIMENTAL APPARATUS AND PROCEDURE

APPARATUS

The design of the apparatus used to measure the pressure-temperature loading characteristics of the samples is shown in Figure 37. It consisted of four major components: The sample oven, a cesium reservoir, a capacitance manometer, and a 15 ℓ /sec ion pumped vacuum system. The original intention was to mount all four samples on the apparatus at one time, with each sample isolated by a nickel pinch off. When the time came to test each sample, the pinch off could be opened.

Unfortunately, it was discovered that after bakeout at 600°C the nickel pinch offs would not open. Therefore, the samples were welded into the apparatus one at a time. As it was necessary to expose the samples to air for a short period, they were outgassed again on the apparatus at 1100°C before loading them with cesium.

The sample housing is shown in Figure 38. The samples were held in a cup made of 0.003" tantalum foil and suspended in a heavy niobium cylinder. The cylinder was designed to produce an isothermal environment for the sample. Figure 38a shows the arrangement used for the preliminary outgassing of the samples. Figure 38b shows the original arrangement that would have allowed the samples to be opened to the system one at a time. Figure 38c shows the amended arrangement for testing one sample on the apparatus at a time.

The sample heater is shown in Figure 39. It consisted of six vertical 0.015 inch diameter tantalum filament wires surrounded by approximately 10 layers of tantalum, molybdenum, and stainless steel radiation shielding. About 150 watts was required to bring the niobium oven to 1000°C.

The cesium reservoir consisted of a stainless steel tube brazed into a copper block (nickel plated) which contained a sheathed heater and an air

B2

Figure 37--Plan View of Pressure-Temperature-Loading Apparatus

Figure 39--Heater Used for Niobium Sample Holders

cooling line. The capacitance manometer (manufactured by Granville-Phillips) was of stainless steel, welded construction on the side exposed to cesium and could be operated at temperatures up to 450°C. The device is not an absolute pressure monitor and had to be calibrated against the liquid-reservoir temperature. It was used in only the first test (carbon) due to difficulties encountered when minute quantities of cesium got in the reference side of the instrument and made it inoperable.

An ion pump was used to evacuate the apparatus after mounting a new sample, as well as to maintain a vacuum on the reference side of the capacitance manometer. Three stainless steel, welded, bellows sealed valves were included in the apparatus (HOKE 4235Q6Y, stellited 316 SS plug) to allow various parts of the system to be closed off. However, these valves would not seal helium leak tight after bakeout. Therefore, a Varian 1½" bakeable valve was installed in the line to the vacuum system to insure vacuum tight closures. The valves separating the cesium reservoir from the sample oven and capacitance manometer were used to allow the calibration of the manometer without involving the sample, as well as to allow the cesium reservoir to be brought up to the proper pressure before opening the valve to the sample, in order to get equilibrium time measurements.

The environment for the valves, cesium reservoir, and capacitance manometer was controlled by enclosing all parts in a stainless steel box and purging continuously with nitrogen. This was required to control oxidation of the parts as well as to prevent release of the radioactive cesium should a leak occur. The sample holder was in an 18" diffusion pumped bell jar equipped with a liquid-nitrogen trap. Pressures in the jar were normally less than 10⁻⁷ torr. All parts which were included in the vacuum system were bulk degassed (with the exception of the bellows, valves, and capacitance manometer, which were degassed when assembled on the apparatus). The stainless steel parts were heated for $\approx$ 50 hours at 900-950°C, copper and nickel parts for $\geq$ 50 hours at approximately 750°C, and niobium parts for $\geq$ 20 hours at 1800°C. Prior to degassing, all parts were chemically cleaned.

CESIUM LOADING AND CALIBRATION

The cesium loading in the sample was monitored by using activated cesium. Cesium was activated by irradiating a 10 gram nickel ampoule of cesium metal in a TRIGA reactor to a Cs^{134} intensity of approximately 50 micro curie/gram (two primary gamma rays at 0.605 MeV and 0.80 MeV with a 2.06 year half-life). After irradiation, the cesium ampoule was placed in a stainless steel container and the cesium was distilled into the reservoir. The cesium loading in the sample was monitored with a well shielded 2" NaI crystal and photomultiplier tube. The output of the phototube was fed into a preamplifier, amplifier, count-rate meter, and scaler. The output of the count-rate meter was recorded in order to establish that equilibrium had been achieved at each data point.

The counting equipment was set up to integrate all gamma rays with energies $\gtrsim 350$ keV. The drift of the electronics was checked after each data point with a $0.167 \mu\text{c}$ source of Cs^{134} . The counting system was calibrated with vials containing known quantities of CsNO_3 which were irradiated in the capsule along with the cesium metal. Two calibrations were performed: First, at the end of the test of each sample, a vial of CsNO_3 was placed in a niobium cylinder and counted in the same location as occupied by the sample. Second, all samples and standards were counted in a good geometry after the samples were removed from their ovens. These two calibrations agreed within 10%.

INSTRUMENTATION

Chromel/alumel thermocouples were used on the tubing to insure that all temperatures were $\gtrsim 50^\circ\text{C}$ above the cesium reservoir temperature. Calibrated chromel/alumel thermocouples (with cold junctions in an ice bath) were used in the sample oven and cesium reservoir. Temperature accuracy was considered to be $\pm 2^\circ\text{C}$. Leeds and Northrup temperature controllers were used on the cesium reservoir and sample oven.

CESIUM VAPOR PRESSURE-TEMPERATURE RELATIONSHIP

Cesium vapor pressures were determined from the temperature of the liquid pool which was assumed to be in equilibrium with the pressure over

the sample. The P-T curve used for the cesium metal was that recommended by Nottingham and Breitwieser⁽¹⁸⁾ as that giving the best fit to the experimented vapor-pressure data. The equation is:

$$\log_{10} p(\text{N/sq m}) = \frac{-3920.38}{T} - 0.519781 \log_{10} T + 10.71914$$

Table 5 gives the pressure-temperature data for cesium in the range of interest here.

TABLE 5
VAPOR PRESSURE OF CESIUM
(Liquid Reservoir)
torr

$^{\circ}\text{K}$	0	1	2	3	4	5	6	7	8	9
400	.276-2	.291.-2	.308.-2	.325-2	.343-2	.362-2	.382-2	.403-2	.425.-2	.448-2
410	.472-2	.498-2	.524-2	.552-2	.581-2	.612-2	.644-2	.677-2	.713-2	.749-2
420	.788-2	.828-2	.870-2	.914-2	.960-2	.101-1	.106-1	.111-1	.117-1	.122-1
430	.128-1	.135-1	.141-1	.148-1	.155-1	.162-1	.170-1	.178-1	.186-1	.195-1
440	.204-1	.214-1	.224-1	.234-1	.245-1	.256-1	.267-1	.279-1	.292-1	.305-1
450	.319-1	.333-1	.344-1	.363-1	.378-1	.395-1	.412-1	.430-1	.448-1	.457-1
460	.487-1	.508-1	.529-1	.551-1	.574-1	.598-1	.623-1	.648-1	.675-1	.703-1
470	.731-1	.761-1	.791-1	.823-1	.856-1	.890-1	.925-1	.962-1	.100-0	.104-0
480	.108-0	.112-0	.116-0	.121-0	.126-0	.130-0	.135-0	.140-0	.146-0	.151-0
490	.157-0	.163-0	.169-0	.175-0	.181-0	.188-0	.195-0	.202-0	.209-0	.216-0
500	.224-0	.232-0	.240-0	.249-0	.258-0	.267-0	.276-0	.286-0	.295-0	.306-0
510	.316-0	.327-0	.338-0	.350-0	.361-0	.373-0	.386-0	.399-0	.412-0	.426-0
520	.440-0	.454-0	.469-0	.484-0	.500-0	.516-0	.533-0	.550-0	.568-0	.586-0
530	.604-0	.623-0	.643-0	.663-0	.684-0	.705-0	.727-0	.749-0	.772-0	.796-0
540	.820-0	.845-0	.871-0	.897-0	.924-0	.952-0	.980-0	.101+1	.104+1	.107+1
550	.110+1	.113+1	.117+1	.120+1	.124+1	.127+1	.131+1	.134+1	.138+1	.142+1
560	.146+1	.150+1	.156+1	.159+1	.163+1	.168+1	.173+1	.177+1	.182+1	.187+1
570	.192+1	.197+1	.203+1	.208+1	.214+1	.220+1	.226+1	.232+1	.238+1	.244+1
580	.250+1	.257+1	.264+1	.270+1	.278+1	.285+1	.292+1	.300+1	.307+1	.315+1
590	.323+1	.331+1	.340+1	.348+1	.357+1	.366+1	.375+1	.384+1	.394+1	.403+1
600	.413+1	.423+1	.434+1	.444+1	.455+1	.466+1	.477+1	.489+1	.500+1	.512+1
610	.524+1	.537+1	.549+1	.562+1	.575+1	.589+1	.603+1	.616+1	.631+1	.645+1
620	.660+1	.675+1	.691+1	.706+1	.722+1	.738+1	.755+1	.772+1	.789+1	.807+1
630	.824+1	.843+1	.862+1	.881+1	.900+1	.919+1	.939+1	.960+1	.981+1	.100+2
640	.102+2	.105+2	.107+2	.109+2	.111+2	.114+2	.116+2	.119+2	.121+2	.124+2
650	.126+2	.129+2	.131+2	.134+2	.137+2	.140+2	.143+2	.145+2	.148+2	.151+2
660	.154+2	.158+2	.161+2	.164+2	.167+2	.170+2	.174+2	.177+2	.181+2	.184+2
670	.188+2	.192+2	.195+2	.199+2	.203+2	.207+2	.211+2	.215+2	.219+2	.223+2
680	.227+2	.232+2	.236+2	.240+2	.245+2	.250+2	.254+2	.259+2	.264+2	.269+2
690	.273+2	.278+2	.284+2	.289+2	.294+2	.299+2	.305+2	.310+2	.316+2	.321+2
700	.327+2	.333+2	.339+2	.345+2	.351+2	.357+2	.363+2	.370+2	.376+2	.383+2

APPENDIX C
CLEANING AND OUTGASSING OF SAMPLES

CLEANING PROCEDURES

The samples were cleaned and outgassed before being tested with cesium. The alumina, carbon, and graphite samples were chemically cleaned, primarily to remove contaminants introduced during sample preparation, and then outgassed. The tungsten 10% tantalum sample was received infiltrated with copper. After the copper de-infiltration, the sample was outgassed, no chemical cleaning was attempted. The chemical cleaning procedures are listed in Table 6.

The Al_2O_3 cleaning procedure listed in Table 6 and used for the sample which was tested was later modified because the procedure left brown stains on the ceramic which were attributed to an acetone-acid reaction. The modified procedure is:

- a. 3 minute ultrasonic cleaning in chloroform.
- b. 1 minute ultrasonic cleaning in H_2O .
- c. 10 seconds in acid solution of equal volumes of HF , HNO_3 , and H_2O .
- d. 1 minute ultrasonic cleaning in H_2O .
- e. Vacuum dry.

The graphite cleaning procedure was used in the sample which was tested. However, it is now recommended that graphite samples be cleaned using the same technique used with carbon.

The tungsten 10% tantalum sample was de-infiltrated by heating in vacuum. This sample, along with a group of others, was heated for one hour at 1500°C and one hour at 1600°C at pressures less than 5×10^{-6} torr. Because of the presence of copper, the samples were weighed and again

heated to 1500°C for one hour. After weighing, the samples were heated to 1550°C for one hour and weighed again to confirm that the copper had been removed.

TABLE 6
CHEMICAL CLEANING PROCEDURES

<u>Al₂O₃¹⁹</u>	<u>Carbon</u>	<u>Graphite</u>
a. 3 minute ultrasonic cleaning in following solution: 35 parts Methyl Ethyl Ketone 10 parts acetone 15 parts toluene 15 parts isopropyl alcohol 25 parts ethyl acetate 5 parts xylene	a. 3 minute ultrasonic cleaning in chloroform. b. 1 minute ultrasonic cleaning in H ₂ O. c. Vacuum dry.	a. 3 minutes in same cleaner as used for Al ₂ O ₃ . b. 3 minute ultrasonic cleaning in acetone. c. Vacuum dry.
b. 10 seconds in acid. 1 part HF 1 part HNO ₃ 1 part H ₂ O		
c. 1 minute ultrasonic cleaning in H ₂ O.		
d. 3 minute ultrasonic cleaning in acetone.		
e. Vacuum dry.		

OUTGASSING PROCEDURES

After cleaning, the samples were welded into the niobium sample ovens (previously described) and outgassed. The sample holder was mounted in a diffusion pumped bell jar with a connection to a 15ℓ/sec ion pump, quadrupole mass spectrometer, and roughing valve. After a preliminary bakeout of the tubing leading to the sample, after which the base pressure of the system was typically less than 10^{-7} torr at the mass spectrometer, the sample was heated. The outgassing temperature for the carbon, alumina, and W-10 Ta samples was set at 1200°C for two reasons: First, this temperature was 200°C above the highest operating temperature. Second, this temperature was low enough so that sintering effects in any of these materials should have been small. The CARB-I-TEX graphite sample was outgassed at 1500°C, the temperature limit of our oven, since there are no sintering problems with graphite.

Table 7 lists outgassing temperatures, time at temperature, pressure at end of outgassing, and major gases detected for the samples which were outgassed with the mass spectrometer attached. The alumina, graphite and tungsten 10% tantalum samples were brought up to temperature in a few hours while keeping the pressure below 10^{-5} torr (at the pump). They were then run until the pressure leveled out, a process that usually took 10-15 hours. Final pressures with the samples hot were $\leq 2 \times 10^{-8}$ torr.

Approximately 50 hours were required to bring the carbon sample to temperature. So much gas was evolved while first heating the sample that the roughing line was kept open until the sample reached approximately 150°C. The sample was held at temperature for 50 hours. A plot of the major gases evolved during the outgassing of this sample is shown in Figure 40. At the beginning of the outgassing, large quantities of high mass constituents were evolved (mass 50-250).

As noted in Table 7, the major gases evolved in all samples were H₂ and CO. In addition, H₂ was the major gas in the system at the end of the outgassing. After outgassing, the samples were pinched off and kept sealed.

Sample	Outgassing Temperature	Time at Temperature	Pressure at End of Outgassing x(10 ⁻⁸ torr) Hot/Cold						Major Gases (in order of amounts)
			Total	H ₂	CH ₄	N ₂	CO	CO ₂	
No. 141 Alumina	1150°C	16.0 hours	1.53	1.41	0.011	0.017	0.087	0.0022	H ₂ , CO, CH ₄
			1.19	1.10	0.0093	0.010	0.063	0.0022	
No. 251 Carbon	1170°C	50 hours	2.66	1.94	0.0093	0.62	< 0.01	0.0004	H ₂ , CO, N ₂ , CH ₄
			0.83	0.72	0.0093	0.066	< 0.003	0.0003	
No. 332 Graphite	1530°C	1.6 hours	-	-	-	-	-	-	H ₂ , CO, CO ₂
			0.88	0.81	0.0078	0.0069	0.029	0.0008	
No. 526 W-10Ta	1200°C	30.0 hours	1.29	1.16	0.011	0.013	0.068	0.0011	H ₂ , CO, CO ₂ , CH ₄
			1.21	1.13	0.0078	0.0037	0.055	0.0020	

TABLE 7
OUTGASSING DATA FOR SELECTED SAMPLES

Figure 40--Outgassing History of Pure Carbon FC-50 Sample