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NERVA FUEL ELEMENT DEVELOPMENT PROGRAM SUMMARY REPORT - JULY 1966 THROUGH JUNE 1972

Characterization of Vapor-Deposited Niobium and Zirconium Carbides

UNION CARBIDE

OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

prepared for the U.S. ATOMIC ENERGY COMMISSION
under U.S. GOVERNMENT *Contract W-7405 eng 26*

MASTER

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Characterization of Vapor-Deposited Niobium and Zirconium Carbides

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Date Issued - September 21, 1973

This report presents a summary of work performed on the characterization of vapor-deposited niobium and zirconium carbides of NERVA Fuel Elements for the Space Nuclear Systems Office, under Purchase Orders SNC-51, SNC-73, SNC-81, and SNC-95 during the period July 1966 through June 1972.

Prepared for the U.S. Atomic Energy Commission
Under U.S. Government Contract W-7405-eng-26

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ABSTRACT

Chemical and physical properties of vapor-deposited niobium carbide and zirconium carbide have been determined by the fabrication of thick-wall tubes of each carbide under varying deposition conditions. The effects studied included coefficient of thermal expansion, density, impurity level, carbon-to-metal ratio, and metallographic structure. The niobium carbide coatings contained less than 3,000 parts per million impurities, and the impurity level decreased when the deposition temperature was increased. Some of the zirconium carbide coatings contained four percent oxygen and chlorine, and the impure coatings were unstable when heated above the deposition temperature of 1,100°C. The amount of instability was primarily related to the oxygen and chlorine content; an increased deposition temperature reduced the impurity contents to less than 500 ppm. The higher-temperature process conditions produced coatings with a predictable and consistent coefficient of thermal expansion value which could be repeatedly heated to 2,000°C (~ 700°C above the deposition temperature) without any detrimental effects such as weight and volume changes. The weight and volume changes were related to the impurities being evolved when the coatings were heated to temperatures of 1,600 to 1,800°C.

CONTENTS

FOREWORD

The NERVA graphite fuel element program, which was funded for several years by the Space Nuclear Systems office, has been terminated at the Oak Ridge Y-12 Plant.(a) This report was abstracted from a series of progress reports which were issued routinely during the course of the fuel element studies, and covers data collected during the vapor deposition studies of the carbides of niobium and zirconium. These vapor-deposited carbides were examined for chemical purity and the effect of the impurities were studied in relation to the thermal stability of the deposited carbides.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.

SUMMARY

Chemical and physical properties of vapor-deposited niobium carbide and zirconium carbide were determined on thick-wall tubes of both carbides which were deposited under varying plating conditions.

NIOBIUM CARBIDE RESULTS

Tubes of niobium carbide were made using a low-temperature (900 to 1,250°C) process referred to as GEM[b] and a high-temperature (1,800 to 2,100°C) process referred to as GED.[c] The feed salts used were either niobium pentachloride or niobium pentabromide. The main results of the study are summarized by the following statements:

1. The coefficient of thermal expansion (CTE) of the GEM tubes deposited from niobium pentachloride salt was $7.0 \times 10^{-6}/^{\circ}C$ (20-1,000°C). This value compares favorably with a value of 7.2 for GEM tubes plated from niobium pentabromide and 6.6 for GED tubes plated from niobium pentachloride.
2. The CTE of the tubes was linearly related to the carbon-to-niobium ratio, with the CTE varying from a low of $6.6 \times 10^{-6}/^{\circ}C$ (20-1,000°C) at a carbon-to-niobium ratio of 0.80 to a high of $7.35 \times 10^{-6}/^{\circ}C$ (20-1,000°C) at a carbon-to-niobium ratio of 0.97.
3. The carbon-to-niobium ratio was lowest for the GED tubes and highest for the GEM tubes from niobium pentabromide.
4. GEM tubes from niobium pentachloride salt had an oxygen and chlorine contamination level of up to 1,000 ppm. GEM tubes from niobium pentabromide salt had essentially the same level of oxygen and bromine. GED tubes had a lower content with an oxygen impurity of about 150 ppm and the chlorine content ranging up to 375 ppm.
5. GEM tubes from niobium pentachloride had impurities (iron and silicon) ranging up to 1,000 ppm. However, in the GEM tubes from niobium pentabromide and the GED tubes, these impurities were generally below the detectable limits of the analysis.

(b) GEM - A vapor-deposition process where the carbon required to form the carbide is supplied from decomposing methane gas during the coating operation. The process can be controlled over a temperature range of 1,000 to 1,400°C. Methane is thermally decomposed into carbon and hydrogen. The carbon then reacts with the niobium pentachloride salt and other furnace gases to form niobium carbide. "GEM" stands for the G-end (E) methane (M) process. The "G" end is defined as the gas inlet end of the NERVA fuel element.

(c) GED - A vapor-deposition (D) process where the carbon required to form the carbide is supplied by carbon diffusing from the carbon surface which is being plated. The carbon diffusion process can be controlled over a temperature range of 1,500 to 2,300°C. A common plating temperature for this process is 2,000°C.

6. Although there were some variations between the coating processes, the density of all the tubes ranged between 7.3 and 7.8 gms/cc.

7. Both GEM processes gave a small, columnar-type grain structure, while the GED process provided a rather large grain structure.

ZIRCONIUM CARBIDE RESULTS

Tubes of zirconium carbide were made using the low-temperature GEM process and zirconium tetrachloride feed salt. The primary goal was for these coatings to be stable when heated to relatively high temperatures (2,000°C) and have a known and reproducible CTE. A knowledge of the other chemical and physical properties was also needed. The results of this study can be summarized by the following statements:

1. The most significant part of this study was the fact that the stability (and thus a consistent CTE) was related to the impurity level (mainly oxygen and chlorine).

2. Stable coatings (no weight or length change upon cycling to 2,000°C) were obtained when deposited at 1,330°C or above, and with an oxygen content of 0.2 percent or lower and a chlorine content of 0.1 percent or lower.

3. The CTE of these coatings was 7.7 to 7.8 x 10^{-6}/°C (20 to 2,000°C). The CTE value did not change on additional heat cycles.

4. Coatings deposited at lower temperatures (ie, less than 1,330°C) had higher oxygen and chlorine contents and were unstable upon heating to 2,000°C, undergoing length and/or weight changes and producing erratic CTE values.

5. The carbon-to-zirconium ratio could not be determined by X-ray diffraction due to broad and diffuse patterns. These nondefinitive X-ray patterns were partially due to the effect of the impurities. Carbon-to-zirconium ratios were determined by chemical analysis and found to be a function of the deposition temperature. These ratios were 0.90 for zirconium carbide deposited at 1,200°C, 0.95 when deposited at 1,300°C, and approaching 1.0 when deposited at 1,400°C.

6. The oxygen and chlorine contents of the tubes were also a function of the plating temperature. The oxygen level was 4 percent for zirconium carbide plated at 1,000°C and 0.04 percent for zirconium carbide plated at 1,400°C. The chlorine ranged from 1.5 to 0.04 percent between the same plating temperatures.

7. Impurities (mainly aluminum, iron, and silicon) were also related to the plating temperature. Values ranged to a maximum of 1,000 ppm for zirconium carbide deposited near 1,000°C and a minimum that was equivalent to the detectable limits of the analytical method used for these measurements for zirconium carbide deposited between 1,300 and 1,400°C.

8. The metallographic structure of GEM zirconium carbide coatings was very dependent upon the coating temperature. For zirconium carbide plated at 1,100 to 1,200°C, the

zirconium carbide structure was nearly amorphous; but, at a plating temperature of approximately 1,300°C, the growth of a columnar zirconium carbide structure was developed.

9. Thermogravimetric outgas analysis of a stable, low-impurity zirconium carbide coating showed only Mass 2 (H_2) being evolved between 1,200 and 2,400°C. However, a higher-impurity-level coating showed Mass 36 (HCl) being evolved between 1,400 and 1,800°C plus Mass 2.

10. Ion-beam microprobe analyses showed oxygen present as zirconium monoxide and dioxide but not oxychloride. Uncombined chlorine was also detected.

11. Density of the tubes was also dependent upon the coating temperature, reaching a maximum of essentially theoretical density (6.56 gms/cc) at about 1,300°C. At higher temperatures the density decreased.

INTRODUCTION

The NERVA graphite development program had specific goals which extended over a period of several years. One goal was to produce a fuel element which would result in a reactor capable of operating up to 60 cycles with run durations of ten minutes per cycle.

During the program tenure, routine progress reports on the development program were prepared. One phase of the development program included the deposition of niobium and zirconium carbides which were used as a barrier to protect the graphite matrices from attack by the hot hydrogen propellant gas. Effects of trace levels of impurities in the coatings were studied.

This compilation of niobium and zirconium carbide data was gained from information previously reported during the course of the studies. Similar compilations on other phases of the program are included in reports Y-1852, Parts 1 and 2, Y-1852, Parts 4 and 5, Y-1857, and Y-1868.

CHARACTERIZING VAPOR-DEPOSITED METAL CARBIDES

NIOBIUM CARBIDE THICK-WALL TUBES

Thick-wall tubes of niobium carbide were made from niobium pentachloride and niobium pentabromide at low (900 to 1,250°C) and high (1,800 to 2,100°C) plating temperatures and with various gas flows.(1 - 5) The low-temperature process (referred to as GEM) used methane as the main source of carbon, but the high-temperature process (GED) depended on the diffusion of carbon from a carbon tube which was used as a coating mandrel. Niobium carbide tubes were obtained by vapor coating the inside diameter (0.50 inch) of a carbon tube that was about 52 inches long. Each carbon tube was first coated with a thin (1 to 3-mil) layer of pyrocarbon to reduce the adherence of the niobium carbide coating to the carbon mandrel and facilitate removal of the niobium carbide tubes.

Low-Temperature Deposition Using Niobium Pentachloride Feed Salt

Three coating runs were made where the niobium carbide tubes were deposited at low temperatures (GEM) using niobium pentachloride feed salt. Deposition conditions for the three runs are listed in Table 1.

Table 1

COATING CONDITIONS FOR TUBES USING NIOBIUM PENTACHLORIDE FEED SALT

	Run 1		Run 2		Run 3	
Parameter	PyC	NbC	PyC	NbC	PyC	NbC
Time (hrs)	13	3 + 76	5	58	6	133
Weight Gain (gms)	~ 6	150 to 350	~ 3	219	~ 3	163
Coating Rate (gms/hr)	-	1.9 to 4.4	-	3.77	-	1.22
Gas Flow (1/min/tube)						
Ar	9.0	9.00	9.0	9.00	9.0	4.50
HCl	-	1.50	-	1.50	-	0.75
H_2	-	0.164	-	0.164	-	0.082
CH_4	0.4	0.040	0.4	0.040	0.4	0.020
$NbCl_5$	-	0.171	-	0.178	-	0.092
Coating Temperature (° C)						
0-Inch Location	1,080	930	-	-	-	933
10-Inch Location	1,205	1,040	1,200	1,040	1,205	1,050
23-Inch Location	1,215	1,090	-	-	-	1,080
37-Inch Location	1,210	1,140	1,210	1,140	1,205	1,080
47-Inch Location	1,225	1,225	-	-	-	1,100
52-Inch Location	1,230	1,250	1,230	1,245	1,220	1,110
Coating Thickness (mils)						
0-Inch Location	1	4 to 8	~ 0.5	-	~ 0.5	16
20-Inch Location	2	12 to 14	~ 1.0	-	~ 1.0	17
30-Inch Location	3	16 to 22	~ 1.5	16	~ 1.5	18
40-Inch Location	4	18 to 50	~ 2.0	43	~ 2.0	19
52-Inch Location	8	10 to 180	~ 4.0	90	~ 3.0	26

For the coating studies, two tubes of niobium carbide were produced in each plating run. The first coating run was not typical because of a malfunction within the load cell (used to determine the $NbCl_5$ usage) at the beginning of the run, and the base film of pyrocarbon was too thick. It appeared that a portion of the niobium carbide coating in one of the carbon mandrels pulled away from the graphite matrix and eventually almost plugged the mandrel bore. This action diverted most of the coating gas flows to the second mandrel and resulted in an abnormally thick coat, especially at the hot end of the mandrel. A view of the hot-end (50 to 52-inch) region of the niobium carbide tube produced in the second run is provided in Figure 1.

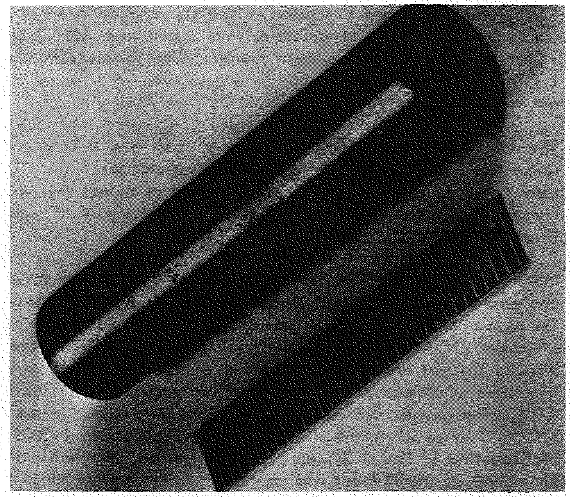

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Figure 1. NIOBIUM CARBIDE THICK-WALL TUBE. (Hot End)

The third run was made with the total gas flow per mandrel reduced from 10.8 to 5.4 liters per minute. This run was made to determine if minor process changes would produce any significant changes in the properties of the niobium carbide tube. There appeared to be no appreciable difference in the densities, coefficients of thermal expansion, or impurity contents of the vapor-deposited niobium carbide tubes.

Coefficient of Thermal Expansion - Free-standing tubes of niobium carbide were obtained at deposition temperatures that ranged from 1,080 to 1,240°C, and CTE values were determined on these pieces. A summary of the values is provided in Table 2.

Table 2

COEFFICIENT OF THERMAL EXPANSION VALUES FOR NIOBIUM CARBIDE TUBES MADE USING NIOBIUM PENTACHLORIDE

Tube Position (in)	Deposition Temperature (° C)	Run	Wall Thickness (mils)	Coefficient of Thermal Expansion(1) (° C x 10^{-6}) As Deposited	After Reheat to 2,000° C
23	1,085	1	16	7.1	7.3(2)
26	1,100	2	14	6.7	-
30	1,115	1	21	7.1	-
42	1,090	3	24	7.0	-
44	1,190	2	64	6.9	-
50	1,230	2	87	6.8	-
51	1,240	1	160	7.1	-

(1) From 20 to 1,000° C.

(2) This sample broke after reheating to 2,000°C, leaving just a one-inch sample for CTE determination. The accuracy with such a short sample is questionable.

Data from this study show that the CTE did not vary much over a wide thickness range and a moderate range of deposition temperatures and deposition rates. The average value of 7.0 x 10^{-6}/°C (20 - 1,000°C) compared favorably to the reported literature value of 7.2 x 10^{-6}/°C.(6) A limitation of CTE determinations up to 1,000°C to discover minor CTE variations was recognized and, in later zirconium carbide work, values were obtained up to 2,000°C.

Chlorine and Oxygen Contents - Chlorine contents of the thick-wall niobium carbide tubes were investigated. Determinations by both the pyrohydrolysis chemical analysis and electron microprobe methods showed reasonable agreement, as indicated in Table 3. The chemical analysis data given in Figure 2 indicate that the chlorine concentration was dependent on the deposition temperature and sample location, and varied from a high of 1,000 ppm at the gas inlet end (1,000°C) to a low of 120 ppm at the gas exit end (1,250°C).

Table 3

CHLORINE CONTENT OF NIOBIUM CARBIDE THICK TUBES

Tube Position (in)	Deposition Temperature (°C)	Chlorine Content (ppm) By Chemical Analysis	Chlorine Content (ppm) By Microprobe Analysis
28	1,110	467	No Sample
38	1,150	172	200 - 300
46	1,210	108	< 200

Oxygen contents (Figure 2) were found to be approximately equal to the chlorine level at each of the sample points. Oxygen levels varied from a high of 1,100 ppm at the gas inlet end (1,000°C) to a low of 100 ppm at the exit end (1,250°C).

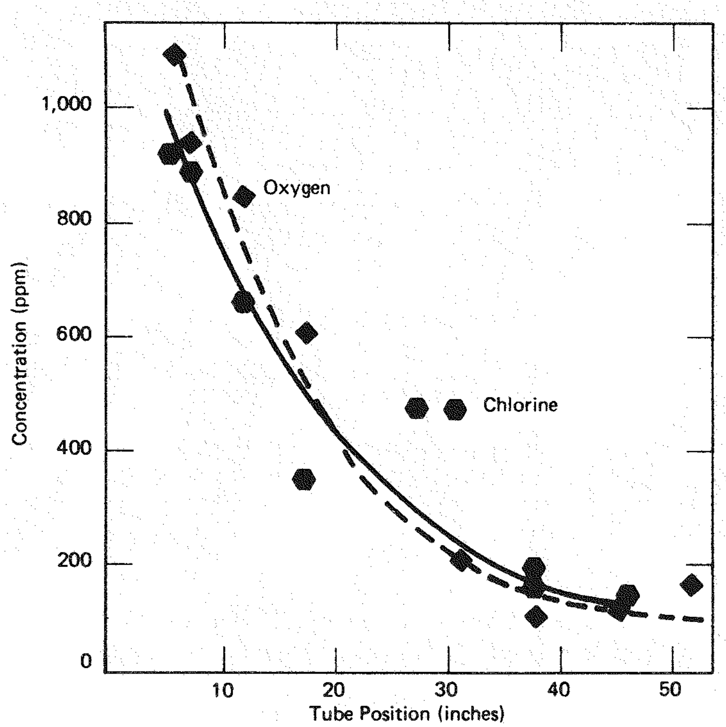

Figure 2. IMPURITIES CONTENT OF NIOBIUM CARBIDE THICK-WALL TUBES USING NIOBIUM PENTACHLORIDE FEED SALT.

Other Impurities - Samples were taken along the niobium carbide tube length and analyzed for impurities other than oxygen and chlorine. Results of these tests are listed in Table 4. Significantly high impurities were noted for silicon, iron, and aluminum. These impurities were higher toward the middle of the tube than at either of the ends. The concentration of these impurities as a function of the deposition temperature is noted in the graph of Figure 3. Iron concentrations were highest in the 1,050 to 1,075°C range, while silicon tended to peak nearer 1,200°C.

Density - Densities of the tubes (by mercury porosimetry) are listed in Table 5 and also given in Figure 3. As noted, the density increased slightly as the plating temperature increased.

One of the samples was heated to 2,000°C for one hour in carbon, but the sample broke so it was not possible to get a weight loss. Changes in density and oxygen values are reported in Table 6.

Carbon Content and the Carbon-to-Niobium Ratio - The carbon content (chemical analysis) and carbon/niobium ratio (X-ray diffraction) are also given in Table 5. The combined carbon increased when the niobium carbide was plated between 1,070 and 1,120°C, but decreased as the plating temperature was increased to 1,200 - 1,250°C. A

Table 4

IMPURITIES IN A NIOBIUM CARBIDE TUBE MADE
USING NIOBIUM PENTACHLORIDE

	Tube Length (in)					
	10	17 to 19	31 to 32	42 to 46	47 to 51	Exit Line
Deposition Temperature (°C)	1,040	1,070	1,120	1,200	1,250	< 1,250
Impurities (ppm)						
Ag	< 10	15	10	< 10	< 10	< 10
Al	10	30	100	100	10	10
B	< 1	3	3	3	3	3
Be	< 3	< 3	< 3	< 3	< 3	< 3
Bi	< 10	< 10	< 10	< 10	< 10	< 10
Ca	< 100	< 100	< 100	< 100	< 100	< 100
Cd	< 10	< 10	< 10	< 10	< 10	< 10
Co	< 3	65	25	40	15	15
Cr	< 10	35	20	25	15	15
Cu	< 10	< 10	< 10	20	< 10	< 10
Fe	20	> 1,000	1,000	600	400	500
Ga	< 3	< 3	< 3	< 3	< 3	< 3
In	< 10	< 10	< 10	< 10	< 10	< 10
Mg	< 10	< 10	20	20	< 10	< 10
Mn	< 1	6	6	2	2	2
Mo	< 30	< 30	< 30	< 30	< 30	< 30
Ni	20	10	10	< 10	< 10	< 10
Pb	< 3	20	< 3	50	60	25
Si	< 30	600	900	1,000	30	< 30
Sn	< 3	3	< 3	< 3	< 3	< 3
Ta	< 300	< 300	< 300	< 300	< 300	< 300
Ti	< 10	< 10	< 10	< 10	< 10	< 10
V	< 10	< 10	< 10	< 10	< 10	< 10
W	300	< 100	< 100	< 100	< 100	< 100
Y	< 10	< 10	< 10	< 10	< 10	< 10
Zn	< 300	< 300	< 300	< 300	< 300	< 300
Zr	< 100	350	500	< 100	< 100	< 100

further decrease was noted as the temperature was lowered below 1,250°C in the exit line. This trend seems a little unusual, but the X-ray diffraction data followed a similar cyclic pattern.

There were no reported difficulties in the X-ray diffraction analyses; ie, no weak-line intensities, no broad and diffuse lines, and no minor or intermediate phases.

Electrical Resistivity - The niobium pentachloride salt produced thick tubes having electrical resistivity values of 110 to 125 μohm-cm when measured at room temperature. Tubes reheated to 1,000°C in a carbon-free atmosphere produced no significant changes. A comparison with values obtained when using niobium pentabromide feed salt is made in a later section of this report. (Page 16)

Thermal Gravimetric Analysis (TGA) - TGA studies indicated essentially no weight loss from room temperature to 1,600°C for any of the samples.

Table 5

PROPERTIES OF VAPOR-DEPOSITED NIOBIUM CARBIDE THICK-WALL TUBES MADE USING NIOBIUM PENTACHLORIDE

	Tube Length (in)						
Property	10	18	22(1)	31	44	52	Exit Line
Deposition Temperature (°C)	1,040	1,070	1,085	1,120	1,200	1,250	< 1,250
Carbon Content (%)							
Total	-	10.942	-	11.096	10.649	10.686	10.327
Combined	-	10.942	-	11.096	10.439	10.549	10.214
Free	-	None	-	None	0.210	0.137	0.113
X-Ray Diffraction							
Major Phase(2)	NbC	NbC	-	NbC	NbC	NbC	NbC
Lattice Parameter (A)	4.4663	4.4661	-	4.4665	4.4655	4.4657	4.4643
C/Nb (ratio)	0.916	0.914	-	0.918	0.907	0.909	0.894
Oxygen Content (ppm)	580	210	310	160	140	< 100	< 100
Mercury Porosimetry							
Bulk Density (gms/cc)	7.43	7.58	7.34	7.57	7.57	7.72	7.67
Porosity (%)	0.58	0.50	2.92	0.50	1.57	0	0
Real Density (gms/cc)	7.47	7.62	7.56	7.61	7.69	7.72	7.67
Thermal Gravimetric Analysis							
Weight Loss(3) (%)	-	0.012	0.018	-	None	-	None
Material Evolved (mass number)	-	None	None	-	None	-	None

(1) Reheated to 2,000°C for one hour in a carbon atmosphere.

(2) No intermediate or minor phases reported.

(3) Between room temperature and 1,600°C.

Table 6

CHANGE IN NIOBIUM CARBIDE TUBES HEATED TO 2,000° C IN CARBON

Sample	NbC Position (in)	Deposition Temperature (°C)	Bulk Density (gms/cc)	Real Density (gms/cc)	Open Porosity (%)	Oxygen Content (ppm)
As Deposited	18	1,070	7.58	7.62	0.50	210
After Reheat to 2,000° C	22	1,085	7.33	7.55	2.92	310

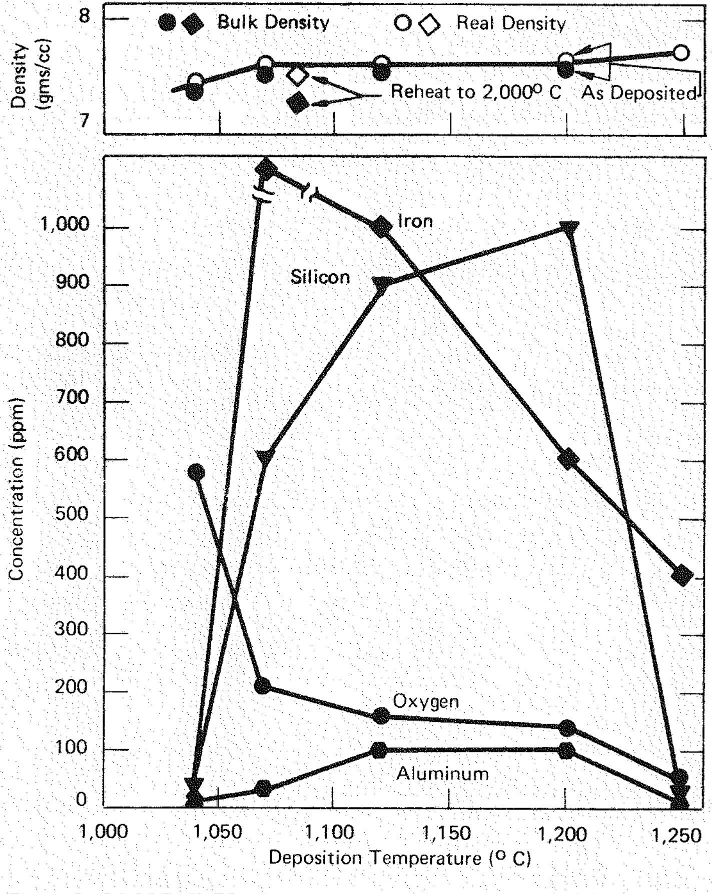

Figure 3. PROPERTIES OF NIOBIUM CARBIDE TUBES MADE FROM NIOBIUM PENTACHLORIDE.

Metallographic Structure - Photographs of the as-deposited crystal structure are provided in Figures 4 and 5. These structures varied along the niobium carbide tube length and were dependent on the plating temperature, gas composition, and other plating conditions. These photographs show a typical wide range in deposited structures. Discontinuities in the structure were due to interruptions in the deposition due to process difficulties.

Figure 6 shows a niobium carbide section heated to 2,000°C in a carbon atmosphere. This structure, when compared to Figure 4, shows larger grains and that porosity had developed at the grain boundaries. Porosity in niobium carbide-coated films was not noted in any of the as-deposited structures. This phenomenon is believed to be caused by micro impurities which caused grain growth and sintering of the niobium carbide. Porosity at grain boundaries can occur because of the movement of the micro impurities.

Formation of Dendrites - As previously mentioned, the first niobium carbide plating run had an interruption at the very beginning of the coating run due to a malfunction of the load cell. Some of the coating pulled away from the carbon mandrel and a very large number of "wart-like" bumps were evident in the niobium carbide tube which was nearly plugged. One of the nodules which may have originated on a "site" on the pyrocarbon surface can be seen in Figure 7. The center of the nodule is carbon surrounded by a niobium carbide coating.

Low-Temperature Deposition Using Niobium Pentabromide Feed Salt

Two coating runs were made at low temperatures (GEM) using niobium pentabromide feed salt to determine if the vapor-deposited tubes had physical properties different from those made by using niobium pentachloride salt. Although no major differences were detected, the niobium pentabromide process seemed to produce tubes which had physical properties which were at least equivalent to or, in most cases, slightly better than those deposited from niobium pentachloride. The more desirable physical properties included a slightly higher CTE, greater density, higher carbon-to-niobium ratio, a better grain structure, less open porosity, lower electrical resistivity, and more stability on heating to 2,000°C. Properties

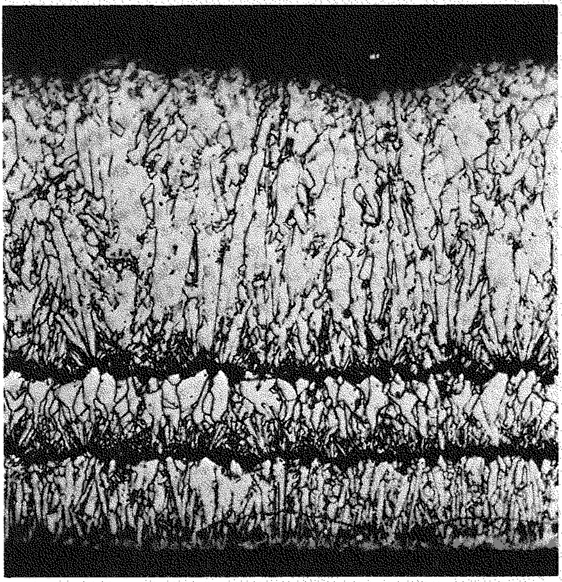

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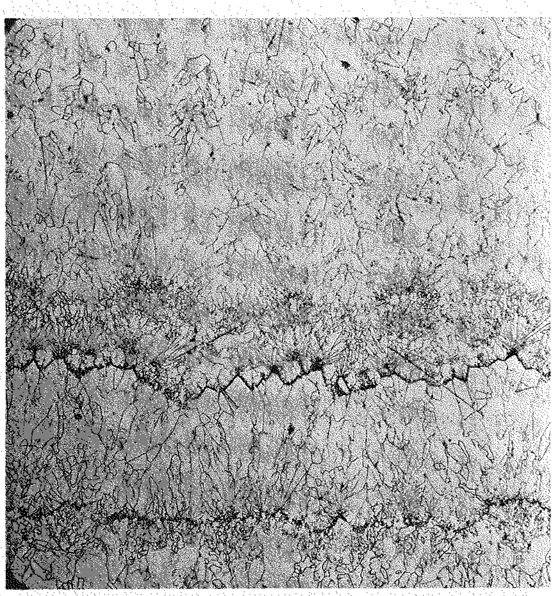
Figure 4. AS-DEPOSITED CRYSTAL STRUCTURE AT 25 INCHES WHEN THE NIOBIUM CARBIDE WAS COATED AT 1,100°C. (Bright Field Illumination; 400X)



G156-10

Figure 5. AS-DEPOSITED CRYSTAL STRUCTURE AT 52 INCHES WHEN THE NIOBIUM CARBIDE WAS COATED AT 1,250°C. (Bright Field Illumination; 75X)

that were essentially the same included the amount of impurity and their oxygen and halide contents.

Coating conditions are summarized in Table 7 and, as noted, are essentially the same as those when the niobium pentachloride feed salt was used. Run time for the first run was not long enough to produce enough tubes of sufficient thickness; thus, the second run was essentially a duplication of the first run, but with an increased plating time.

Coefficient of Thermal Expansion - CTE values of the niobium carbide tubes produced from niobium pentabromide ranged between 7.1 and 7.2 x 10^{-6}/°C (20-1,000°C). These values are slightly higher than the values of the niobium carbide tubes made from the niobium pentachloride feed salt. Comparative CTE values are reported in Table 8. Within the accuracy of the equipment, the CTE (20 - 1,000°C) of the niobium carbide produced from niobium pentabromide did not change appreciably after heating to 2,000°C for one hour in a carbon atmosphere.

Oxygen and Bromine Impurities - Levels of the oxygen and bromine impurities are indicated by the graph of Figure 8 and listed in Table 9. These impurity concentrations are nearly equal to the concentrations noted in the tubes coated using niobium pentachloride feed salt except that the chlorine has been replaced by bromine. The oxygen content of a sample was lowered (143 to 43 ppm) by reheating to 2,000°C in a carbon atmosphere.

Other Impurities - In general, the niobium carbide tubes made using niobium pentabromide did not contain any significant amount of other impurities. The only significant impurities that appeared in the tubes made using niobium pentachloride (aluminum, iron, and silicon) did not appear in the tubes made using niobium pentabromide. No doubt, this difference was due to the difference in the impurity level of the feed salt and to a deposition of the impurities in the preheater zone of the coating equipment. The actual impurities of the tubes made using niobium pentabromide are listed in Table 9. Note that heating the tubes to 2,000°C did not significantly change the values.

Density - The real density of the tubes was about the same as those made using niobium pentachloride. However, there was essentially no open porosity in the tubes deposited from niobium pentabromide so their bulk density was slightly higher. As with the niobium pentachloride system, the density increased slightly as the deposition temperature increased. The various values are given in Table 9.

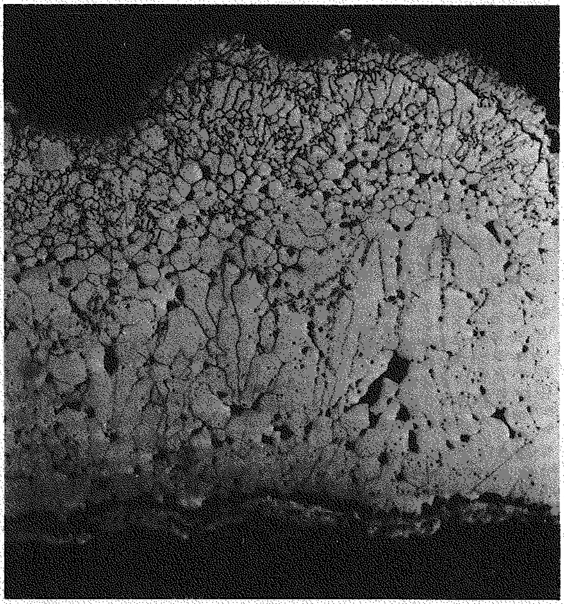


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Figure 6. SAMPLE COATED AT 1,090°C, TAKEN AT 24 INCHES, AND REHEATED TO 2,000°C IN CARBON. (Bright Field Illumination; 400X)

The sample reheated to 2,000°C had an increase in density from 7.57 to 7.73 gms/cc, and no open porosity. By comparison, the niobium pentachloride process tube on reheating to 2,000°C had 2.92 percent open porosity, a bulk density of 7.34 gms/cc, and a real density of 7.56 gms/cc (see Table 5).

Carbon Content and the Carbon-to-Niobium Ratio - The carbon content and carbon-to-niobium ratio for tubes from the niobium pentabromide process are also given in Table 9. Both values were higher for the niobium pentabromide process than for the niobium pentachloride process, but the values decreased faster along the tube length. For example, the niobium pentabromide system produced tubes which had a carbon-to-niobium ratio of 0.944 at the gas inlet end and 0.916 at the gas exit end; while, for the niobium pentachloride system, the comparable carbon-to-niobium values were 0.916 at the inlet end and 0.909 at the outlet end. The carbon-to-niobium ratio for the sample reheated to 2,000°C increased from 0.928 to 0.935.

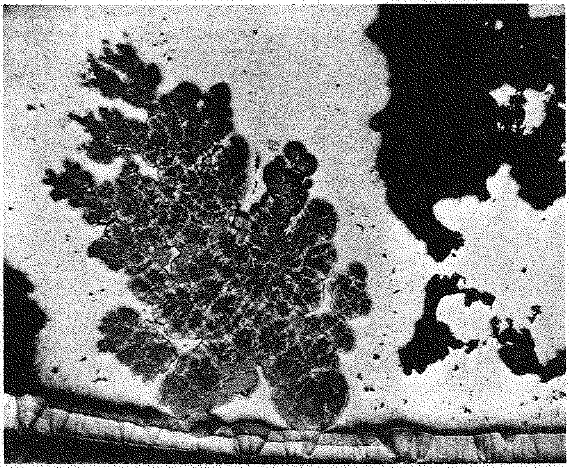

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Figure 7. DENDRITIC GROWTH IN THE NIOBIUM CARBIDE TUBE. (Sensitive Tint; 100X)

Electrical Resistivity - Room-temperature electrical resistivity values of niobium carbide tubes made using niobium pentabromide feed salt were 65 to 75 μohm-cm. This range of resistivities can be compared to 110 to 125 μohm-cm for tubes made using niobium pentachloride. In both cases, tubes heated to 1,000°C in a carbon-free atmosphere produced no significant changes. Results of these tests are summarized in Table 10.

Metallographic Structure - The as-deposited crystal structure of tubes made from the niobium pentabromide process is detailed in Figure 9. When compared with Figure 4, which is the coating deposited using niobium pentachloride salt at about the same deposition temperature, it can be noted that the niobium pentabromide salt (disregarding the laminations due to process interruptions) produced fewer but larger crystals. This difference, along with the other data comparison (such as higher carbon content, higher real and bulk densities, and fewer impurities) would explain the more dense structure of the niobium carbide made using niobium pentabromide salt which occurred after it was heated to 2,000°C in a carbon atmosphere, as emphasized in Figure 10. The reheated tube from niobium pentabromide salt showed practically no porosity when compared to the reheated tube from the niobium pentachloride process (Figure 10 versus Figure 6).

Table 7

COATING CONDITIONS FOR NIOBIUM CARBIDE THICK-WALL TUBES USING NIOBIUM PENTABROMIDE FEED SALT

	Run 4		Run 5	
	PyC	NbC	PyC	NbC
Time (hrs)	6	31	6	59 1/2
Weight Gain (gms)	-	85	-	136
Coating Rate (gms/hr)	-	2.76	-	2.34
Gas Flow (l/min/tube)				
Ar	9.0	9.0	9.0	9.0
HBr	-	1.5	-	1.5
H_2	-	0.164	-	0.164
CH_4	0.4	0.040	0.4	0.040
$NbBr_5$	-	0.175	-	0.175
Coating Temperature (° C)				
0-Inch Location	-	915	1,100	925
10-Inch Location	1,220	1,040	1,210	1,040
23-Inch Location	1,210	1,095	1,210	1,092
36-Inch Location	-	1,140	1,190	1,140
47-Inch Location	-	1,215	1,205	1,215
52-Inch Location	1,210	1,250	1,210,	1,250
Coating Thickness (mils)				
10-Inch Location	1.0	-	1.0	1 1/2
20-Inch Location	1.3	2	1.3	4
30-Inch Location	1.4	4	1.4	8
40-Inch Location	1.4	14	1.4	20
52-Inch Location	2.1	40	2.1	75

Table 8

COEFFICIENT OF THERMAL EXPANSION OF NIOBIUM CARBIDE TUBES

Sample Location (in)	Deposition Temperature (° C)	NbC Thickness (mils)	Coefficient of Thermal Expansion(1) (x 10^{-6}/° C)	
			$NbCl_5$ Salt	$NbBr_5$ Salt
23	1,085	16	7.1	
26	1,100	14	6.7	
30	1,115	25	7.1	
32	1,125	9	-	7.1
42	1,090	24	7.0	
42	1,180	25	-	7.2
44	1,190	64	6.9	
46(2)	1,205	22	-	7.1(2)
49	1,230	63	-	7.2
50	1,240	87	6.8	-
51	1,240	160	7.1	-

(1) Temperature - 20 to 1,000° C; all samples measured in the as-coated state.

(2) After reheating to 2,000° C for one hour in a carbon atmosphere.

High-Temperature Deposition Using Niobium Pentachloride Feed Salt

Only one coating run was made in which niobium carbide tubes were made from niobium pentachloride feed salt using the high-temperature (1,800 to 2,100°C) diffusion-type process (GED). This GED process required that the carbon for the carbide be obtained by diffusion from the carbon mandrel instead of the addition of methane. Coating conditions and the thickness profile are reported in Table 11.

Oxygen and Chlorine Content - As noted in Table 12, the oxygen content was low (< 150 ppm) and

Table 9

PROPERTIES OF VAPOR-DEPOSITED NIOBIUM CARBIDE THICK-WALL TUBES MADE USING NIOBIUM PENTABROMIDE

	Tube Position (in)					
	11	28	35	38(1)	44	51
Deposition Temperature (°C)	1,040	1,110	1,140	1,150	1,190	1,240
Chemical Carbon Content (%)						
Total	-	11.422	11.263	10.8777	10.977	10.687
Free	0.592	0.157	0.116	0	0.010	0
Combined	-	11.265	11.147	10.8777	10.967	10.687
X-Ray Diffraction Major Phase(2)	NbC	NbC	NbC	NbC	NbC	NbC
Lattice Parameter (A)	4.4684	4.4679	4.4673	4.4678	4.4666	4.4663
Carbon/Niobium Ratio	0.944	0.936	0.928	0.935	0.920	0.916
Oxygen Content (ppm)	610	258	143	43	81	< 50
Bromine Content (ppm)	842	210	132	-	200	52
Mercury Porosimetry Bulk Density (gms/cc)	7.350	7.354	7.571	7.731	7.686	7.752
Porosity (%)	0	0	0	0	0	0
Real Density (gms/cc)	7.350	7.354	7.571	7.731	7.686	7.752
Metallic Impurities (ppm)						
Aluminum	10	10	10	< 10	10	10
Iron	25	15	12	30	< 10	< 10
Molybdenum	30	30	< 30	30	< 30	< 30
Nickel	30	10	< 10	< 10	< 10	< 10
Silicon	30	< 30	< 30	< 30	< 30	< 30
Tungsten	300	100	< 100	< 100	< 100	< 100

(1) Reheated to 2,000° C for one hour in a carbon atmosphere.
(2) No other phases reported.

Table 10

ELECTRICAL RESISTIVITY OF NIOBIUM CARBIDE TUBES

Sample Location (in)	Deposition Temperature (°C)	Wall Thickness (mils)	Resistivity (μohm-cm) As Coated	Resistivity (μohm-cm) After Heating to 1,000°C(1)
		Using $NbCl_5$ Feed Salt		
23	1,085	16	125	125
30	1,175	25	110	115
		Using $NbBr_5$ Feed Salt		
32	1,125	9	65	60
42	1,180	25	65	60
49	1,230	63	75	75

(1) Heating to this temperature was done in a carbon-free furnace.

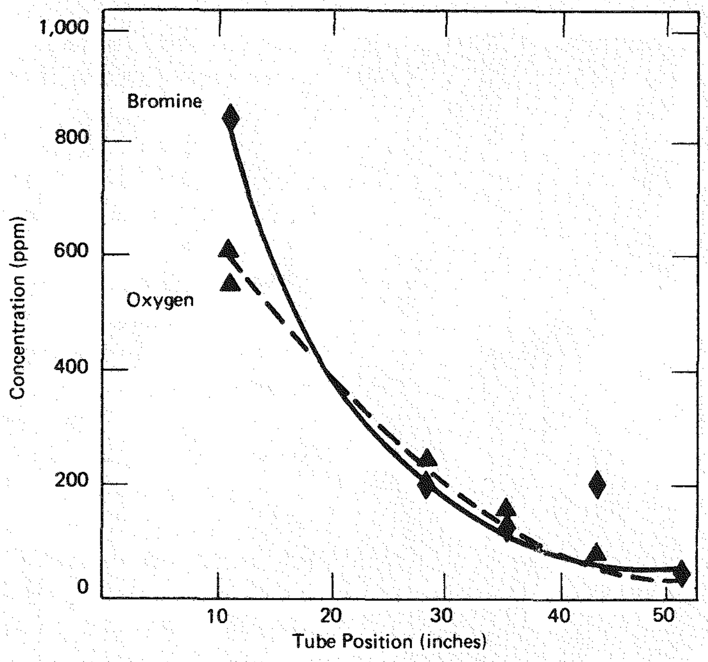

Figure 8. IMPURITIES CONTENT OF NIOBIUM CARBIDE THICK-WALL TUBES USING NIOBIUM PENTABROMIDE FEED SALT.

essentially constant along the entire tube length. The chlorine content was also low (in the range from 50 to 375 ppm). Comparable values for tubes made from the low-temperature (GEM) process were 1,000 ppm at the gas inlet end to 125 ppm at the exit end for both oxygen and chlorine.

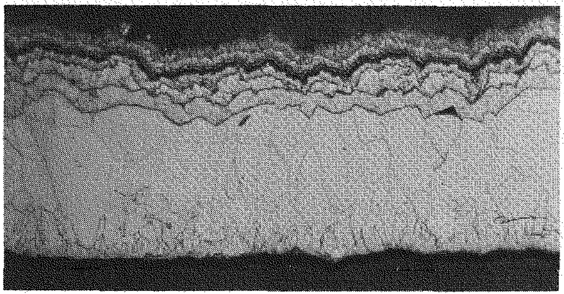

Figure 9. AS-DEPOSITED NIOBIUM CARBIDE (USING $NbBr_5$) AT THE 25-INCH LOCATION. (Coated at 1,100°C; Bright Field Illumination; 500X)

Other Impurities - Other impurities were very low, generally below the detectable limits (Table 12). The exception was tungsten which was present in the feed salt.

Density - Bulk and real densities were 7.735 and 7.797 gms/cc, respectively. Open porosity was 0.79 percent at the low-temperature end (gas inlet) of the tube (Table 12). As the deposition temperature and coating rate increased along the tube length, the open porosity increased and thus lowered the density. However, the densities (even with a large amount of open porosity) were higher than those obtained in the low-temperature (GEM) tubes.

Electrical Resistivity - Electrical resistivity of the GED tubes ranged from 140 to 170 μohm-cm. These values are higher than the 110 to 130 μohm-cm for the GEM niobium carbide from niobium pentachloride and 65 to 75 μohm-cm for GEM niobium carbide from niobium pentabromide.

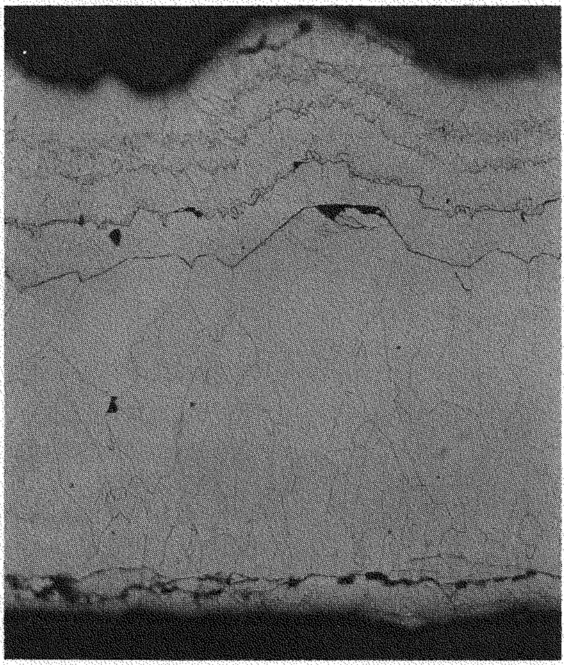

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Figure 10. NIOBIUM CARBIDE (USING $NbBr_5$), COATED AT 1,150°C (AT THE 38-INCH LOCATION), AND REHEATED TO 2,000°C IN CARBON. (Bright Field Illumination; 250X)

Carbon and Niobium Contents and the Carbon-to-Niobium Ratio - Carbon and niobium contents of the tubes were determined by chemical analysis. These data (Table 12) showed that the tubes were niobium rich, having a niobium content of 90.2 to 90.7 weight percent compared to 88.55 weight percent for theoretical niobium carbide. Niobium contents increased with increasing deposition temperatures. Carbon contents of 9.8 to 9.3 weight percent were considerably lower than theoretical (11.45 wt %). This difference was as expected due to the high coating temperatures and the fact that the carbon was being supplied from the carbon mandrel by diffusion through the deposited niobium carbide coating. As noted in Table 12, the average carbon-to-niobium ratio (from chemical analysis) ranged from 0.840 at the gas inlet end (1,800°C) to 0.795 at the gas outlet end (2,100°C). No free carbon was found in the samples.

Samples were also analyzed by X-ray diffraction. These data showed two carbon-to-niobium ratio levels. One level, which was higher and essentially constant (0.878 to 0.880), is believed to be the matrix side of the coating which had an available supply of carbon; the lower ratio was probably on the gas side of the coating, thus away from the supply of carbon from the substrate (element matrix). This lower ratio decreased along the element length from 0.780 at the gas inlet end (1,800°C) to 0.726 at the gas exit end (2,100°C), indicating that, as the coating thickness increased, the supply of carbon at the deposition surface was lower.

X-ray diffraction data for all the niobium carbide tubes deposited under the various processes are summarized in Figure 11. Effect of the high-temperature (GED) process is quite evident.

Also given in Figure 11 are the ratios of the low-temperature (GEM) niobium carbide tubes made using niobium pentachloride. These carbon-to-niobium values are higher (0.90 to 0.91) and show a slight drop off when going down the tube length. The slight difference between Runs 1 and 3 was probably due to coating-rate effects.

Another significant difference noted in Figure 11 was the carbon-to-niobium ratios for the niobium carbide tubes that were made using niobium pentabromide. These ratios were higher (0.945 to 0.915) and dropped off at a much faster rate along the tube length. These decreasing carbon-to-niobium ratios along the tube length were a result of temperature changes and coating gas changes, plus other effects.

Table 11

DIFFUSION COATING CONDITIONS FOR NIOBIUM CARBIDE TUBES

(Run 6)

Run Time (hrs)	48
Weight Gain (gms)	103
Coating Rate (gms/hr)	2.14
Gas Flow (l/min/tube)	
Ar	9.0
HCl	1.5
H_2	0.244
$NbCl_5$	0.181

Tube Position (in)	Coating Temperature (°C)	Coat Thickness (mils)
0	1,800	7
10	1,900	11
25	1,950	18
35	2,000	20
52	2,100	30

Coefficient of Thermal Expansion - The CTE value (20-1,000°C) of the GED niobium carbide tubes was 6.6 x 10^{-6}/°C (20-1,000°C). This value compared favorably with the 7.0 for the GEM-niobium carbide tubes from niobium pentachloride and about 7.2 for the GEM-niobium carbide tubes from niobium pentabromide.

Since the GED tubes had a significantly lower CTE and carbon-to-niobium ratio than the GEM tubes, it was desirable to determine if there was a relationship between the two properties. Selected tubes of each type (GEM NbC-$NbCl_5$, GEM NbC-$NbBr_5$, and GED NbC-$NbCl_5$) having a variety of carbon-to-niobium ratios were again measured to determine their CTE values. The tubes were next heated to 2,500°C in a carbon atmosphere in order to increase the carbon-to-niobium ratio. X-ray diffraction analyses and CTE values were again determined. The available data are reported in Table 13 and Figure 12. These data show that the CTE values increased linearly with increasing carbon-to-niobium ratios from a low of 6.6 x 10^{-6}/°C (20-1,000°C) to a high of 7.35 x 10^{-6}/°C (20-1,000°C) for carbon-to-niobium ratios of 0.80 and 0.97, respectively. All niobium carbide tubes produced by both the GEM and GED processes had the same CTE value when the carbon-to-niobium ratios were equal.

Metallographic Structure - The as-deposited grain structure of the GED process is emphasized in Figure 13. As expected, this high-temperature process produced a very large grain size when compared to the low-temperature process. Also, large horizontal cracks were apparent in the cracking; due, probably, to the fact that the lower section (carbon mandrel) side) of the coating had the higher carbon-to-niobium ratio and, thus, a higher CTE while the upper region (gas phase side) had the lower ratio and CTE. In other words, a severe CTE gradient across the niobium carbide film was probably present with an estimated CTE value of 7.0 x 10^{-6}/°C for the carbon mandrel side and 6.4 x 10^{-6}/°C for the gas stream side. These CTE estimates were made using the X-ray diffraction data (Table 12) which show carbon-to-niobium ratios of 0.879 and 0.780 for the tube plated at 1,800°C.

ZIRCONIUM CARBIDE THICK-WALL TUBES

The primary-coating program goal was to produce tubes of zirconium carbide that were stable when heated to relatively high temperatures (above 2,000°C)(1, 2, 6, 7) Zirconium carbide coatings were to be deposited at relatively low temperatures (1,000 to 1,400°C), and various chemical and physical properties were to be determined. One very important goal was for the zirconium carbide coating to have a known and consistent coefficient of thermal expansion. Earlier work with niobium carbide indicated that the amount of instability of the coating was related to the level of various impurities. Thus, a likely area of success seemed to be to obtain deposition conditions which produced zirconium carbide coatings which contained a minimum amount of impurities.

Table 12

PROPERTIES OF GED PROCESS NIOBIUM CARBIDE TUBES FROM NIOBIUM PENTACHLORIDE

Property	Tube Position (in)			
	0	10	35	52
Deposition Temperature (°C)	1,800	1,900	2,000	2,100
Chemical Analysis(1)				
Niobium (%)	90.211	90.344	90.426	90.686
Carbon (%)				
Total	9.797	9.781	9.673	9.315
Free	None	None	None	None
Combined	9.797	9.781	9.673	9.315
Carbon/Niobium Ratio	0.840	0.837	0.827	0.795
X-Ray Diffraction				
Major Phase	NbC	NbC	NbC	NbC
Carbon/Niobium Ratio(2)	0.879	0.878	0.878	0.880
Carbon/Niobium Ratio(2)	0.780	0.761	0.750	0.726
Oxygen Content (ppm)	120	146	148	146
Chlorine Content (ppm)	NS(3)	NS	377	54
Mercury Porosimetry				
Bulk Density (gms/cc)	7.735	7.694	7.611	7.425
Porosity (%)	0.79	1.55	0	4.06
Real Density (gms/cc)	7.797	7.814	7.611	7.739
Impurities (ppm)				
Aluminum	10	< 10	< 10	10
Iron	10	10	< 10	10
Silicon	< 30	< 30	< 30	< 30
Tungsten	1,000	500	< 100	< 100

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(1) Theoretical NbC = 88.55 weight percent niobium and 11.45 weight percent carbon.

(2) Higher values believed to be from the matrix side of the coating; lower values were probably from the gas side.

(3) NS = no sample.

Table 13

COEFFICIENT OF THERMAL EXPANSION VALUES FOR VAPOR-DEPOSITED NIOBIUM CARBIDE TUBES

Feed Salt *Material*	Deposition *Process*	Coefficient of Thermal Expansion(1) $(\times 10^{-6}/^{\circ}C)$	Carbon-to-Niobium Ratio		
			Average	*Maximum*(2)	*Minimum*(2)
$NbCl_5$	GED	6.60	0.800	0.88	0.73
$NbCl_5$	GED	6.60	0.810	0.88	0.75
$NbCl_5$	GEM	7.01	0.910		
$NbCl_5$	GEM	7.01	0.900		
$NbBr_5$	GEM	7.20	0.920		
$NbBr_5$	GEM	7.22	0.924		
Reheated to 2,500° C in carbon for three hours.					
$NbCl_5$	GED	7.35	0.978		
$NbCl_5$	GEM	7.01	0.931		
$NbCl_5$	GEM	7.13	0.972		
$NbBr_5$	GEM	7.35	0.976		

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(1) Temperature - 20 to 1,000° C.

(2) Two-phase coatings were found. The maximum value is assumed to be the matrix side and the minimum value is assumed to be the gas side.

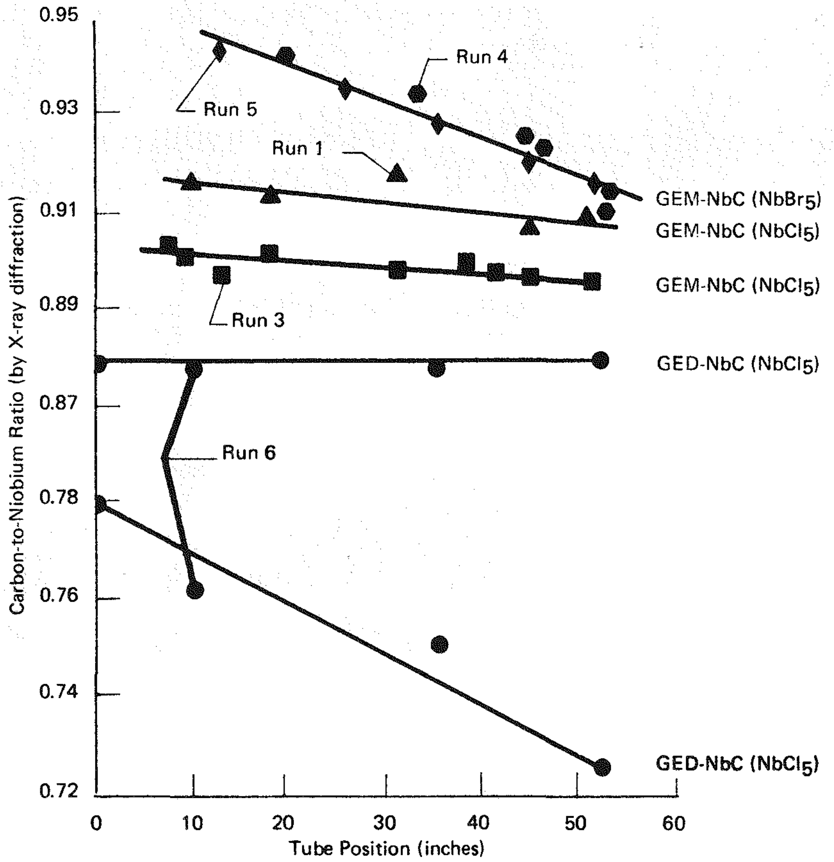

Figure 11. CARBON-TO-NIOBIUM RATIOS FOR VARIOUS NIOBIUM CARBIDE TUBES.

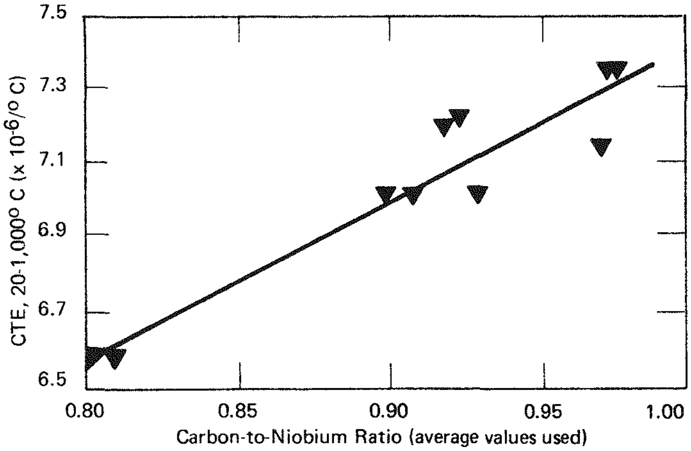

Figure 12. COEFFICIENT OF THERMAL EXPANSION VERSUS CARBON-TO-NIOBIUM RATIOS FOR VAPOR-DEPOSITED NIOBIUM CARBIDE.

Low-Temperature Deposition Using Zirconium Tetrachloride Feed Salt

All thick tubes of zirconium carbide were made using the low-temperature (GEM) process. Methane was used as the main source of carbon and the feed salt used was zirconium tetrachloride. Five runs were made using moderate variations in the deposition temperature,

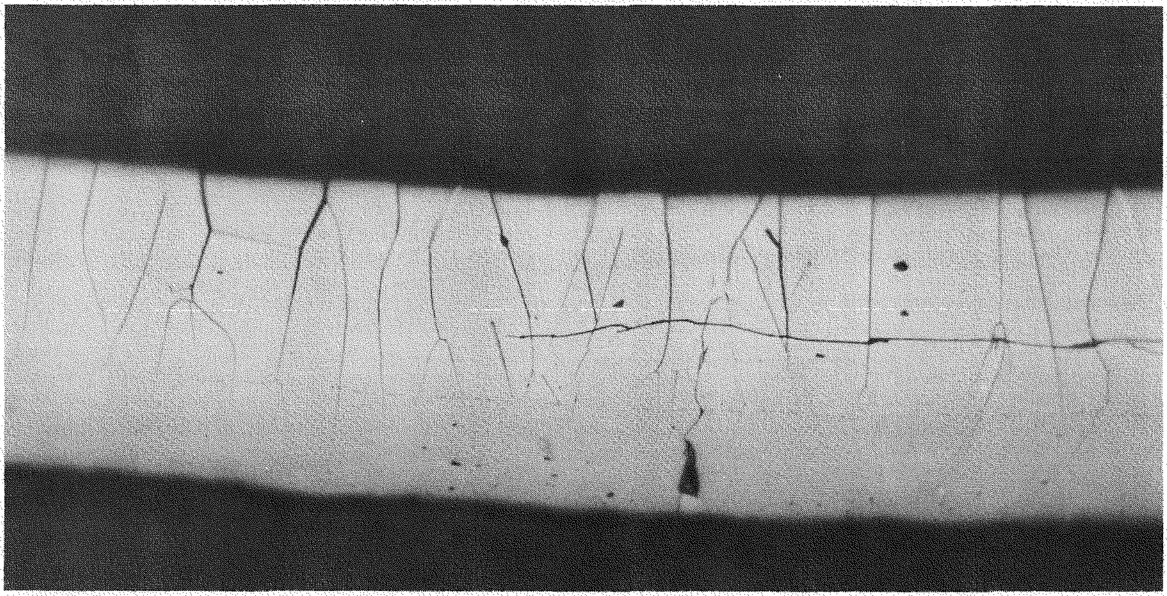

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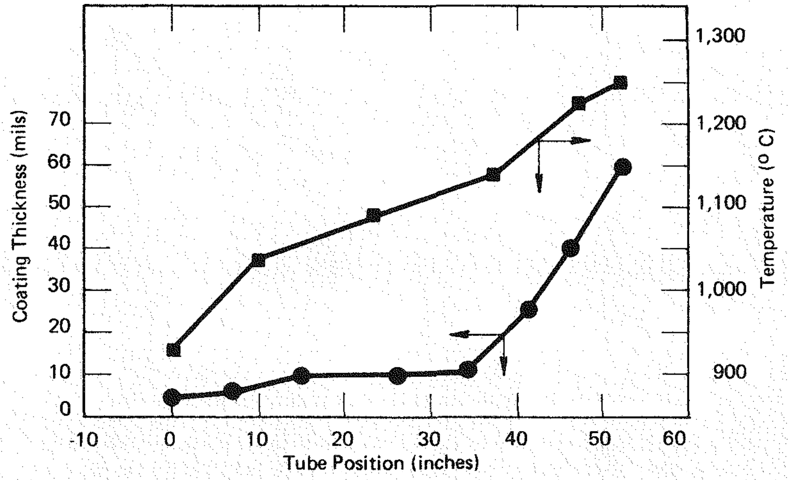
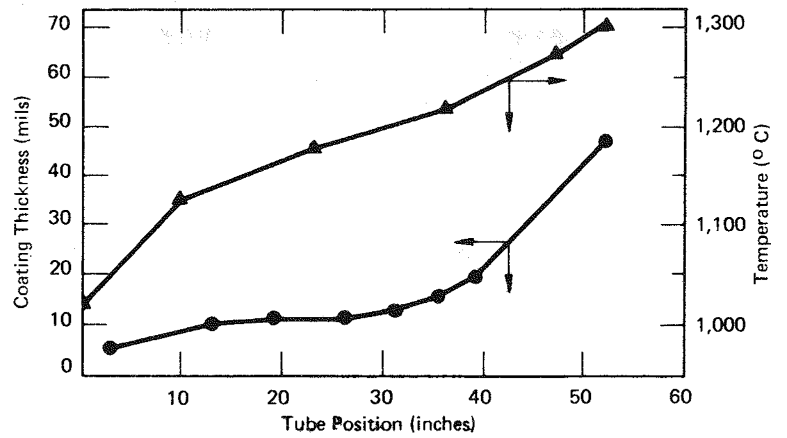
Figure 13. HIGH-TEMPERATURE (1,800°C) DEPOSITION OF NIOBIUM CARBIDE USING NIOBIUM PENTACHLORIDE. (Bright Field Illumination; 250X)

total gas flow, coating run time, and various concentrations of feed salt, hydrogen, and methane. Deposition conditions and thickness profile data for each run are recorded in Figures 14 through 18. An overall comparison of the main variables of the five plating runs is easily seen in Table 14. Although not apparent from the data of Table 14, when the feed salt concentration was changed, proportional changes were also made in the hydrogen and methane concentrations (Figures 14 to 18).



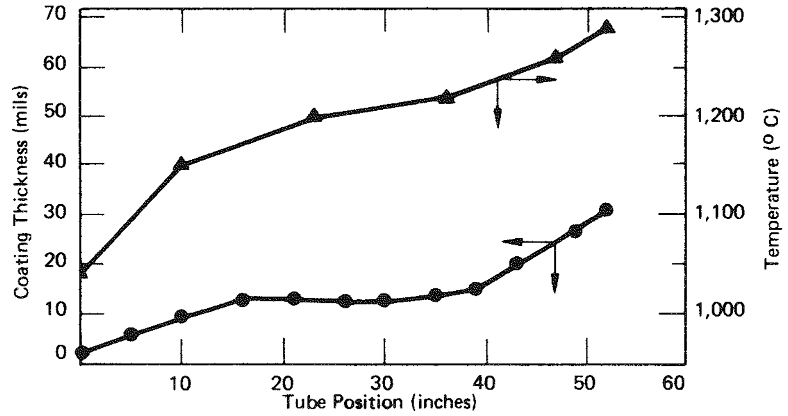
Date	Run Number	Type	Run Time (hrs)	Weight Gain (gms)				Pre-Heater (gms)	Number of Tubes	Gas Flow (vol %)					Total Gas (l/m/tube)
				High	Low	Avg	Gms/Hr			Ar	HCl	H_2	CH_4	Salt	
11-17-70	558	ZrC	80 + 10	119.0	117.2	118.1	1.31	-	2	95.63	-	1.91	0.43	2.03	9.41

Figure 14. THICK TUBES OF GEM ZIRCONIUM CARBIDE. (Run 1; Temperature Span of 930 to 1,250°C)



Date	Run	Type	Run Time (hrs)	Weight Gain (gms)				Pre-Heater (gms)	Number of Tubes	Gas Flow (vol %)					Total Gas (l/m/tube)
				High	Low	Avg	Gms/Hr			Ar	HCl	H_2	CH_4	Salt	
8-2-71	568	ZrC	53	-	-	128.1	2.42	14	2	95.66	-	1.91	0.43	2.00	9.41

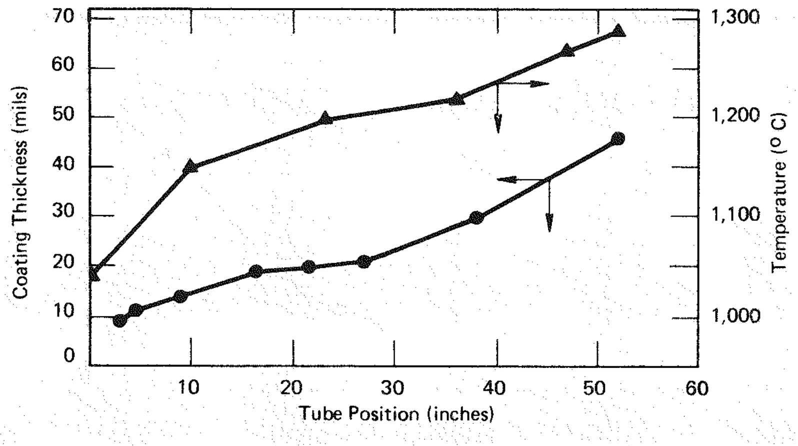
Figure 15. THICK TUBES OF GEM ZIRCONIUM CARBIDE. (Run 2; Temperature Space of 1,020 to 1,300°C)



Date	Run	Type	Run Time (hrs)	Weight Gain (gms)				Pre-Heater (gms)	Number of Tubes	Gas Flow (vol %)					Total Gas (l/m/tube)
				High	Low	Avg	Gms/Hr			Ar	HCl	H_2	CH_4	Salt	
9-13-71	569	ZrC	100	-	-	117.4	1.17	8	1	98.25	-	0.77	0.17	0.81	23.41

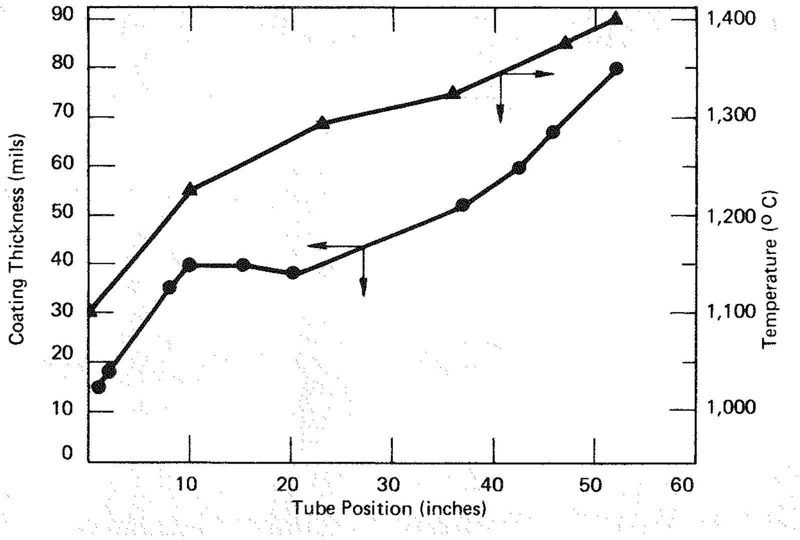
Figure 16. THICK TUBES OF GEM ZIRCONIUM CARBIDE. (Run 3; Temperature Span of 1,040 to 1,290°C)

A moderate plating temperature increase between Runs 1 and 2 increased the coating rate from 1.31 to 2.42 gms/hr. Repeating the Run 2 temperatures, Run 3 showed that an increase in the inert (argon) gas flow and subsequent decrease in salt, hydrogen, and methane concentrations reduced the coating rate to 1.17 gms/hr. For Run 4, the same temperatures were used as for Run 3, but the salt, hydrogen, and methane concentrations were substantially increased and the coating rate increased to 3.26 gms/hr. At these high gas concentrations, another temperature increase was made for Run 5 which further raised the coating rate to 7.20 gms/hr.



Date	Run	Type	Run Time (hrs)	Weight Gain (gms)				Pre-Heater (gms)	Number of Tubes	Gas Flow (vol %)					Total Gas (l/m/tube)
				High	Low	Avg	Gms/Hr			Ar	HCl	H_2	CH_4	Salt	
9-28-71	570	ZrC	56 2/3	-	-	185	3.26	17	1	91.81	-	3.67	0.82	3.70	9.80

Figure 17. THICK TUBES OF GEM ZIRCONIUM CARBIDE. (Run 4; Temperature Span of 1,040 to 1,290°C)



Date	Run	Type	Run Time (hrs)	Weight Gain (gms)				Pre-Heater (gms)	Number of Tubes	Gas Flow (vol %)					Total Gas (l/m/tube)
				High	Low	Avg	Gms/Hr			Ar	HCl	H_2	CH_4	Salt	
10-18-71	571	ZrC	50 1/3	-	-	362.2	7.20	21 1/2	1	91.74	-	3.67	0.82	3.77	9.81

Figure 18. THICK TUBES OF GEM ZIRCONIUM CARBIDE. (Run 5; Temperature Span of 1,100 to 1,400°C)

All of the zirconium carbide runs produced free-standing, thick tubes of GEM zirconium carbide of varying lengths (up to 35 inches). The tubes were sectioned into sample pieces for various analyses. A view of one of the sections of one of the tubes is provided in Figure 19.

Table 14

SUMMARY PROCESS CONDITIONS FOR GEM-ZIRCONIUM CARBIDE THICK TUBES

Run	Temperature Span (°C)	Total Gas Flow (1/min/tube)	Feed Salt Concentration (vol %)	Run Time (hrs)	Total Deposition (gms)	Coating Rate (gms/hr)
1	930 - 1,250	9.41	2.03	90	118	1.31
2	1,020 - 1,300	9.41	2.00	53	128	2.42
3	1,040 - 1,290	23.41	0.81	100	117	1.17
4	1,040 - 1,290	9.80	3.70	57	185	3.26
5	1,100 - 1,400	9.81	3.77	50	362	7.20

Impurities - Samples from the first run were taken along the tube length, and the impurities were determined by spectrographic analysis (Table 15). The niobium impurity may be a process contamination problem since a portion of the coating equipment was the same as that used for the niobium carbide coating studies. Other high impurities were silicon, iron, and aluminum which were present in the feed salt. The impurity concentrations were highest either at the cold end (gas inlet) or near the middle of the tube and the lowest at the hot end (gas outlet). Concentrations of these impurities as a function of the deposition temperature are given in Figure 20. A major reduction in the concentration of all three materials occurred at about 1,125°C, which was at 35 inches along the tube length. In subsequent runs the temperatures were increased, and the 1,125°C temperature point in Run 1 which occurred at the 35-inch location now occurred at about 10 inches from the gas inlet end. This increased temperature greatly reduced the impurities for the major length of the zirconium carbide tube. A summary of the major impurities of all five runs is given in Table 16. The lower level of major impurities (aluminum, iron, and silicon) for the later runs is quite evident. These three elements are common impurities in the zirconium tetrachloride feed salt. The low level of impurity concentration in the deposited zirconium carbide tubes was not considered to be a problem in reactor operations. Impurity levels also decreased along the tube length as the plating temperatures were raised.

Electrical Resistivity - A cursory check of the room-temperature resistivity of one of the tubes deposited in the first run gave a value of 100 μohm-cm. The tube was deposited at a temperature of 1,240°C and had a wall thickness of 55 to 59 mils.

Carbon-Zirconium Content and the Carbon-to-Zirconium Ratio - In the first run, the carbon content was determined by chemical analysis but the determination of the carbon-to-zirconium ratio was attempted by X-ray diffraction. These latter determinations were severely hampered due to very weak and/or very broad and diffuse lines. The ease with which various impurities enter the zirconium carbide structure and disturb the X-ray determinations was recognized, but the concentrations of oxygen and chlorine were higher than anticipated. As pointed out in Table 17, the only meaningful X-ray pattern for the first run was from the very hot end of the tube (1,250°C) where the impurities were the lowest (~ 0.5%). Once the impurity problem was realized, there were not sufficient samples remaining from Run 1 for a chemical analysis of the zirconium carbide. For the second run, both the zirconium and carbon contents were determined by chemical analysis and this ratio was again compared to the ratio obtained by X-ray data. As seen in Table 17, this run again showed the wide difference in the ratios and reinforced the conclusion that the ratio by chemical analysis was a more accurate analysis. For the later runs, the carbon-to-zirconium ratio was determined only by chemical analysis.

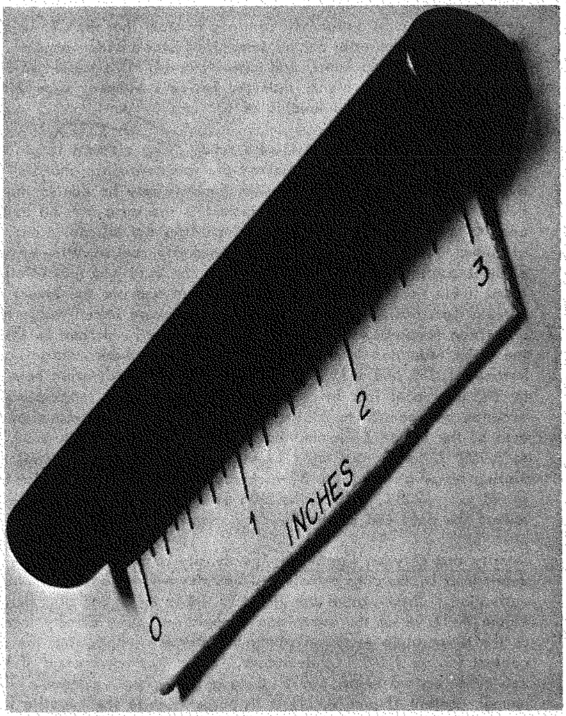


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Figure 19. SECTION OF A GEM ZIRCONIUM CARBIDE THICK TUBE.

Total carbon, free carbon, and zirconium content, along with the carbon-to-zirconium ratio (by chemical analysis) for all five runs are summarized in Table 16. Although there is some variability in the data (especially the free carbon, the carbon, zirconium, and carbon-to-zirconium ratio generally increased as the deposition temperature increased, as shown in Figure 21. In summary, a lower carbon-to-zirconium ratio ($ZrC_{0.9}$) was formed at about 1,200°C, a higher ratio ($ZrC_{0.95}$) at about 1,300°C, but the theoretical ratio ($ZrC_{1.0}$) was not formed until the temperature approached 1,400°C.

Metallographic Structure - The metallographic structure of the coatings was very dependent upon the deposition temperature and deposition rate. Generally, at temperatures of less than 1,200°C the coatings had a very-fine-grain crystal structure, as the photomicrographs of Figures 22 and 23 indicate. As the deposition temperature approached 1,300°C, the structure began to show larger grain sizes (Figures 24 and 25). At temperatures near 1,400°C the deposition rate was sufficiently high to show the inclusion of appreciable porosity (see Figure 26).

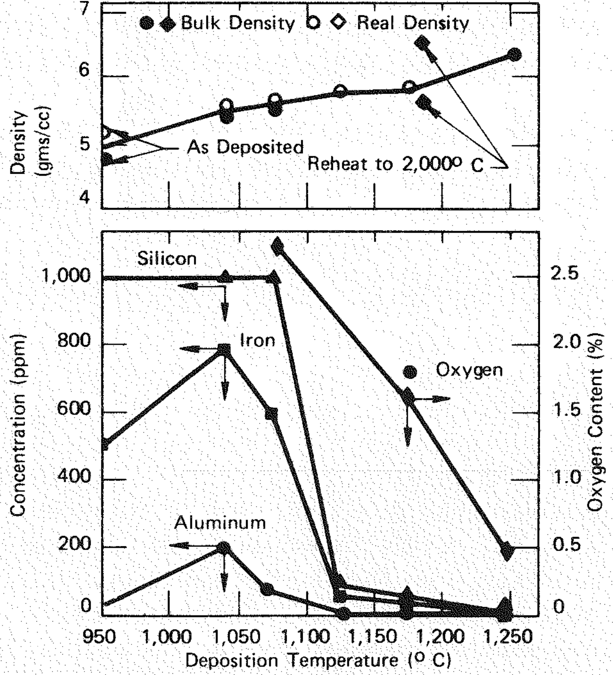

Figure 20. PROPERTIES OF VAPOR-DEPOSITED THICK-WALL TUBES OF GEM ZIRCONIUM CARBIDE.

Figure 27 provides a view of the structure of a coating originally deposited at 1,180°C and then reheated to 2,000°C for one hour in a carbon-rich atmosphere. Although there was some coalescence of the crystals, the fine-grain structure was still prevalent.

Laminations noted in some of the figures were due to flow interruptions and/or pressure fluctuations because of the large amount of recondensed salt that accumulated in the exit filtering system.

Oxygen and Chlorine Content - For each of the five runs, the oxygen and chlorine impurities in the zirconium carbide coatings decreased along the tube length as the coating temperatures were increased. As the temperatures

Table 15

IMPURITIES IN THE THICK-WALL TUBES OF
GEM ZIRCONIUM CARBIDE
(Run 1)

	Tube Position (in)						
	0 to 5	9 to 13	18 to 22	32 to 34	41 to 42 1/2	51 1/2 to 52	Exit Line
Deposition Temperature (° C)	950	1,040	1,075	1,125	1,175	1,250	< 1,250
Impurities (ppm)							
Al	10	200	60	6	6	5	10
B	4	1	1	1	< 1	< 1	3
Ba	2	< 2	< 2	< 2	< 2	< 2	< 2
Be	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.10	< 0.1
Ca	30	40	30	10	< 10	< 10	< 10
Cd	> 100	2	1	100	40	45	< 0.4
Co	< 4	4	< 4	< 4	< 4	< 4	100
Cr	400	10	5	8	4	< 4	400
Cu	90	< 2	< 2	8	4	< 2	2
Fe	500	800	600	40	30	10	500
Hf	< 100	< 100	< 100	< 100	< 100	< 100	< 100
K	< 100	< 100	< 100	< 100	< 100	< 100	< 100
Li	< 1	< 1	< 1	< 1	< 1	3	10
Mg	< 10	60	40	< 10	< 10	< 10	< 10
Mn	< 4	< 4	< 4	< 4	< 4	< 4	4
Mo	< 10	< 20	< 20	< 20	< 20	< 20	< 20
Na	4	6	6	< 1	< 1	< 1	< 1
Nb	1,200	200	150	100	30	10	50
Ni	12	< 4	< 4	< 4	< 4	< 4	5
P	< 200	< 200	< 200	< 200	< 200	< 200	< 200
Pb	50	10	10	75	10	60	< 4
Si	1,000	1,000	1,000	50	40	< 10	< 10
Sn	45	10	12	12	< 10	18	< 10
Ta	< 20	< 20	< 20	< 20	< 20	< 20	500
Ti	40	20	20	20	< 10	< 10	< 10
V	< 20	< 20	< 20	< 20	< 20	< 20	< 20
W	10	10	10	10	< 10	10	20
Zn	< 1,000	< 100	< 100	< 100	< 100	< 100	< 100

were varied between runs, the gaseous impurity levels decreased with increasing temperature regardless of the position along the tube length (see Table 16). Runs 1 through 4, which were made at nearly the same temperature but with different coating gas flows and coating rates, had essentially the same level of impurities. Coating temperatures were raised substantially in Run 5 and the impurity level decreased significantly.

To summarize, the coating temperature was found to be the major factor in determining the oxygen and chlorine impurity level in GEM zirconium carbide coatings. Oxygen data for all of the runs are plotted in the graph of Figure 28 as a function of the coating temperature. Figure 29 is a similar plot for the chlorine data. Chlorine data for Run 1 were proportionally higher than for the other runs. There appeared to be no explanation for this except for possible sampling or analytical error.

In general, the oxygen content was about three times as high as the chlorine content at comparable temperatures. A sample reheated to 2,000°C in a carbon atmosphere showed an

Table 16

PROPERTIES OF THICK-WALL TUBES OF GEM ZIRCONIUM CARBIDE

Run	Average Position (in)	Average Temperature (° C)	Approximate Average Thickness (mils)	Chemical Analysis (wt %)				Combined Carbon/ Zirconium Mole Ratio	Impurity Concentration				
				Carbon									
				Total	Free	Combined	Zirconium		O (wt %)	Cl (wt %)	Al (ppm)	Fe (ppm)	Si (ppm)
1	11	1,040	8	9.622	0.097	9.525	-	~ 0.8(1)	-	-	200	800	1,000
1	20	1,075	10	9.929	0.073	9.856	-	~ 0.8(1)	2.74	-	60	600	1,000
1	33	1,125	11	10.620	0.084	10.536	-	~ 0.8(1)	-	-	6	40	50
1	42	1,175	28	9.248(1)	0.095	9.153(1)	-	~ 0.8(1)	1.58	1.61	6	30	40
1	52	1,250	60	11.593	0.266	11.327	-	~ 0.95(2)	0.47	0.93	5	10	< 10
2	5	1,075	6	8.493	0.055	8.438	85.16	0.752	3.69	1.20	80	500	600
2	10	1,125	8	8.754	0.056	8.698	85.09	0.776	3.27	0.91	60	300	400
2	16	1,150	10	8.684	0.297(2)	8.387	86.13	0.739(2)	2.81	0.69	50	300	300
2	30	1,200	13	10.078	0.119	9.959	83.79(2)	0.903	1.97	0.63	60	175	600
2	37	1,225	18	10.198	0.054	10.144	86.43	0.892	1.35	0.61	50	100	400
2	45	1,265	30	10.744	0.040	10.704	86.64	0.938	0.77	0.21	75	50	300
2	52	1,300	45	10.850	0.125	10.725	87.99	0.926	0.41	0.11	2	30	< 10
3	9	1,135	8	9.553	0.079	9.474	86.30	0.834	2.86	0.64	< 1	50	125
3	17	1,175	13	9.480	0.0073	9.407	86.72	0.824	2.33	0.34	< 1	30	50
3	32	1,215	13	10.117	0.123	9.994	86.19	0.881	2.04	0.30	-	-	-
3	51	1,280	29	11.430	0.095	11.335	88.38	0.974	0.79	0.15	-	-	-
4	1	1,055	7	9.374	0.098	9.276	85.64	0.823	2.98	1.29	-	-	-
4	4	1,090	10	9.711	0.096	9.615	85.88	0.850	2.53	1.06	-	-	-
4	9	1,150	14	9.740	0.063	9.677	86.58	0.849	2.45	0.98	100	100	100
4	19	1,185	20	10.280	0.068	10.212	86.34	0.898	2.19	0.85	40	30	40
4	37	1,225	30	10.600	0.112	10.488	87.48	0.911	1.18	0.77	-	-	-
4	52	1,290	46	10.980	0.088	10.892	88.06	0.939	0.59	0.51	-	-	-
5	1	1,120	15	9.712	0.119	9.593	86.08	0.846	1.15	1.23	-	-	-
5	10	1,225	40	10.790	0.162	10.628	87.77	0.920	0.90	0.56	< 1	115	15
5	20	1,280	38	11.035	0.100	10.935	87.96	0.944	0.47	0.42	-	-	-
5	37	1,325	52	11.120	0.144	10.976	88.30	0.944	0.20	0.10	2	< 10	10
5	43	1,360	62	11.617	0.536	11.081	88.32	0.953	0.12	0.03	-	-	-
5	52	1,400	80	12.323	0.595	11.728(2)	87.54	1.017(2)	0.04	0.04	-	-	-

(1) Approximate value based on the combined carbon content. Zirconium analysis not performed.

(2) Questionable value.

Table 17

CARBON-TO-ZIRCONIUM RATIO FOR VARIOUS GEM ZIRCONIUM CARBIDE THICK-WALL TUBES

			X-Ray Diffraction Analysis				Chemical Analysis		
Run	Average Position (in)	Average Temperature (° C)	Major Phase	Minor Phase	Lattice Parameter (A)	Carbon/ Zirconium Ratio (1)	Carbon/ Zirconium Ratio	Oxygen Content (wt %)	Chlorine Content (wt %)
1	11	1,040	ZrC	ZrO_2	(2)	-	~ 0.8(3)	-	-
1	20	1,075	ZrC	ZrO_2	(2)	-	~ 0.8(3)	2.74	-
1	33	1,125	ZrC	None	4.6836(4)	< 0.5	~ 0.8(3)	-	-
1	42	1,175	ZrC	None	4.6905(4)	< 0.6	~ 0.8(3)	1.58	1.61
1	52	1,250	ZrC	None	4.6987	~ 0.97	~ 0.95(3)	0.47	0.93
2	5	1,075	ZrC	ZrO_2	4.6800(4)	< 0.5	0.752	3.69	1.20
2	10	1,125	ZrC	ZrO_2	4.6826(4)	< 0.5	0.776	3.27	0.91
2	16	1,150	ZrC	ZrO_2	4.6817(4)	< 0.5	0.739	2.81	0.69
2	30	1,200	ZrC	ZrO_2	4.6904(4)	< 0.6	0.903	1.97	0.63
2	37	1,225	ZrC	None	4.6930(4)	< 0.6	0.892	1.35	0.61
2	45	1,265	ZrC	None	4.6944(4)	< 0.6	0.938	0.77	0.21
2	52	1,300	ZrC	None	4.6943	< 0.6	0.926	0.41	0.11

(1) Data taken from Storms, Edmund, K.; **Refractory Carbides**, p 25; Academic Press, New York, New York (1967).

(2) Unable to measure lines due to a very weak intensity.

(3) Approximate value based on the combined carbon content. Zirconium analysis not performed.

(4) Lines very broad and diffuse (used point of maximum intensity) thus questionable values. Undoubtedly due to impurity levels.

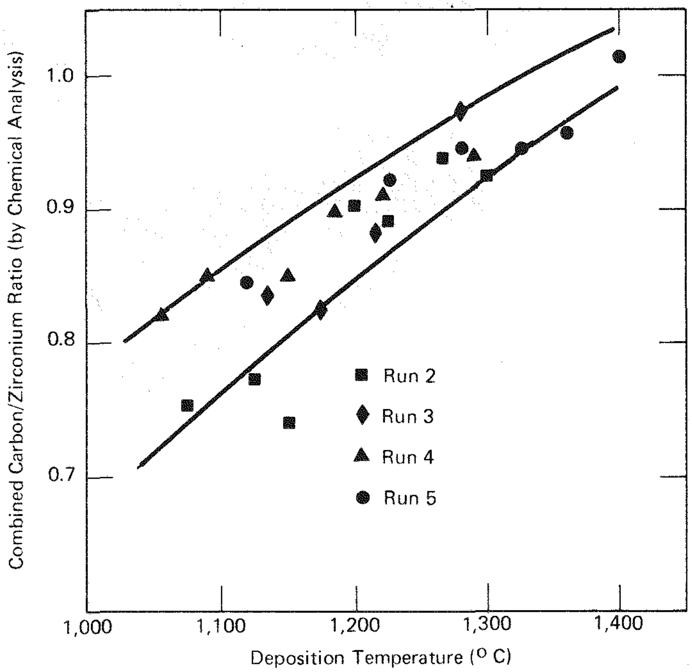

Figure 21. CARBON-TO-ZIRCONIUM RATIO OF GEM ZIRCONIUM CARBIDE THICK-WALL TUBES.

approximate reduction of 10 fold, in the chlorine content and 2 fold in the oxygen content.

Coefficient of Thermal Expansion - One of the most significant parts of these studies was the relationship of the impurity level (mainly oxygen and chlorine) to the CTE of the

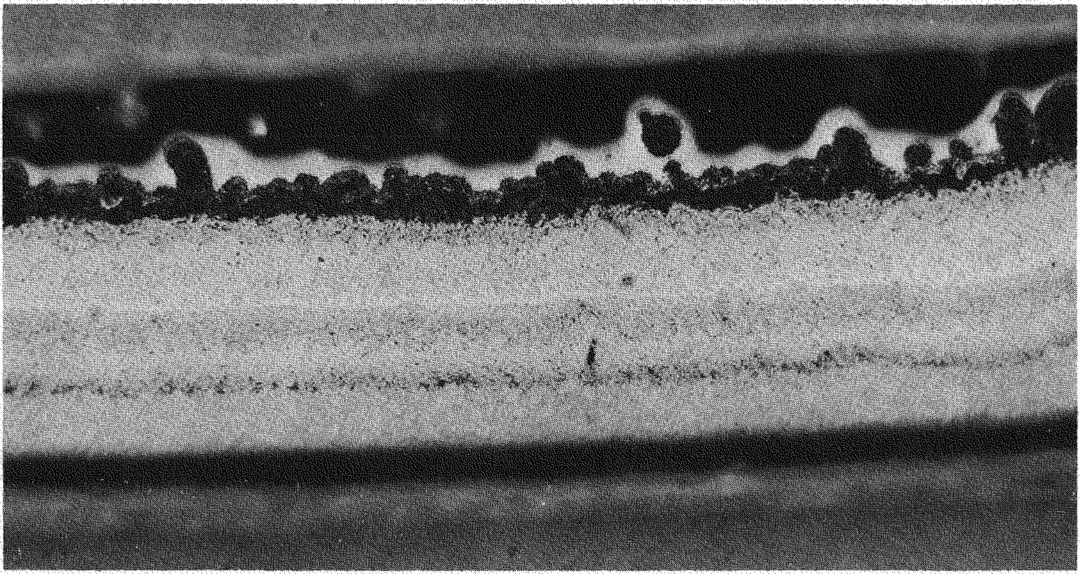

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Figure 22. GEM ZIRCONIUM CARBIDE DEPOSITED IN RUN 4 AT THREE INCHES AND AT 1,070°C. (Bright Field Illumination: 250X)

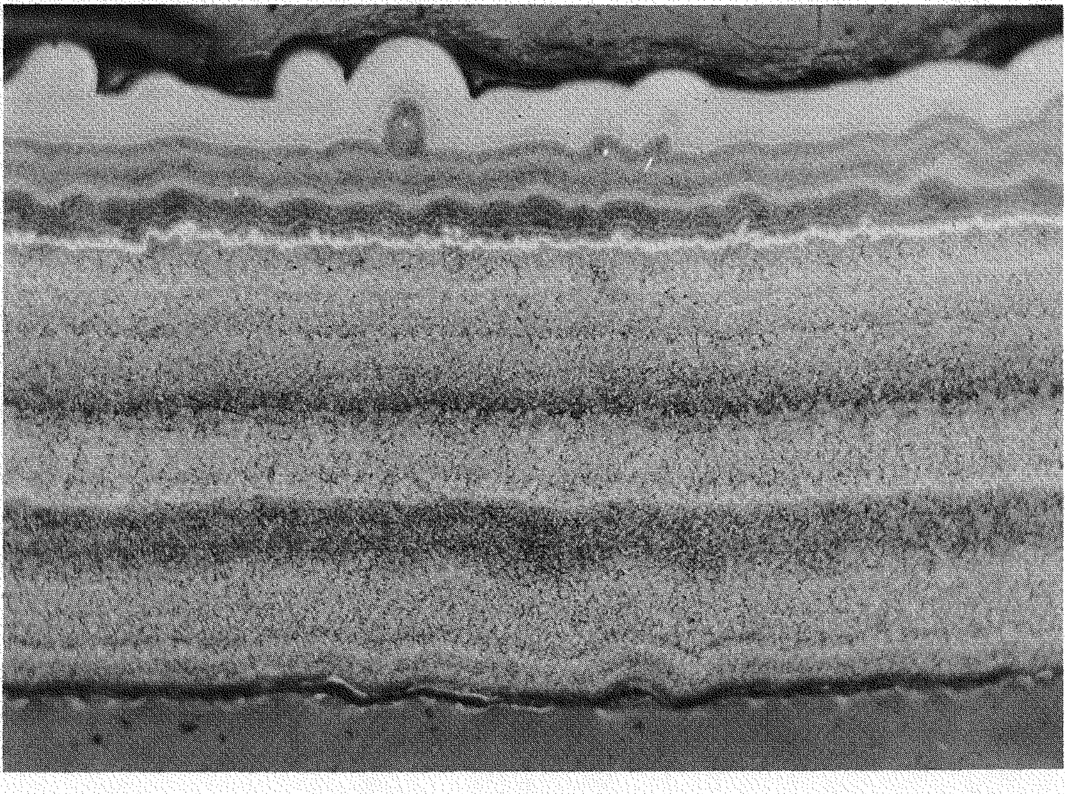

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Figure 23. GEM ZIRCONIUM CARBIDE DEPOSITED IN RUN 3 AT 19 INCHES AND AT 1,190°C. (Note White Line—PyC—Due to Flow Interruption; Bright Field Illumination; 250X)

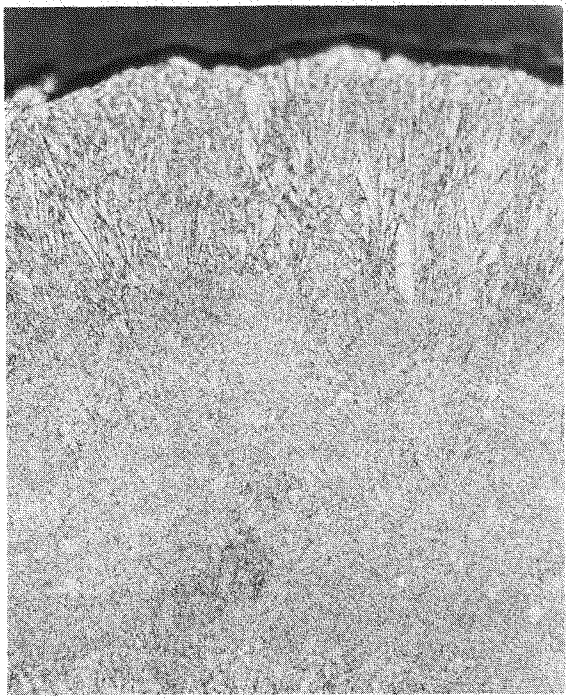

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Figure 24. GEM ZIRCONIUM CARBIDE DEPOSITED IN RUN 2 AT 52 INCHES AND AT 1,300°C. (Bright Field Illumination; 400X)

MS 71-1009-1

Figure 25. GEM ZIRCONIUM CARBIDE DEPOSITED IN RUN 5 AT 37 INCHES AND AT 1,330°C. (Bright Field Illumination; 100X)

coatings. Several tubes, having a length of five inches, were shipped to the Los Alamos Scientific Laboratory (LASL) for CTE determination up to 2,000°C. All of the CTE data (up to 2,000°C) presented in this report were obtained at LASL.

The zirconium carbide tubes represented a range of temperatures and also a range of impurity levels. Each tube was heated to approximately 2,000°C for one or more times and the expansivity measured. The weight loss and volume change after each cycle were also recorded.

Figures 30 and 31 report the expansion data for two zirconium carbide tubes which had low impurity levels. Both tubes were plated above 1,330°C and both had CTE values of 7.7 - 7.8 x 10^{-6}/°C (20-2,000°C range). Neither tube showed any weight loss or length change after heating to 2,000°C.

Below a zirconium carbide plating temperature of about 1,300°C, and at oxygen and chlorine levels of 0.7 percent or greater, the zirconium carbide coatings were unstable. On the first heating to 2,000°C, weight losses and length changes occurred and were erratic, but high CTE values were also obtained ($\sim$ 9 x 10^{-6}/°C). On the second and subsequent cycles to 2,000°C, the zirconium carbide coatings appeared to be stable. Figure 32 shows a zirconium carbide tube plated at 1,250 to 1,280°C and having an oxygen level of 0.5 to 0.7 percent. Up to approximately 1,600°C it appeared to be stable, but had a large and abrupt change in expansivity beginning at about 1,800°C.

Figure 33 provides a plot taken from a zirconium carbide tube plated at 1,270 to 1,300°C (oxygen content of 0.41 to 0.77%). These heating cycle data show that the first heating

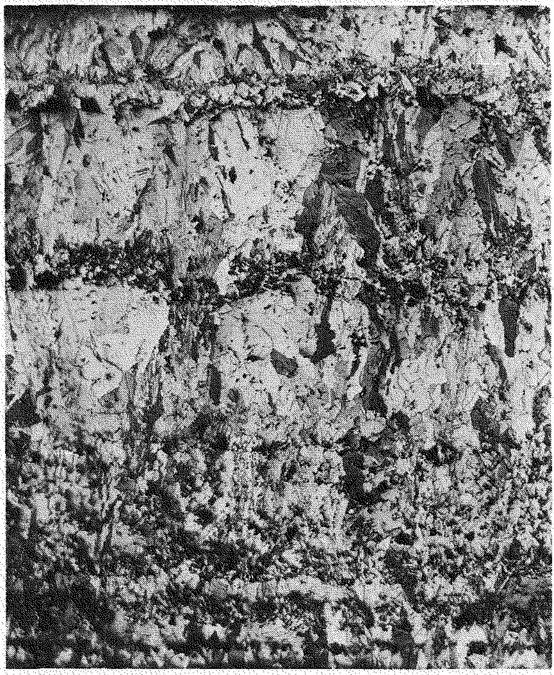

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Figure 26. GEM ZIRCONIUM CARBIDE DEPOSITED IN RUN 5 AT 52 INCHES AND AT 1,400°C. (Bright Field Illumination; 75X)

cycle had a high CTE value (~ 9.0 x $10^{-6}/^{o}C$; 20 to 2,000°C). A weight loss of 0.35 percent was experienced by the tube, but no measured length change was noted after the first heating cycle. The second heating cycle was normal and produced a CTE value of 7.9 x $10^{-6}/^{o}C$ (20-2,000°C), which was equal to the tube data obtained from the impurity-free zirconium carbide tubes.

Figure 34 gives a plot of a zirconium carbide tube plated at a lower temperature (1,235-1,265°C) and had an oxygen content of 0.77 - 1.35 percent. For information purposes it should be stated that the tubes, being five inches in length, were not plated at a constant temperature point. One end of the five-inch tube was plated at a lower temperature than the other end because of the plating furnace temperature profile. Each end was chemically sampled. The low-plating-temperature end always had the higher impurity level. All tube data in this report have two reported temperatures for the tubes and two reported impurity levels which represent each end of the tube.

The first-cycle data, given in Figure 34, showed a high expansion level up to 1,600°C, but no expansion was measured from 1,600 to 1,950°C. After the first cycle, a weight loss of 1.16 percent and a length change of 0.27 percent were measured. The second cycle data on this tube were similar to the ones obtained on the impurity-free zirconium carbide tubes (CTE value of 7.5 x $10^{-6}/^{o}C$; 20 - 2,000°C).

A plot of the data obtained on a zirconium carbide tube that was plated at 1,200 - 1,220°C is presented in Figure 35. This tube contained an oxygen content of 1.34 - 1.97 percent. The tube was initially heated to 1,000°C and then cooled. Other data, discussed in the section that follows, indicate that this heat cycle would not affect the sample. The zirconium carbide tube was reheated to 2,000°C. Up to approximately 1,550°C, a high expansion value was measured, but between 1,550 and 2,000°C, the expansion stopped and decreased a substantial amount. A weight loss of 2.15 percent and a length change of 0.11 percent were measured on the specimen after this heat cycle.

Figure 36 gives data obtained on a zirconium carbide tube that was plated at 1,190 - 1,205°C and had an oxygen level of 1.7 - 2.2 percent. Up to approximately 1,300°C, a high level of expansion was measured; but, above 1,300°C, the expansion rapidly decreased. After the heating cycle, a weight loss of 3.3 percent and a length change of two percent were measured.

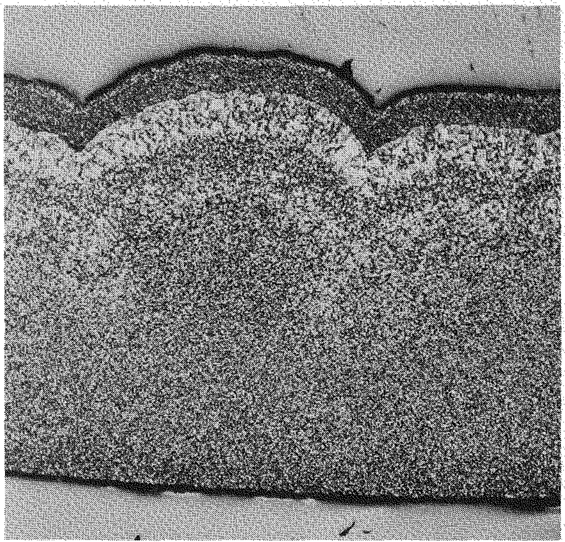

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Figure 27. GEM ZIRCONIUM CARBIDE DEPOSITED IN RUN 1 AT 42 INCHES AND AT 1,180°C, THEN REHEATED TO 2,000°C FOR ONE HOUR IN CARBON. (Bright Field Illumination; 100X)

The most important factors determined from the data showed that stable coatings (upon heating to 2,000°C) of zirconium carbide were obtained with a CTE of 7.7 to 7.8 x 10^{-6}/°C (20-2,000°C) when deposited at 1,330°C or above and with an oxygen content of 0.2 percent or lower and a chlorine content of 0.1 percent or lower. Coatings deposited at lower temperatures and with higher oxygen and chlorine contents were unstable on heating to 2,000°C, undergoing length and/or weight changes and giving very erratic CTE values.

Density - Densities of the zirconium carbide tubes were also dependent upon the coating temperature. Below approximately 1,100°C, the open porosity ranged from 2 to 7 volume percent. However, between 1,100 and 1,300°C there was very little open porosity resulting in very little difference between the bulk and real densities. Above 1,300°C, the open porosity reappeared.

Up to 1,200°C, the bulk and real densities increased slowly with increasing temperature. However, at about 1,200°C, both densities increased much more rapidly, reaching a maximum of essentially theoretical density (6.56 gms/cc for hafnium-free ZrC(8)) around 1,300°C. Above this temperature, as the open porosity reappeared, both the bulk and real densities decreased. Table 18 summarizes the data for all the runs; Figure 37 shows how the relation of the real densities to the coating temperature varies at different temperature ranges. A plot of the bulk densities would give an essentially identical curve.

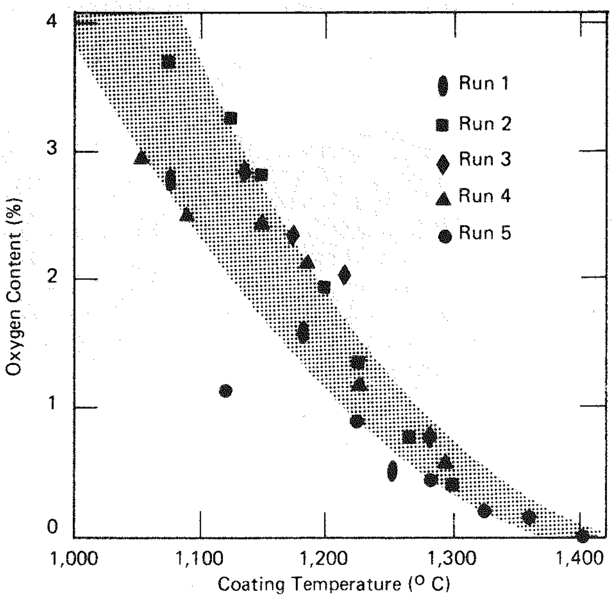

Figure 28. OXYGEN CONTENT OF THICK-WALL TUBES OF GEM ZIRCONIUM CARBIDE.

Thermogravimetric-Outgas Analysis

As part of the overall program, a thermogravimetric-outgas analysis of zirconium carbide tubes was made on several samples. Coatings deposited above 1,330°C, which had a stable CTE, were heated to 2,400°C (in vacuum). The weight loss was measured as a function of temperature, and the mass loss of the evolved gases as a function of temperature was obtained. Up to 2,100°C, no weight losses occurred nor were any detectable gases evolved,

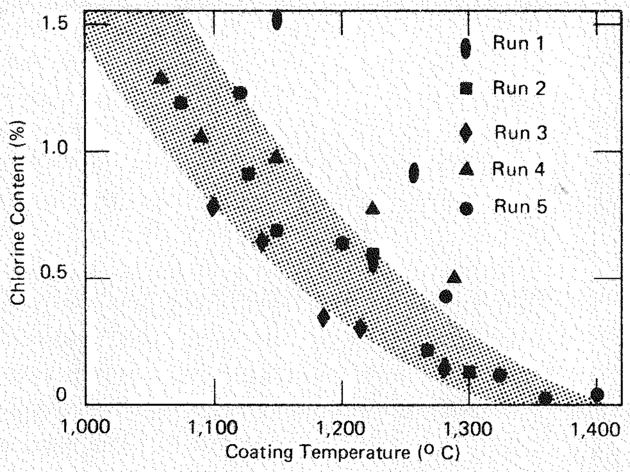

Figure 29. CHLORINE CONTENT OF THICK-WALL TUBES OF GEM ZIRCONIUM CARBIDE.

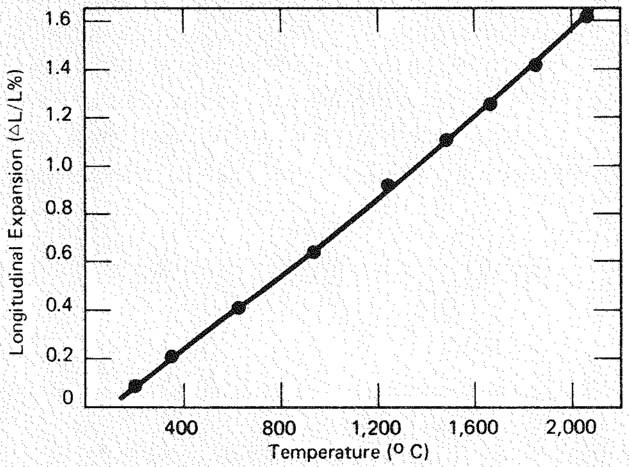

Figure 30. LONGITUDINAL THERMAL EXPANSION OF GEM ZIRCONIUM CARBIDE. (Run 5; Coating Temperature, 1,370 - 1,400°C; Tube Position, 46 - 51 Inches; O Content, 0.12 - 0.04%; Cl Content, 0.03 - 0.04%; CTE from 20 to 1,000°C, 6.9 x 10^{-6}/°C; CTE from 20 to 2,000°C, 7.8 x 10^{-6}/°C; No Weight or Length Change)

but from 2,100 to 2,400°C, the weight loss was 0.05 percent. The only gas detected to be outgassed from the samples was hydrogen (Mass 2) which occurred over the range from 1,000 to 2,400°C.

A problem with the use of the thermogravimetric equipment used for these studies was that the gases were evolved at a high temperature and then passed through tubing at room temperature to the detector device. If the evolved gases were not stable at room temperature, the detector would not "see" the evolved-gas species.

Thermogravimetric analysis data, reported in Figure 38, give the loss data for a zirconium carbide tube plated at 1,300°C, and represents the slightly unstable CTE shown in an earlier graph (Figure 33). In this zirconium carbide tube, a weight loss occurred which started at 1,600°C, peaked at 1,900°C, and then decreased to 2,200°C. This loss was followed by a second weight loss in the range from 2,200 to 2,400°C. The total weight loss to 2,400°C was 0.9 percent. Outgas analysis data for this zirconium carbide tube are given in Figure 39. Data from this analysis indicate that the Mass 2 gas (H_2) was evolved from 1,200 to 2,400°C, and peaked at about 1,850°C. As previously stated, unless a particular gas species was stable at room temperature, it could not be detected.

CTE data for the zirconium carbide tubes plated at 1,220°C is presented in Figure 40. The initial weight loss started at 1,400°C, peaked at 1,600°C, and then fell. From about 1,700 to about 2,200°C, the losses continued at about a constant rate and then rose from 2,200 to 2,400°C. In this tube, the total weight loss to 2,400°C was 2.7 percent. Outgas data are summarized in Figure 41 and these data show that Mass 36 gas (HCl) was evolved over the range from 1,400 to 1,900°C. Mass 2 gas (H_2) was evolved from 1,400 to 2,200°C. The detected hydrogen chloride is believed to result from the presence of chlorine in the zirconium carbide which reacted with the hydrogen before it reached the detector sensor device. This conclusion is based on a study of the ion-beam probe data which is discussed in the section that follows.

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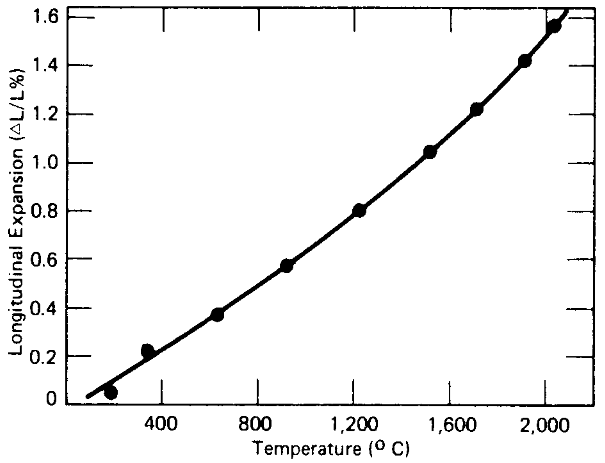

Figure 31. LONGITUDINAL THERMAL EXPANSION OF GEM ZIRCONIUM CARBIDE. (Run 5; Coating Temperature, 1,330 - 1,350°C; Tube Position, 37 - 42 Inches; O Content, 0.20 - 0.12%; Cl Content, 0.10 - 0.03%; CTE from 20 to 1,000°C, 6.4 x 10^{-6}/°C; CTE from 20 to 2,000°C, 7.7 x 10^{-6}/°C; No Weight or Length Change)

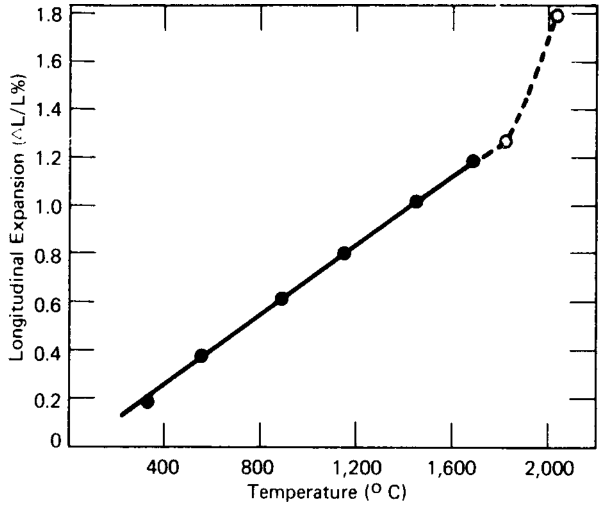

Figure 32. LONGITUDINAL THERMAL EXPANSION OF GEM ZIRCONIUM CARBIDE. (Run 5; Coating Temperature, 1,250 - 1,280°C; Tube Position, 15 - 20 Inches; O Content, 0.7 - 0.5%; Cl Content, 0.5 - 0.4%; CTE from 20 to 1,000°C, 7.0 x 10^{-6}/°C; CTE from 20 to 2,000°C, – x 10^{-6}/°C; Weight Change for First Cycle, –0.9%; Length Change for First Cycle, +0.1%)

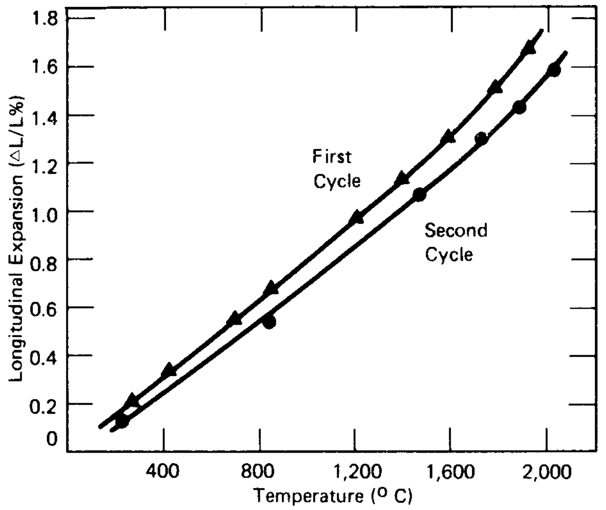

Figure 33. LONGITUDINAL THERMAL EXPANSION OF GEM ZIRCONIUM CARBIDE. (Run 2; Coating Temperature, 1,270 - 1,300°C; Tube Position, 46 - 51 Inches; O Content, 0.77 - 0.41%; Cl Content, 0.21 - 0.11%; CTE from 20 - 1,000°C, 6.9 x 10^{-6}/°C; CTE from 20 to 2,000°C, 7.9 x 10^{-6}/°C–Both CTE Values from Second Cycle; Weight Change for First Cycle, –0.35%; No Length Change for First Cycle or Weight or Length Changes for Second Cycle)

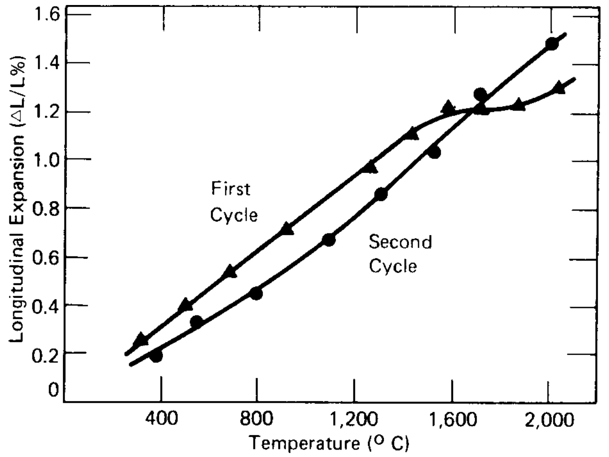

Figure 34. LONGITUDINAL THERMAL EXPANSION OF GEM ZIRCONIUM CARBIDE. (Run 2; Coating Temperature, 1,235 - 1,265°C; Tube Position, 40 - 45 Inches; O Content, 1.35 - 0.77%; Cl Content, 0.61 - 0.21%; CTE from 20 to 1,000°C, 6.1 x 10^{-6}/°C; CTE from 20 to 2,000°C, 7.5 x 10^{-6}/°C–Both CTE Values from Second Cycle; Weight Change from First Cycle, –1.16%; Length Change from First Cycle, +0.27%; No Weight or Length Change for the Second Cycle)

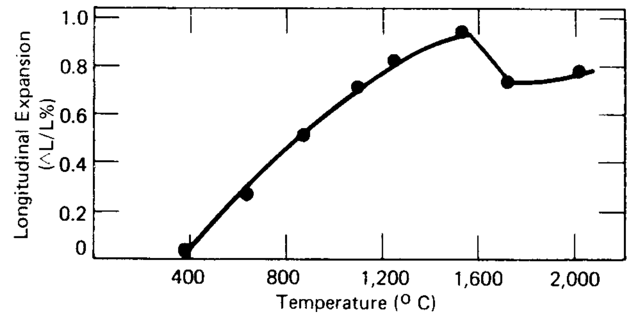

Figure 35. LONGITUDINAL THERMAL EXPANSION OF GEM ZIRCONIUM CARBIDE. (Coating Temperature, 1,200 - 1,220°C; First Cycle Heated to 1,000°C, but Run was Terminated Due to a Furnace Malfunction; Data Obtained on Second Cycle; O Content, 1.97 - 1.35%; Cl Content, 0.63 - 0.61%)

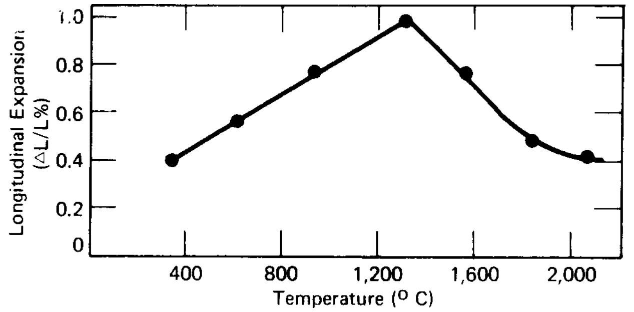

Figure 36. LONGITUDINAL THERMAL EXPANSION OF GEM ZIRCONIUM CARBIDE. (Coating Temperature, 1,190 - 1,205°C; O Content, 2.2 - 1.7%; Weight Change for First Cycle, –3.3%; Length Change for First Cycle, –2%; No Weight or Length Change for Second Cycle)

Table 18

DENSITIES OF VARIOUS THICK TUBES OF GEM ZIRCONIUM CARBIDE

Run	Position (in)	Deposition Temperature (°C)	Porosity (vol %)	Bulk Density(1) (gms/cc)	Real Density(1) (gms/cc)	Real Density(2) (% Theoretical)
1	5	950	7.04	4.79	5.15	78.5
1	11	1,040	0.61	5.50	5.53	84.3
1	20	1,075	0.79	5.60	5.64	86.0
1	33	1,125	0	5.79	5.79	88.3
1	42	1,175	0	5.86	5.86	89.3
1	52	1,250	0	6.34	6.34	96.6
2	6	1,080	4.52	5.73	6.00	91.5
2	37	1,220	2.36	6.09	6.24	95.1
2	45	1,265	0.39	6.46	6.49	98.9
3	38	1,230	0	6.25	6.25	95.3
3	51	1,280	0.50	6.43	6.46	98.5
4	3	1,065	3.06	5.78	5.96	90.9
4	38	1,230	0	6.04	6.04	92.1
4	50	1,285	0	6.50	6.50	99.1
5	8	1,200	0.14	5.87	5.88	89.6
5	22	1,290	1.06	6.48	6.55	99.8
5	36	1,325	0.52	6.55	6.58	100.3
5	43	1,360	0.85	6.42	6.48	98.8
5	52	1,400	1.11	6.16	6.23	95.0

(1) By mercury porosimetry.

(2) Based on a theoretical density of 6.56 gms/cc for hafnium-free zirconium carbide (from **Engineering Properties of Selected Ceramic Materials**, compiled by the Battelle Memorial Institute).

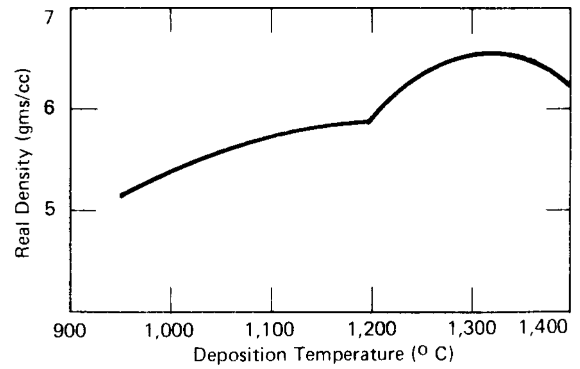

Figure 37. REAL DENSITIES OF GEM ZIRCONIUM CARBIDE THICK-WALL TUBES.

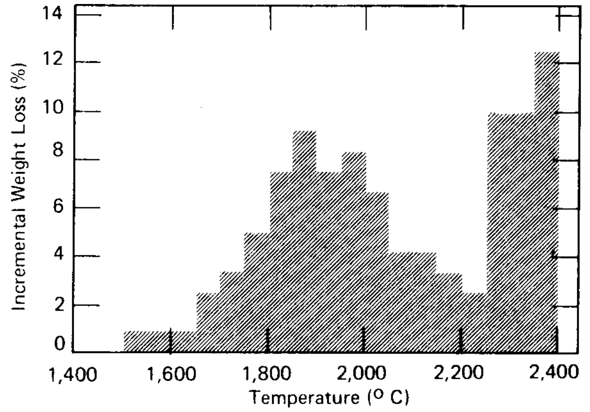

Figure 38. THERMOGRAVIMETRIC ANALYSIS OF GEM ZIRCONIUM CARBIDE. (Coating Temperature, 1,300°C; O Content, 0.41%; Cl Content, 0.11%; Weight Loss from 20 to 2,400°C, 0.9%; Weight Loss After One Hour at 2,400°C, 0.9%; Incremental Weight Loss Percent is the Percent Loss of the Total of 0.9%)

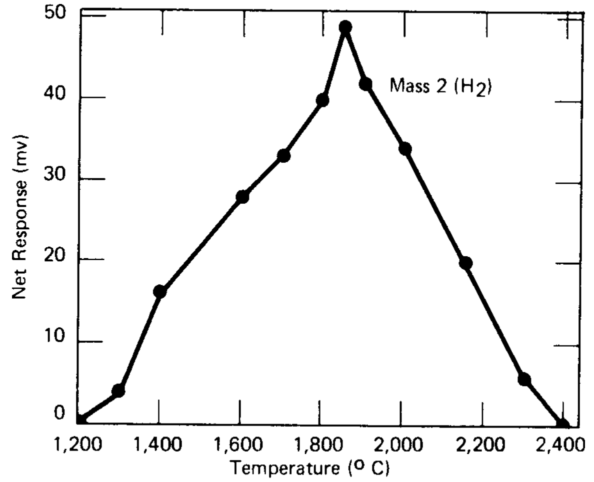

Figure 39. OUTGAS ANALYSIS OF GEM ZIRCONIUM CARBIDE. (Coating Temperature, 1,300°C; O Content, 0.41%; Cl Content, 0.11%)

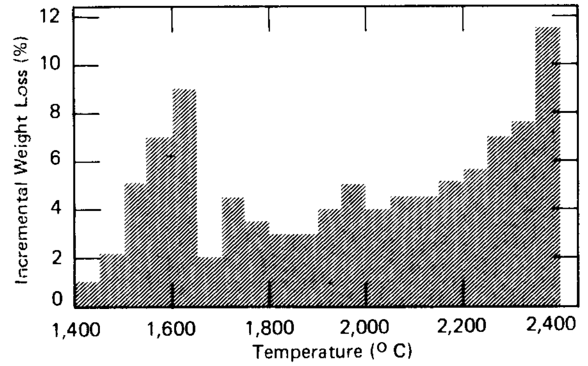

Figure 40. THERMOGRAVIMETRIC ANALYSIS OF GEM ZIRCONIUM CARBIDE. (Coating Temperature, 1,220°C; O Content, 1.35%; Cl Content, 0.61%; Weight Loss from 20 to 2,000°C, 2.7%; Incremental Weight Loss Percent is the Percent Loss of the Total of 2.7%)

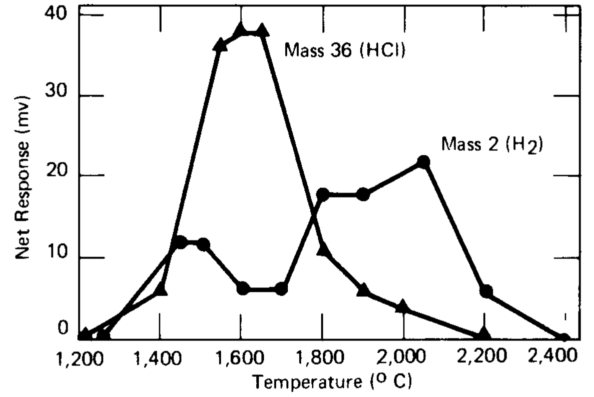

Figure 41. OUTGAS ANALYSIS OF GEM ZIRCONIUM CARBIDE. (Coating Temperature, 1,220°C; O Content, 1.35%; Cl Content, 0.61%)

The most significant points made by the outgas studies were:

1. Chlorine was evolved at 1,600 to 1,800°C from samples plated below 1,330°C.

2. Substantial weight losses occurred on the zirconium carbide coatings deposited below 1,330°C when heated to temperatures of 1,600°C or more.

3. Outgas data and the erratic CTE data on the impure zirconium carbide coatings are in agreement. The erratic CTE data can be explained by the releasing of the gaseous impurities from the zirconium carbide coatings.

Ion-Beam Microprobe

An ion-beam microprobe analysis was performed on two zirconium carbide samples. One sample contained low impurities (0.4% O_2, 0.1% Cl_2) and one sample had high impurities (2% O_2, 0.6% Cl_2). The ion-beam probe bombarded the specimen with a gas and detected the evolved gaseous species. Results showed that, for both samples, the evolved masses were not equal to the oxychloride, but mass peaks equivalent to zirconium monoxide and dioxide were observed. Chlorine was detected in both samples (Mass 35) but no gas equivalent to Mass 36 (HCl), Mass 231 ($ZrCl_4$), or a subspecies of zirconium chloride was detected.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be made as a result of this study:

1. The most important vapor-deposition process variable is the deposition temperature for niobium carbide and zirconium carbide.

2. Within the low-temperature span studied (1,000 to 1,400°C), coatings of niobium carbide and zirconium carbide, which were stable when heated to 2,000°C, were produced as the plating temperature was increased toward 1,400°C.

3. Low-temperature coatings of niobium carbide had a higher CTE than the high-temperature coatings, which could be explained by the carbon-to-niobium ratio effect.

4. Stable coatings of zirconium carbide were obtained when deposited with low impurity levels, such as total oxygen and chlorine contents below 0.3 weight percent.

5. The CTE of stable zirconium carbide was 7.7 to $7.8 \times 10^{-6}/^{\circ}C$ (20 to 2,000°C).

It is recommended that if zirconium carbide coatings stable at 2,000°C are required, they should be deposited with a total oxygen and chlorine content preferably below 0.3 percent.

The carbon-to-metal ratio was shown to have a significant effect on the CTE of niobium carbide. It is recommended that a study of the carbon-to-zirconium ratio and CTE be conducted to obtain data on zirconium carbide.

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(2) *Rover Fuel Element Development Activities*, Y-DA-3618; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; May 11, 1970.

(3) *Rover Fuel Element Development Activities*, Y-DA-3811; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; August 26, 1970.

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