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July 1, 1966

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~~Progress Report On~~

~~Laboratory Coating Studies~~

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NOV 17 1966

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Respectfully,

H. F. Faught
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Abstract

Information obtained in limited studies of the vapor deposition of TaC and ZrC by the hydrogen reduction of $TaCl_5$ and $ZrCl_4$ is presented. The data on TaC describe the deposition as a function of the $TaCl_5$ concentration in the gas stream and show that Ta_2C is present in coatings deposited at $2150^\circ C$ when the volume of $TaCl_5$ in the gas stream is greater than 2%. The data on ZrC are presented as a function of temperature and disclose that with the gas composition used diffusion-controlled deposition conditions were obtained only at the higher coating temperatures.

Low temperature metal deposits formed by the hydrogen reduction of $MoCl_5$ and $NbCl_5$ were investigated as a means of filling the cracks present in high temperature NbC coatings. Molybdenum is found to penetrate into the cracks, but is not adherent to NbC. In the process of depositing molybdenum metal from the chloride, etching of the NbC grain boundaries takes place.

A study of hydrogen chloride attack of niobium carbide coatings shows that the attack is inhibited to some extent by the presence of niobium chlorides in the gas stream. In depositing niobium metal over niobium carbide, etched grain boundaries are not in evidence. Although niobium does not penetrate into the cracks the way molybdenum does, it forms a diffusion bond with NbC and bridges over the cracks to seal them. This offers a potential method of increasing the resistance of a NERVA fuel element to hydrogen corrosion.

INTRODUCTION

Although the major emphasis of coating development in the Process Development Group of the Fuel Development Section at WANL is the improvement of NbC coatings on NERVA fuel⁽¹⁾, there has been occasion to investigate, to a limited extent, other coating systems. This report will present and discuss some of the data obtained on depositing TaC and ZrC, on overcoating NbC with ZrC and Mo and Nb metals, and on attacking NbC coatings with HCl. The metals and carbides were deposited from their respective chlorides under a variety of experimental conditions. In each case the data constitute only a small part of what would be considered a complete study of each coating system. These data are presented solely for information purposes, and possibly to serve as the groundwork for further development of the coating system.

EQUIPMENT AND PROCEDURES

The basic requirements for vapor deposition are a means of containing and supplying the coating source material; a means of containing and heating the substrate to the desired reaction temperature; a method of collecting and and/or disposing of the effluent products of the coating reaction; and a method of control of the entire coating system.

Figure 1 shows a flow diagram of the coating system used in this work. It shows the coating sequence from the gases used in the coating studies to the traps used for collecting reactive products. Argon or helium flows into the outer chamber to keep it pressurized with respect to both the sample

Figure 1 - Flow Diagram of Coating System

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chamber and the atmosphere. A measured amount of helium flows through the chloride salt to sweep its vapors into the main stream of the gases (He , HCl , and H_2), to mix with them, and to be transported to the deposition site. The lines through which the salt flows are heated to prevent condensation of the salt before the vapors enter the high temperature coating furnace. After depositing a coating, the unreacted salts condense and are removed in traps containing glass wool, and the reactive chloride gases are absorbed in a trap containing soda lime. The inert gases are then exhausted to the atmosphere.

Containers which hold the coating source material are referred to as "saturators". Their essential features are an inlet for an inert gas, a thermowell, a valve for relieving pressure during heating, and an exit for transporting the salt-saturated vapors to the coating substrate. Because the chlorides used in this work react readily with the atmosphere, valves constitute a part of the saturator so that it can be completely and independently isolated from the rest of the coating system and from the atmosphere.

Beyond these basic considerations, the design of the saturator depends upon the temperature limitations of the materials of construction, and upon the temperature required to increase the vapor pressure of the salt to the point where adequate quantities of the salt can be delivered to the substrate. The saturator shown in Figure 2 (glass cap mated to a stainless steel plate with a teflon gasket and spring-loaded bolts) is satisfactory for operation to about 250°C and is used to bubble helium through liquid NbCl_5 , TaCl_5 , and MoCl_5 . However, at temperatures around 330°C required to sublime ZrCl_4 ,

ALL PIPE, PLATE, AND TUBING OF T304 STAINLESS STEEL
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Figure 2 - Saturator for Molten Chloride Salts

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the use of normal gasketing materials is not satisfactory and it was necessary to use the all-metal saturator shown in Figure 3.

The saturators are heated in a thermostatically controlled oven. The oven also contains gas preheaters for the saturator inlet gas and for the supplemental reactive and non-reactive gases which are introduced into the coating gas stream directly above the saturator. The short length of pipe between the oven and furnace is kept heated to prevent condensation of material prior to entering the furnace.

The induction heated coating furnace used in this work is shown schematically in Figure 4. The outer quartz shell is sealed from the atmosphere by compression against silicone rubber gaskets placed in a recess in the water-cooled top and bottom stainless steel plates. A flow of inert gas is maintained in this chamber. Argon or helium are normally used, even though they are subject to glow discharge phenomena at high coating temperatures. When nitrogen can be tolerated in the system, a commercial 85% argon - 15% nitrogen mixture in which the nitrogen functions as an arc suppressor is preferred.

The outer quartz shell is constructed by ultrasonically drilling 7/8 in. diameter holes to accommodate quartz tubes to which optically clear quartz sight glasses are fused. The shell is wrapped with the induction coil prior to fusing the quartz tubes onto the shell. The extension tubes are necessary to prevent fogging of the lens by substances baked out of the graphite parts and lampblack insulation. The lampblack is contained in an inner quartz

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Figure 3 - Saturator for Zirconium Tetrachloride

Figure 4 - Coating Furnace Schematic

shell which sits on a graphite support ring. Graphite sight tubes pass through the lampblack from holes in the inner quartz shell to the susceptor and are aligned with the optical lens tube of the outer quartz jacket. The susceptor contains a graphite pre-heater and suitable fixturing to hold the sample.

The effluent salt vapors readily condense in the exit system. A glass pipe air condenser removes most of the solids from the stream. The fine carry-over is removed by glass wool in a bank of horizontal traps. The noncondensable gases pass through a soda-lime trap which removes the acid constituents before the gases are exhausted to a flame. The flame burns any hydrogen or hydrocarbons present in the gas before it is exhausted to the atmosphere.

A control panel holds the flowmeters, pressure gauges, temperature recorders, and electrical equipment necessary to operate and monitor the runs. Substrate temperatures are read using an I&N optical pyrometer.

There are at present 3 furnaces that are set up to be operated from a 20 Kw generator. These are pictured in Figure 5. Although only one furnace can be operated at a time it is necessary to have several available to permit coating from several different systems without contaminating the coatings with material deposited on the furnace parts during previous coating runs. Multiple furnaces eliminate the need to tear down and rebuild a furnace each time a change is made from one coating system to another.

Runs are made according to pre-selected conditions. While the furnace is being purged with an inert gas the graphite samples are heated to coating temperatures. During this time power is supplied to the oven to heat the salts

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Figure 5 - Laboratory Vapor Coating Facility

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to the required temperatures. A valve is open to a mercury seal and trap to relieve pressure and prevent back diffusion of air into the saturator. Upon reaching operating temperatures in both the furnace and oven this valve is closed and the valve connecting the saturator to the furnace is opened. The valve on the flowmeter supplying the carrier gas to the saturator is opened to slowly build up a positive line pressure before opening the inlet valve to the saturator. Hydrogen and hydrogen chloride are then supplied to the system and the flows and pressures regulated. The inert gas flow in the jacket had been previously increased so that the jacket pressure is 2 to 5 mm Hg positive with respect to pressure of the coating gases. At the end of the coating run the valve between the saturator and the coating furnace is closed first. This builds up a pressure in the saturator inlet gas line and prevents back transport of the salt while closing the valve on the inlet line. The hydrogen chloride and hydrogen flows are then stopped, power to the furnace turned off, and an inert gas purge maintained in the furnace. The furnace cools at approximately $40^{\circ}\text{C}/\text{min.}$ from 2000° to 1400°C. It is generally cooled to room temperature before removing the sample.

Temperatures, flowmeter readings, and operating pressures are recorded every 10 or 15 minutes during a run and averaged to obtain data for calculations. Coating weight is the weight gained by the sample during the run. Salt delivery rate is determined by the difference in weight in the saturator before and after the run divided by the length of the run in minutes. The important variables are usually temperature, total coating gas flow, gas stream composition (especially hydrogen to salt ratio), and time.

TANTALUM CARBIDE

A total of 8 runs were made in which tantalum carbide was deposited on graphite at temperatures around 2200°C. Data from these runs are given in Table I. It is seen that in six of the runs tantalum carbide was deposited by hydrogen reduction of tantalum pentachloride in a gas stream containing hydrogen chloride. In the other two runs tantalum carbide was deposited by thermal decomposition of tantalum pentachloride in a helium atmosphere.

Transport of the tantalum pentachloride to the substrate is accomplished by passing helium through the molten salt using the saturator shown in Figure 2. The amount of salt moved is a function of the flow rate of helium and of the vapor pressure and consequently the temperature of the salt. A constant problem in using a "bubble through" saturator with niobium pentachloride is blocking of the helium inlet to the saturator with niobium oxychloride. However, tantalum pentachloride does not readily form an oxychloride and no problems are encountered in operating the tantalum pentachloride saturator.

In the first several coating runs made the salt delivery was below expectations and it was therefore increased in each of the succeeding runs. The experimentally determined salt delivery from the saturator used in this work is shown as a function of the rate of helium flow through the molten salt in Figure 6. Increasing the saturator helium flow causes a slight increase in the total flow, a steady increase in the concentration of salt in

TABLE I

Summary of Data From the Vapor Deposition of Tantalum Carbide

Run No.	Time (hr)	Temperature (°C) ⁽¹⁾		Total Gas Flow (lpm)	Gas Composition (%)				H ₂ /TaCl ₅	Wt. of Ta Deposit ⁽²⁾ (gr)	Efficiency (%)	Bore Thickness at Inlet (mils)
		1 in.	5 in.		HCl	He	H ₂	TaCl ₅				
C-1 ⁽³⁾	2	2080	2143	1.75	46.6	48.1	3.5	1.9	1.8	15.44	48	1.34
C-2	2	2150	2216	1.70	46.9	48.1	3.5	1.5	2.3	19.77	79	1.70
C-3	2	2160	2222	1.72	45.7	48.3	3.5	2.5	1.4	25.68	62	1.96
C-4	2	2165	2224	1.76	45.3	48.4	3.5	3.0	1.2	31.48	62	2.84
C-5	2	2160	2218	1.78	45.4	48.0	3.4	3.2	1.1	27.15	49	2.10
C-6	2	2180	2247	1.79	45.1	47.9	3.4	3.6	1.0	33.62	54	2.94
C-7	2	2130	2191	1.67	0.0	97.2	0.0	2.8	0.0	17.98	39	2.48
C-8	1.5	2115	2237	1.71	0.0	97.0	0.0	3.0	0.0	11.98	33	--

Temperatures measured at 1" and 5 in. from the sample inlet.

- (1) Estimated in Runs C-2 through C-7 because of fogged lens at the 1 in. location. Reliable readings were obtained at the 5 in. location.
- (2) Coating up 9 to 11 inches of a 15 inch sample. Temperature at 10 inch location around 1700°C.
- (3) Initial run; some salt consumed in coating of preheater thereby diluting stream in salt at element inlet.

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Figure 6 - Salt Delivery from TaCl_5 Saturator

the gas stream, and a decrease in the hydrogen to salt ratio. All of the other factors are held constant within the limitations of the equipment. These runs show that the amount of material deposited increases as the salt concentration increases and the hydrogen to salt ratio decreases. This is contrary to the effect expected in a system requiring hydrogen reduction and carbon diffusion to promote deposition, and in two subsequent runs it was found that hydrogen was not essential to the deposition of material.

A schematic of the thickness and the composition of the coating and the deposition rate as functions of salt concentration for runs two through six is given in Figure 7. X-ray diffraction analysis showed that coatings deposited from gas streams containing more than 2% $TaCl_5$ or at rates greater than about 0.15 grams/minute contained both TaC and Ta_2C . At lower concentrations only TaC was found. Figure 8 is a photomicrograph which shows that Ta_2C makes up at least 50% of the coating thickness deposited from gas streams containing 3% or more of $TaCl_5$ and 3.5% hydrogen. The presence of Ta_2C indicates that unless appropriate adjustments are made in the chemistry of the coating stream, deposition occurs too rapidly to permit complete carburization.

X-ray diffraction analysis showed that the coating deposited solely by the thermal decomposition of $TaCl_5$ is entirely TaC . Metallographic examination of these coatings, as seen in the photomicrograph in Figure 9, showed that the outer 25% of the coating is very porous and the mid-area has deep grain boundary cracks.

Figure 7 - Relationship Between Coating Thickness, Composition, and Per Cent of TaCl_5 in Coating Gas Stream.
 (In addition to the TaCl_5 content given, the coating gas in Runs C-1 through C-6 contained 46% HCl, 48% He, and 3.5% H_2 ; the gas in Run C-7 contained 97.2% He and 2.8% TaCl_5 .)

Figure 8 - Tantalum Carbide Coating on Graphite Formed by H_2 Reduction of $TaCl_5$. (sample from Run C-4; 200X, etched.)

Figure 9 - TaC Deposited by Thermal Decomposition of $TaCl_5$ (sample from Run C-7; 200X; unetched.)

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Figure 7 shows that the thickness of the TaC layer is about 1.4 mils and is virtually independent of the gas stream composition. The differences in thickness are probably due to uncontrolled temperature fluctuations. TaC growth under diffusion controlled conditions can be expressed by:

$$d = 8.3 \times 10^3 (\exp - 87,000/2RT) t^{1/2}$$

where d is the thickness in mils, T the temperature in degrees Kelvin, and t is the time in hours. This equation was arrived at by using the average experimental temperature of 2150°C, a thickness of 1.4 mils, and the expression

$$D_c^{TaC} = 1.8 \exp(-87,000/RT)$$

as determined by Brizes and Tobin⁽²⁾.

The few runs that were made to deposit tantalum carbide showed that it is readily deposited, but because diffusion of carbon through tantalum carbide is slower than it is through niobium carbide, substrate temperatures of about 300°C higher than that used in depositing niobium carbide are required to obtain equivalent thicknesses of tantalum carbide in runs of equal duration. The rate of tantalum deposition can easily exceed the rate of carbon diffusion through the coating to give the lower carbide, Ta₂C. Gas chemistry adjustments such as higher hydrogen chloride or lower salt percentages are required to reduce the deposition rate to obtain uniform diffusion-controlled coatings. A completely carburized coating can also be obtained by holding the coated piece at temperature for a period of time after stopping the flow of coating gas.

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ZIRCONIUM CARBIDE

A total of 31 runs were made to study the deposition of zirconium carbide on graphite. Data from these runs are given in Table II.

Zirconium chloride (ZrCl_4) sublimes above 300°C . For this reason it is necessary to operate the saturator at temperatures above 300°C in order to get adequate transport of the salt vapors to the substrate. At these temperatures the salt has a tendency to cake and better results are obtained by flowing the carrier gas over, instead of through, the salt. For these reasons the saturator shown in Figure 3 is used for ZrCl_4 . By operating the saturator slightly above 330°C , fairly consistent salt deliveries are obtained. Most of the useful data is based on runs with constant salt deliveries and hydrogen-to-salt ratios of between 4 to 5.

The first several runs made it apparent that the gas compositions used in depositing TaC could not be applied to the deposition of ZrC. The presence of about 50% HCl in the gas stream precludes deposition. In the absence of HCl satisfactory coatings form at 1400°C and above. Calculations for the reaction $\text{ZrCl}_4(\text{g}) + 2\text{H}_2(\text{g}) + \text{C}(\text{s}) = \text{ZrC}(\text{s}) + 4\text{HCl}(\text{g})$ show that good yields are thermodynamically possible above 2000°K at a hydrogen to salt ratio of 5 (Figure 10), and this was the basis for all runs made after D-10. Figure 10 shows that the H_2/salt ratio makes little difference in the theoretical yield

TABLE II
 SUMMARY OF DATA FROM THE VAPOR DEPOSITION OF ZIRCONIUM CARBIDE

Run No.	Time (hr)	Inlet Temperature ⁽²⁾		Total Gas Flow (lpm)	Gas Composition (%)				H ₂ /ZrCl ₄	Wt. of Zr Deposit (gr)	Efficiency (%)	Bore ⁽²⁾ Thickness at Inlet (mils)
		1.5 in.	6.5 in.		HCl	He	H ₂	ZrCl ₄				
D-1	2	1850	1939	1.58	51.0	39.9	3.9	5.3	0.74	Loss of 2.6 gr. -	-	-
D-2	2	2011	2060	0.79	-	85.7	10.2	4.1	2.47	1.22	23.3	0.57
D-3	0.5	1997	2057	1.72	-	92.4	1.7	5.9	0.30	2.68	11.4	-
D-4	1	1956	2028	6.51	2.3	52.5	38.3	0.9	42.8	2.47	34.9	0.72
D-5	2	1800	1871	4.69	-	77.6	20.8	1.6	13.4	0.97	2.6	0.11
D-6	3.5	1786	1857	6.15	-	59.0	40.5	0.5	89.7	4.88	34.6	0.45
D-7	1.5	1711	1766	6.32	-	59.9	39.4	0.6	64.3	3.49	23.8	1.72
D-8	2	2135	2154	2.40	-	57.4	40.8	0.8	53.7	4.24	47.7	1.06
D-9	2	2153	2171	2.55	-	60.4	38.3	1.3	29.9	11.46	68.8	1.97
D-10	2	2164	2185	2.57	-	60.7	38.4	0.9	45.3	7.06	66.2	2.24
D-11	2	2147	2168	1.77	-	86.6	11.2	2.8	4.2	12.68	54.9	1.70
D-12	2	2130	2187	1.76	-	86.7	11.2	2.1	5.4	1.05	5.6	0.61
D-13	2	2164	2168	1.82	-	85.4	11.0	3.6	3.1	0.39	1.2	0.89
D-14	2	2200	2223	1.78	-	87.5	11.2	1.4	7.9	7.54	60.8	3.54
D-15	2	2144	2201	1.80	-	86.4	11.2	2.4	4.6	15.43	72.2	2.32
D-16	2	2145	2157	1.78	-	86.6	11.2	2.2	5.0	14.80	74.7	2.79
D-17	2	2104	2077	1.84	-	86.6	10.8	2.6	4.2	16.32	70.8	2.39
D-18	2	2158	2237	1.87	-	87.1	10.8	2.1	5.1	15.19	77.6	2.94
D-19	2	2149	2086	1.95	-	87.4	10.4	2.2	4.6	15.65	73.5	2.77
D-20	2	2032	2207	1.87	-	86.9	10.8	2.3	4.6	11.29	53.0	1.36
D-21	2	1916	2089	1.84	-	86.5	10.9	2.6	4.3	9.71	41.9	0.73
D-22	2	1864	2010	1.80	-	86.7	11.1	2.2	5.0	7.21	37.0	0.85
D-23	2	1780	1846	1.77	-	86.2	11.1	2.7	4.2	4.93	21.3	0.80
D-24	2	1670	1758	1.78	-	86.4	11.1	2.4	4.5	3.67	17.3	0.55
D-25	2	1416	1464	1.85	-	86.2	11.0	2.8	4.0	1.52	6.1	0.20
D-26	2	908	927	1.83	-	86.2	11.0	2.8	4.0	-0.15	0.0	0.00
D-27	2	1797	1814	1.82	-	86.5	11.1	2.4	4.6	3.56	16.7	0.87

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TABLE II (Cont'd.)

Run No.	Time (hr)	Inlet Temperature ⁽²⁾		Total Gas Flow (lpm)	Gas Composition (%)					Wt. of Zr Deposit (gr)	Efficiency (%)	Bore ⁽²⁾ Thickness at Inlet (mils)
		1.5 in.	6.5 in.		HCl	He	H ₂	ZrCl ₄	H ₂ /ZrCl ₄			
D-28	2	1886	1928	1.84	-	86.3	11.1	2.6	4.4	4.84	20.9	1.23
D-29	2	2006	2190	1.85	-	86.3	11.1	2.6	4.3	8.21	35.6	2.80
D-30	2	2106	2207	1.83	-	86.1	11.1	2.8	4.0	13.58	54.5	3.76
D-31	2	2000	2078	1.85	-	86.0	11.2	2.8	4.1	7.07	28.6	-

(1) Runs No. 1 through 8 had outer shell gas of 85% Ar-15% N₂ and some of the coatings nitrided.

(2) At 1.5 in. and 6.5 in. from inlet end of sample.

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Figure 10 - Theoretical Yield as a Function of the $H_2:ZrCl_4$ Ratio in $ZrCl_4 + 2H_2 + C = ZrC + 4 HCl$

at low temperatures, but becomes more significant as the temperature approaches 2000°K.

No metal was found in the 1300°C preheater with hydrogen to salt ratios as high as 90, but evidence of metal formation was found above the melting point of zirconium when it was noticed that the metal balled up at the end of the element and then carburized. This observation was confirmed by thermodynamic approximations which showed less than 1% conversion to metal at 1500°K and around 40% conversion at 2000°K. When the 15% nitrogen - 85% argon mixture was used in the shell, nitriding occurred at pressure differentials as low as 2 mm Hg. Zirconium nitride seemed to form in preference to the metal or carbide in the presence of even small amounts of nitrogen at temperatures below the melting point of zirconium. An extreme case of zirconium nitride deposition is shown in Figure 11. Although nitriding was less prevalent at the higher coating temperatures, helium was used as the gas in the outer shell in all runs beyond D-8.

Over half of the runs were made with a nominal gas stream composition of 86.0 to 87.5% He, 10.4 to 11.2% H₂, and 2-3% ZrCl₄ at flows of 1.76 to 1.95 liters per minute. The substrate temperature was the major variable in these 2 hour runs and ranged from 1400 to 2200°C at the sample inlet. The deposition efficiency based on the weight of the deposit relative to the amount of salt used ranged from 6% at the lower temperature to as much as 78% (approximately the theoretical yield) at the higher temperatures; variation was approximately linear with temperature above 1700°C as shown in Figure 12. Although the efficiency was almost linear above 1700°C, the coating thickness increased

Figure 11 - Zirconium Nitride Coating on Graphite
(sample from Run D-7; 200X; unetched.)

Figure 12 - Efficiency of Depositing ZrC by H₂ Reduction of ZrCl₄ as a Function of Coating Temperature

moderately from 0.2 mils at 1400°C to 0.7 mils at 1900°C and then showed a rapid increase from 1.4 mils at 2000°C to 3.5 mils at 2200°C. This variation of coating thickness with temperature is shown in Figure 13. A plot of the coating rate as a function of temperature is compared with the data of Blocher, et.al.,⁽³⁾ in Figure 14. The expression $K_p = 1.74 \exp (-91,500/RT) \text{ cm}^2/\text{sec}$ calculated from Blocher's data is for the parabolic growth of ZrC expected in a diffusion controlled regime. The data obtained above 1800°C can be expressed by a line parallel to that drawn through Blocher's data to give a similar activation energy. The slight curvature of the plot in Figure 14 is typical of reactions with competing mechanisms or which show an increasing homogeneity with increasing temperature.

The effect of temperature, with the gas composition and flows used in this work, upon the coating system, is illustrated in Figure 15. At the lower temperatures the outer surface of the coating has a large number of needle-like growths. Samsonov⁽⁴⁾ attributes the needle-like carbides to the reduction in specific volume in the formation of the carbide from the metal. As the temperature increases the asperities decrease in number and increase in breadth. At the higher temperatures, where the growth is controlled by diffusion of carbon through the coating, the outer surface is reasonably smooth.

Grain size and shape are more irregular than in vapor deposited TaC coatings, and the ZrC-C interface differs from the TaC-C interface in that the

Figure 13 - Inlet Bore Thickness of ZrC Deposited by H₂ Reduction of ZrCl₄ as a Function of Coating Temperature

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Figure 14 - ZrC Coating Rate as a Function of Temperature
(d = thickness, cm.; t = time, sec.,
 T = temperature, °K)

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a) $T = 2032^{\circ}\text{C}$ (Sample from Run D-20)

b) $T = 1864^{\circ}\text{C}$ (Sample from Run D-22)

c) $T = 1670^{\circ}\text{C}$ (Sample from Run D-24)

Figure 15 - Photomicrographs of ZrC Coatings Deposited on Graphite at Different Substrate Temperatures (Channel 10 - 400X)

gap is not uniform. The general appearance of the ZrC coatings suggests a different nucleation and growth phenomena than that observed in depositing TaC.

As expected, no phases other than ZrC are found in the coatings by x-ray analysis (except for those coatings which metallographically showed a sound nitride deposit). However, the low lattice parameters obtained indicate contamination by oxygen or nitrogen even though precautions are taken to minimize their effect. Coatings deposited at the lower temperatures were more discolored than those deposited at the higher coating temperatures.

A series of four samples coated for 2 hours at temperatures from 1800 to 2200°C were subjected to hydrogen corrosion at 2000°C and 350 psi with a hydrogen flow of 400 CFH. The samples ran from 22 minutes to 32 minutes with some of the samples failing because of arcing in the furnace and/or mechanical damage during the run. Photomicrographs of these samples before and after hydrogen corrosion are shown in Figure 16. Hydrogen attack is seen in samples with coating thicknesses below about 2 mils. All of the samples had fewer but larger cracks after the corrosion attack.

The two problems associated with zirconium carbide deposition in the runs that were made were the purity of the deposit and the inadequate amount of salt supplied to the coating gas stream. However, these

- a) Sample from Run D-30 (Deposition Temperature = 2150°C)
- 1) Transverse View Before Hydrogen Corrosion
 - 2) Longitudinal View After Hydrogen Corrosion

- b) Sample from Run D-28 (Deposition Temperature = 1900°C)
- 1) Transverse View Before Hydrogen Corrosion
 - 2) Longitudinal View After Hydrogen Corrosion

Figure 16 - ZrC Coatings Before and After Hydrogen Corrosion (100X)
(corrosion tested at 2000°C and 350 psi with a hydrogen
flow of 400 CFH for 30 minutes)

problems can be rectified without appreciable difficulty if future work is to be performed with this system.

OVERCOATING OF NIOBIUM CARBIDE

Dual coatings are of potential interest because they form a coating system which combines the properties of the individual constituents. ZrC-NbC was the first duplex system attempted and in a single run the feasibility of depositing ZrC over NbC was demonstrated. A photomicrograph of the coating is shown in Figure 17. This system forms a coherent interface, and has the crack and adherence problems inherent in single phase carbide coatings.

The present emphasis on 2-phase coating systems in the NERVA program is the improvement of the corrosion behavior of fuel elements in the "mid-band" region where open cracks provide access of hydrogen to unprotected graphite. These cracks form upon cooling the element from coating temperatures. The number of cracks and their size and distribution are functions of the coating thickness, the temperature from which cooling occurred, the cooling rate and differences in thermal expansion between the coating and the substrate. In hydrogen corrosion tests and in reactor operation the element sees temperatures above and below coating temperatures. At test temperatures above coating temperatures the NbC cracks close, but at lower temperatures these cracks are open and are responsible for what is termed "mid-band" corrosion.

An interesting solution to this problem was developed at Los Alamos (IASL) when it was found that Mo metal and/or carbide deposited from Mo(CO)_6 at low temperatures filled in the coating cracks, and improved the resistance

Figure 17 - ZrC Deposited Over an NbC Coating on Graphite
(sample from Run D-31, Table II, 200X;
lightly etched)

of the element to hydrogen corrosion. This approach is undergoing advanced development at LASL, Y-12, and WANL.

In addition to the carbonyl work the possibility of depositing molybdenum by the H_2 reduction of $MoCl_5$ was explored because the process could be performed in the furnaces used to deposit NbC. The few experiments that were conducted showed that it gave a pure metal foil-like deposit at somewhat higher temperatures than those used in the carbonyl process. Data from the runs that were made are given in Table III. These data show that the best deposition temperature is around $1000^\circ C$. The loss in weight at higher coating temperatures is due to the attack of the NbC coating by the HCl produced in H_2 reduction of $MoCl_5$. This attack is also seen metallographically in Figure 18. The coating subsequently covers the etched boundaries and has good crack penetration. Since the coating is deposited around $1000^\circ C$, expansion partially closes the crack and thin coatings show a slight separation at room temperature. The coating itself is extremely soft and ductile, but has no adherence and is simply mechanically held in place.

Childs, et.al.,⁽⁵⁾ found that at atmospheric pressure metallic molybdenum could be deposited as low as $550^\circ C$, but it was necessary to keep the partial pressure of $MoCl_5$ below 1.5 mm to avoid powdery, non-adherent deposits. Under these conditions the coating rates are extremely slow. Photomicrographs of samples from runs F-5, F-8, and F-10 (Figure 18) show that at temperatures below $1000^\circ C$ powdery deposits are obtained with 1.4% $MoCl_5$ in the gas stream, but at $1200^\circ C$ a thin metallic foil is deposited. Thus, conditions for depositing

TABLE III

SUMMARY OF DATA FROM THE VAPOR DEPOSITION OF PURE MOLYBDENUM METAL

Run ⁽¹⁾ No.	Time (hr)	Temperature (°C) ⁽²⁾		Total Gas Flow (lpm)	Gas Composition (%)				Wt. of Mo Deposit (gr)	Effic- iency (%)	Bore Thickness at Inlet (mils)
		1 1/2"	6 1/2"		He	H ₂	MoCl ₅	H ₂ /MoCl ₅			
F-1	1	--- 951 ---		1.90	87.5	10.5	2.0	5.4	0.364	22.9	-
F-2	1	--- 920 ---		0.35	91.0	7.3	1.7	4.2	0.509	31.9	-
F-3	1	1022	1037	1.86	88.7	10.7	0.7	16.0	0.006	0.2	0.45
F-4	1	815	828	2.71	98.9	1.1	0.1	47.9	0.038	24.1	0.18
F-5	1	1018	1030	2.21	89.7	9.0	1.4	6.4	1.068	13.4	0.71
F-6	1	1030	1052	1.95	88.0	11.4	0.6	17.9	0.002	0.1	0.09
F-7	0.7	1219	1238	2.01	86.7	12.9	0.5	27.7	-0.055	--	--
F-8	2	1215	1223	2.03	83.0	15.6	1.4	11.3	-0.094	--	0.53
F-9	2	1015	1022	1.98	83.3	15.4	1.3	12.3	-0.114	--	0.62
F-10	2	824	830	2.04	83.5	15.2	1.4	11.1	0.648	4.5	1.25 (soot)

- (1) Runs F-1 and F-2 were made using full length elements.
 (2) Temperature measured at 1 1/2 and 6 1/2 in. from sample inlet.

a) Sample from Run F-5
Deposition Temperature = 1020°C
 $H_2/MoCl_5 = 6.4$

b) Sample from Run F-8
Deposition Temperature = 1220°C
 $H_2/MoCl_5 = 11.3$

c) Sample from Run F-9
Deposition Temperature = 1020°C
 $H_2/MoCl_5 = 12.3$

d) Sample from Run F-10
Deposition Temperature = 825°C
 $H_2/MoCl_5 = 11.1$

Figure 18 - Mo Deposited Over NbC Coatings on Graphite (400X)

a suitable coating must be maintained at the sacrifice of coating rate.

Although it appears possible to produce satisfactory metal deposits in this manner, additional development of the chloride process for depositing Mo was abandoned because of the successful application of the carbonyl process to the "mid-band" corrosion problem.

Inasmuch as the nuclear properties of molybdenum are less desirable than niobium some tests were performed on depositing niobium over NbC. These data are given in Table IV and show that deposition takes place somewhere above 800°C for a gas composition of 94.0% He, 3% H₂, and 3% NbCl₅ with an optimum efficiency of the order of 25% between 1000° and 1200°C.

Carbon diffusion is very slow at these temperatures, but a narrow diffusion zone forms to provide an excellent bond between the metal and the carbide. This 0.03 to 0.06 mil zone etched more rapidly than either the metal or carbide, and is visible on the etched samples as a dark band between the metal and carbide coatings in Figure 19. An Arrhenius plot based on the width of this zone is given in Figure 20 and is compared to the data of Bornstein, et.al.,⁽⁶⁾ and an extrapolation of the data obtained above 1700°C by Brizes, et.al.,⁽⁷⁾. It is seen that the data falls between the lines of the other investigators, but at almost one-half their slope. However, although there is not enough data to verify this result, it does appear that reasonable estimates of the diffusion zone thickness can be obtained by using the equations developed at much higher temperatures.

Niobium is deposited without the chloride grain boundary attack observed in the deposition of molybdenum, but the outer surface of the deposit

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TABLE IV

SUMMARY OF DATA FROM THE VAPOR DEPOSITION OF NIOBIUM OVER NbC COATED GRAPHITE

Run No.	Time (hr.)	Temperature (°C) ⁽¹⁾		Total Gas Flow (lpm)	Gas Composition (%)				Wt. of Nb Deposit (gr)	Efficiency (%)	Thickness at Inlet (mils)
		1 in.	6 in.		He	H ₂	NbCl ₅	H ₂ /NbCl ₅			
B-80	1.0	819	846	1.95	93.8	3.0	3.2	0.95	0.075	0.5	0.0
B-81	1.0	1020	1061	1.94	94.1	3.0	2.9	1.05	1.698	12.1	0.4
B-82	1.0	1202	1233	1.96	94.4	3.1	2.6	1.20	2.118	17.0	0.9
B-83	1.0	1103	1079	1.95	91.9	3.1	1.9	1.61	2.256	24.0	0.7
B-84	1.0	1123	1143	1.95	94.4	3.1	2.5	1.21	2.255	18.1	—

(1) Temperature measured at 1 and 6 in. from sample inlet.

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a) Sample from Run B-81
1/2 in. from sample inlet
T = 1020°C

b) Sample from Run B-81
5 1/2 in. from sample inlet
T = 1061°C

Figure 19 - Nb Deposited over NbC Coatings on Graphite
(Channel 10-200X, Metallographically Etched)

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Figure 20 - Total Niobium Carbide (NbC + Nb₂C) Growth Rate as a Function of Temperature

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is irregular and crystalline in contrast to the smooth, thin molybdenum coating. Although niobium does not penetrate into the cracks the way molybdenum does, it bridges over the cracks to effectively seal them and possibly provide some protection from hydrogen corrosion. Niobium, from nuclear considerations, is more desirable than molybdenum and shows considerable promise if hydride formation is not a problem.

Metal deposition by the hydrogen reduction of chloride salts is generally optimum between 1200°-1400°C. By adjusting the temperature to control the equilibrium reactions the distribution of the deposit in long narrow tubes can be controlled. This control of the temperature profile over the length of sample is not possible with the small laboratory coating furnace. In the laboratory runs heavy front end deposits were usually obtained, but in B-81 the coating was well distributed over about 6 inches of the sample. Because profile control is more readily achieved in pilot plant furnaces, plans have been made to coat full length elements at the Westinghouse Experimental Fuel Facility (WEFF) for performance evaluation in the reactor-simulated hydrogen corrosion tests at the Westinghouse Astronuclear Hydrogen Experimental Site (WANHES).

HYDROGEN CHLORIDE ATTACK OF NIOBIUM CARBIDE

Because HCl is a product of the hydrogen reduction of chloride salts, a cursory investigation was made of the effect of HCl on NbC coating in the 800-1200°C range used for metal deposition. As mentioned in the previous section, deposition of molybdenum over NbC by the hydrogen reduction of MoCl₅

etched the NbC, but deposition of niobium by the hydrogen reduction of NbCl₅ gave no evidence of attack.

Six inch samples of non-fuel element stock with NbC coated bores were placed in a coating furnace which had uncoated fixtures. Mixtures of approximately 5% HCl in helium were passed through the bores which had an approximate coated area of 34.7 sq. in. (224 sq. cm). Tests were made at 800-1200°C for times up to 1 hr. The data are given in Table V. The weight loss as a function of time and temperature is given in Figure 21. However, this weight loss is averaged over the six inch sample because the extent of attack is a function of the rate of saturation of the gas stream with reaction products as it progresses through the bores. At 1200°C, for example, all of the coating is removed from the initial 1/4 in. of the sample, but an equilibrium is rapidly approached which diminishes the downstream attack of the coating. Figure 22 shows photomicrographs of the bores at 1/2 inch and 5 1/2 inches from the inlet.

A more detailed study of this system would show that for each temperature there will exist an equilibrium concentration of the predominant niobium chloride which will prevent HCl and/or Cl₂ from attacking Nb or NbC. Likewise, there is a minimum hydrogen-to-hydrogen chloride ratio at each temperature that if maintained will minimize Nb or NbC attack. Free energy considerations based on available data indicate that NbCl₃ will be the predominant species at 1000° and 1500°K. Figure 23 shows the theoretical partial pressure of NbCl₃ in the gas stream as a function of the H₂/HCl ratio for the

TABLE V

SUMMARY OF DATA FROM THE HYDROGEN CHLORIDE ATTACK OF NIOBIUM CARBIDE

Run No.	Time (min)	Temperature (°C) ⁽¹⁾		Gas Flow (lpm)		Weight Loss (gr)
		1/2 in.	5 1/2 in.	He	HCl	
L-1	30	1230	1233	1.77	0.34	0.3256
L-2	30	1013	1011	1.77	0.34	0.1113
L-3	30	809	804	1.77	0.25	0.0804
L-4	60	1213	1216	1.77	0.25	0.1917
L-5	30	1213	1190	1.77	0.25	0.2502
L-6	30	1008	1000	1.77	0.25	0.1077
L-7	60	1026	1025	1.77	0.25	0.1364
L-8	60	814	816	1.77	0.25	0.0918
L-9	60	1210	1200	1.77	0.25	0.3450
L-10	15	806	780	1.77	0.25	0.0382
L-11	15	1007	987	1.77	0.25	0.1436
L-12	15	1207	1175	1.77	0.25	0.0942
L-13	15	985	980	1.77	0.25	0.1130

(1) Temperatures measured at 1/2 and 5 1/2 inches from sample inlet.

Figure 21 - HCl Attack of NbC in the Bores of 6 inch Samples

1/2 in. from sample inlet

5 1/2 in. upstream

a) Run L-3; Inlet T = 809°C; Time = 30 minutes

1/2 in. from sample inlet

5 1/2 in. upstream

b) Run L-4; Inlet T = 1213°C; Time = 60 minutes

Figure 22 - Photomicrographs of HCl Attack of NbC Coatings

reaction

Gas stream compositions that give points to the left of the curve will attack NbC. The effect of temperature becomes more pronounced at low partial pressures of NbCl₃ and a large H₂:HCl ratio is required to prevent attack at the higher temperatures. The calculations made to develop this equilibrium plot did not consider possible side reactions or kinetic effects. Figure 23 shows that for the run conditions given in Table V as little as 5 to 10% reaction is sufficient to give pressures of NbCl₃ and H₂ high enough to inhibit attack. This inhibition has been established by the photomicrographs of Figure 22.

FUTURE PLANS

Niobium carbide has thus far been an adequate coating for protecting fueled and unfueled graphite parts as verified by successful reactor tests. It is a coating which does not have the liabilities of the high neutron absorption cross-section of tantalum carbide or the low eutectic melting point of zirconium carbide-carbon. However, loss of carbon through niobium carbide is greater than it would be with the other carbides.

All of the carbides have deficiencies in one property or another which make them less than ideal for severe NERVA applications. In a comparison of carbide coating for fuel elements, Cadoff⁽⁸⁾ suggests that improvements in

Figure 23 - Equilibrium Plot for the Reaction
 $\text{NbC(s)} + 3\text{HCl(g)} = \text{NbCl}_3\text{(g)} + 3/2 \text{H}_2\text{(g)} + \text{C(s)}$.

properties may be possible through the use of mixed alloy carbide systems. Work has been initiated to study the vapor deposition of mixed alloy carbide systems in general. Because of its desirability for NERVA applications, the zirconium-niobium-carbon system is of particular interest.

Composite coatings are of potential interest for much the same reason as the alloy coatings, i.e., the possibility of combining the properties of the individual elements. Metal coatings with high temperature stability are presently being explored because they can be deposited at low temperatures over cracked niobium carbide coatings to seal paths that would normally contribute to hydrogen corrosion of fuel elements.

The value of using organometallic compounds to deposit metals and/or carbides at low temperatures has been demonstrated by the effective use of molybdenum deposited from the carbonyl. Other organometallic coating systems are yet to be explored. These systems, in addition to their value in filling cracks in NbC, offer a means of depositing a coating over materials that cannot be coated in a high temperature chloride environment.

In addition to continuing work on the deposition of coatings of various materials, an effort will be made to vigorously study some of the basic effects leading to the adherence or non-adherence of carbide coatings on fueled and non-fueled graphite substrates. Work on improving the adherence of NbC on NERVA fuel elements is currently in progress.

A program is also being established to hydrogen corrosion test the small size samples that are coated in the laboratory. This will provide a more immediate evaluation of the effects of process variations in coatings made in the small-scale equipment and establish meaningful comparisons between the variety of coatings that can be applied in the laboratory.

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