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Westinghouse Astronuclear Laboratory

COMPARISON OF CARBIDE COATINGS FOR GRAPHITE BASED FUEL ELEMENTS
(Title Unclassified)

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Introduction

It is well established that carbide coatings can protect graphite bodies at elevated temperatures from the corrosive effect of hydrogen. The effectiveness of any given carbide coating is a function both of the intrinsic properties of the carbide material itself and of its compatability with the system that is being protected.

In this report, several important factors which influence the selection of a coating material for use with graphite based fuel elements in a NERVA type reactor system are reviewed. The discussion will be limited to comparing the mono-carbides of zirconium, niobium, and tantalum, as they are considered to be the most desirable materials for high temperature nuclear reactor applications.

Protection of Graphite Matrix from Hydrogen Corrosion

The effectiveness of various integral carbide coating materials in protecting graphite based fueled matrixes from hydrogen attack is (for a constant coating thickness) a function of two inter-related properties: the carbide carbon activity which is a measure of the reactivity of the carbide with hydrogen and the carbon diffusivity in the carbides which effects the steady-state rate of carbon loss from the matrix.

Little data is available in the literature on the high temperature reaction of the refractory carbides with hydrogen. May and Hoeskstra⁽¹⁾ investigated various refractory compounds at elevated temperatures in a static hydrogen atmosphere. They claim that TaC and ZrC are stable up to 2400°C while NbC is stable above 2760°C. Their data, however, is difficult to interpret in terms of the hydrogen reaction since volatilization and/or decomposition phenomena could be occurring. GE-NMPO⁽²⁾ has reported that at high temperatures hydrogen preferentially removes combined carbon from the TaC lattice as evidenced by a decrease in lattice parameter. The author has heated stoichiometric 10 mil diameter, NbC filaments in a high purity flowing hydrogen atmosphere (2 liters/min at

1 atm). Within two hours at $2100^{\circ} \pm 100^{\circ}\text{C}$ and $2300^{\circ} \pm 100^{\circ}\text{C}$, the filaments at the hydrogen inlet end of the apparatus were completely reduced to the metal. A progressive increase in carbon content was noted in the filaments (as evidenced by the existence of Nb_2C and NbC_x) as a function of position from the hydrogen inlet end, culminating in a C/Nb ratio of > 0.9 at the hydrogen exit position. These data clearly show a specific high temperature hydrogen-NbC reaction but also indicate that a very low carbon concentration (which accumulates in the hydrogen stream) can effectively inhibit the decarburization of the carbide.

The equilibrium reaction between hydrogen and MeC_x ($x = \text{C/Me (metal)}$) can be considered to be similar to the hydrogen-graphite reaction. That is, the hydrogen reacts with the carbon in the carbide according to the following equations:

where

C' = the carbon in the MeC_x phase

a_c = carbon activity in MeC_x .

The equilibrium constants can be written as:

$$K_1 = \frac{(P_{\text{CH}_4})}{(P_{\text{H}_2})^2 a_c} \quad (3)$$

and

$$K_2 = \frac{(P_{\text{C}_2\text{H}_2})}{(P_{\text{H}_2}) a_c^2} \quad (4)$$

where

$(P_{CH_4}), (P_{H_2}), (P_{C_2H_2})$ = partial pressures over the MeC_x phase

K_1, K_2 = equilibrium constants for the $2H_2 + C_{(graphite)} = CH_4$ and $H_2 + 2C_{(graphite)} = C_2H_2$ reactions, respectively.

When $a_c = 1$, the equilibrium is identical to that of the C- H_2 reactions.

In a constant volume system, the hydrogen-MeC equilibria, as a function of hydrogen pressure, can be expressed by equations similar to those given by Bridges⁽³⁾.

That is:

$$K_1 = \frac{b}{(1 - 2b - d)^2 P_{H_2} a_c} \quad (5)$$

and

$$K_2 = \frac{d}{(1 - 2b - d)^2 a_c} \quad (6)$$

where

b = mole fraction CH_4 in equilibrium with MeC_x
 d = mole fraction C_2H_2 in equilibrium with MeC_x
 P_{H_2} = initial H_2 pressure
 a_c = carbon activity of MeC_x .

Thus, if a_c is known, it is possible to determine the mole fraction CH_4 and C_2H_2 in equilibrium with MeC_x . At present, there is insufficient data in the literature on the carbon activity of non-stoichiometric MeC. However, Kaufman et. al.⁽⁴⁾, using the

Schottky-Wagner model for non-stoichiometric compounds of the NaCl structure, have derived equations which can be applied to determine the activities in the Group IV and V carbide systems. The calculated carbon activity values for non-stoichiometric ZrC, NbC, and TaC are given in Table I.

Substituting the calculated activity values, and the equilibrium constants, K_1 and $K_2^{(5)}$ into equations (5) and (6), the condition for equilibrium in hydrogen- MeC_x systems (Me = Nb, Ta, Zr and $x = 0.7, 0.8, 0.9, 0.95$, and 0.98) under an initial hydrogen pressure of 40 atmospheres (NERVA condition) were obtained.

Figure 1 shows the total mole fraction of carbon $\left(\text{CH}_4 + 2(\text{C}_2\text{H}_2)\right)$ formed at equilibrium over NbC_x . The curve for the reaction with graphite is also presented for comparison purposes. It is important to note that very small concentrations of carbon can give rise to high NbC stoichiometries. For example, the reaction products over $\text{NbC}_{0.9}$ is from 2 to 3 orders of magnitude less than that over graphite, for the temperature range shown. To test the above model, values of the mole fraction carbon in the gas stream calculated on the basis of weight loss from hydrogen corrosion tested NERVA fuel elements and the measured stoichiometry values of the hot end channel coatings were compared to the values predicted by Figure 1. Very reasonable agreement was obtained (i. e., experimental $\text{C/Nb} = 0.83$, predicted $\text{C/Nb} = 0.85$) indicating that a near equilibrium condition is achieved between the carbon in the hydrogen stream and the gas interface side of the NbC coating.

Figure 2 is a comparison of the total mole fraction of carbon in the hydrogen stream necessary to maintain a given stoichiometry of NbC, TaC, and ZrC. It can be seen that at 2500°C a carbon mole fraction of 5×10^{-5} in the hydrogen stream would maintain $\text{NbC}_{0.75}$, $\text{TaC}_{0.85}$, and $\text{ZrC}_{0.95}$. Thus, on the basis of reactivity with hydrogen, ZrC is the most desirable carbide material.

Although non-reactivity between the carbide and hydrogen is necessary, it is not a sufficient criteria for the selection of a satisfactory protective coating. The additional requirement is that the carbon diffusivity in the carbide be low.

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TABLE I - Carbon Activity of the Non-stoichiometric Carbides -
ZrC, TaC, and NbC

<u>ZrC</u>	<u>2000°K</u>	<u>2200°</u>	<u>2400°</u>	<u>2600°</u>	<u>2800°</u>	<u>3000°</u>
ZrC _{0.7}	6.81×10^{-5}	1.88×10^{-4}	4.36×10^{-4}	8.89×10^{-4}	1.64×10^{-3}	2.79×10^{-3}
ZrC _{0.8}	1.17×10^{-4}	3.21×10^{-4}	7.46×10^{-4}	1.52×10^{-3}	2.81×10^{-3}	4.78×10^{-3}
ZrC _{0.9}	2.63×10^{-4}	7.25×10^{-4}	1.68×10^{-3}	3.44×10^{-3}	6.33×10^{-3}	1.08×10^{-2}
ZrC _{0.95}	5.56×10^{-4}	1.53×10^{-3}	3.56×10^{-3}	7.25×10^{-3}	1.34×10^{-2}	2.28×10^{-2}
ZrC _{0.98}	1.45×10^{-3}	3.98×10^{-3}	9.25×10^{-3}	1.89×10^{-2}	3.48×10^{-2}	5.91×10^{-2}
<u>TaC</u>						
TaC _{0.7}	2.80×10^{-4}	6.78×10^{-4}	1.42×10^{-3}	2.64×10^{-3}	4.51×10^{-3}	7.16×10^{-3}
TaC _{0.8}	4.80×10^{-4}	1.16×10^{-3}	2.43×10^{-3}	4.52×10^{-3}	7.71×10^{-3}	1.22×10^{-2}
TaC _{0.9}	1.08×10^{-3}	2.62×10^{-3}	5.47×10^{-3}	1.02×10^{-2}	1.74×10^{-2}	2.76×10^{-2}
TaC _{0.95}	2.29×10^{-3}	5.53×10^{-3}	1.15×10^{-2}	2.15×10^{-2}	3.67×10^{-2}	5.83×10^{-2}
TaC _{0.98}	5.94×10^{-3}	1.44×10^{-2}	3.01×10^{-2}	5.60×10^{-2}	9.55×10^{-2}	1.52×10^{-1}
<u>NbC</u>						
NbC _{0.7}	8.73×10^{-4}	1.90×10^{-3}	3.65×10^{-3}	6.33×10^{-3}	1.01×10^{-2}	1.53×10^{-2}
NbC _{0.8}	1.49×10^{-3}	3.26×10^{-3}	6.25×10^{-3}	1.08×10^{-2}	1.74×10^{-2}	2.61×10^{-2}
NbC _{0.9}	3.36×10^{-3}	7.35×10^{-3}	1.41×10^{-2}	2.44×10^{-2}	3.91×10^{-2}	5.88×10^{-2}
NbC _{0.95}	7.11×10^{-3}	1.55×10^{-2}	2.98×10^{-2}	5.17×10^{-2}	8.26×10^{-2}	1.24×10^{-1}
NbC _{0.98}	1.85×10^{-2}	4.04×10^{-2}	7.75×10^{-2}	1.34×10^{-1}	2.15×10^{-1}	3.24×10^{-1}

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FIGURE 1 - Total Mole Fraction Carbon in H_2 Stream (40 atm)
 In Equilibrium with NbC_x vs. Temperature

FIGURE 2 - Total Mole Fraction Carbon in H₂ Stream (40 atm)
 In Equilibrium with NbC_x, TaC_x, and ZrC_x vs. Temperature

Based on data from hydrogen corrosion tested NbC coated NERVA fuel, it is known that the coating (hot end region) at the gas interface is decarburized while the coating at the graphite interface is nearly stoichiometric ($C/Nb = 0.92-0.95$). The concentration gradient remains essentially constant with time for any given hydrogen corrosion test conditions. To maintain this steady-state condition, carbon is transported from the graphite matrix, through the coating and into the hydrogen gas stream. The carbon, as shown by Brizes and Cadoff⁽⁶⁾, is supplied from the NbC-graphite interface of the matrix, thus giving rise to the phenomena of undercutting. It is recognized that undercutting is incompatible with the aim of long time NERVA operation, as loss of coating and exposure of the matrix graphite can result.

The steady-state rate of carbon loss from the matrix (assuming the carbon diffusivity in the carbide is independent of concentration) may be expressed as:

$$J = -D_C \Delta C / \Delta x$$

where

$$J = \text{carbon flux through the coating}$$

$$\Delta C = \text{concentration gradient across the coating}$$

$$\Delta x = \text{coating thickness}$$

$$D_C = \text{carbon diffusivity in the carbide.}$$

It is clear, therefore, that for any given thickness of coating, the carbide with the minimum product of $D_C \times \Delta C$ will offer the greatest protection. The carbon diffusivities in the carbides have been determined at WANL^(6, 7, 8) and are summarized below:

$$D_{TaC}^C = 1.8 \exp -(90,000/RT)$$

$$D_{NbC}^C = 1.0 \exp -(76,000/RT)$$

$$D_{ZrC}^C = 34 \exp -(96,500/RT)$$

Using the above data and that from Figure 2, it is possible to calculate the steady-state carbon loss from a carbide coated graphite element in a hydrogen atmosphere. Table II summarizes the carbon flux, at several temperatures, across a 1 mil coating of NbC, TaC, and ZrC, assuming a carbon concentration of 5×10^{-5} mole fraction in the hydrogen stream. Table II demonstrates that the hot end corrosion losses in NERVA fuel elements could be greatly reduced by employing TaC or ZrC coatings in preference to NbC. Thus, if all other factors are equal, a TaC or ZrC coated fuel element could conceivably increase hot end corrosion performance by a factor of ten.

Coefficient of Thermal Expansion

In the preceding section, a comparison was made between several carbide coating materials as to their ability to protect the graphite from hydrogen attack. The discussion was based on the premise that the coating was integral and crackfree. In actual practice, however, the large dissimilarity in coefficients of thermal expansion between the graphite matrix and the carbide can, under certain conditions, result in a defected coating.

There is considerable variation between reported values of the coefficient of thermal expansion of the carbides. It appears, however, that as a first approximation, the CTE of ZrC, NbC, and TaC are nearly equivalent and range between $6-7 \times 10^{-6}/^{\circ}\text{C}$. This value is considerably higher than that for most graphites ($2-4 \times 10^{-6}/^{\circ}\text{C}$).

Carbide coatings are generally applied to the graphite substrate at temperatures in excess of 1600°C (high coating temperatures are necessary to obtain tolerable carburization kinetics). When the coated bodies are cooled to room temperature, sufficiently high tensile stresses are generated in the carbide, to produce cracks in the brittle coating. The thermal cracks do not heal at temperatures below those during the coating operation, thus exposing the matrix graphite to hydrogen attack. That this is a real problem is evidenced by the so called "corrosion band" (region of severe localized matrix corrosion) which occurs in the mid-region of hydrogen tested NERVA fuel elements.

TABLE II
Steady-State Carbon Flux through Carbide Coatings*

	Carbon Flux (gC/cm ² sec)		
	2200°C	2400°C	2600°C
NbC	1.2×10^{-5}	4.9×10^{-5}	1.7×10^{-4}
ZrC	8.2×10^{-7}	4.9×10^{-6}	2.9×10^{-5}
TaC	5.4×10^{-7}	3.0×10^{-6}	1.4×10^{-5}

* Based on 1 mil thick carbide coating assuming stoichiometric composition at carbide-graphite interface and the equilibrium carbide composition with hydrogen (40 atm + 5×10^{-5} mole fraction carbon) at the carbide-gas interface.

Several alternative ways have been suggested to solve this problem (i.e., high expansion graphites, varying coating temperature profile, etc.), but it is clear that because of the similarity of CTE, there is no basis for singling out any particular carbide as being more desirable than the others.

Melting Point

A high C-carbide eutectic temperature is an important pre-requisite for selection of a carbide coating material for NERVA applications. The approximate eutectic temperatures for some carbide systems are given below:⁽⁹⁾

$$\text{ZrC-C} = 2890^{\circ}\text{C}$$

$$\text{NbC-C} = 3240^{\circ}\text{C}$$

$$\text{TaC-C} = 3450^{\circ}\text{C}$$

It would seem, therefore, that ZrC would be the least promising material of the above group.

The melting data, however, does not necessarily offer a complete picture on the stability of the carbides at high temperatures. The important consideration, at least with respect to current NERVA fuel, is the compatibility of uranium with the coating. At high temperatures ($>2600^{\circ}\text{C}$) and under a temperature gradient (between matrix and coolant channel), uranium from the PyC coated UC_2 fuel particles migrates to the coating-graphite interface. As uranium builds up at this interface, melting of uranium carbide occurs at a temperatures in the vicinity of 2400°C (UC_2 -C eutectic), resulting in undermining and failure of the coating. The accumulation of uranium is, of course, a kinetic consideration dependent on the rate of uranium delivery to the interface and should, therefore, be independent of choice of coating material.* If in the future, a fuel is developed which ties up

* Preliminary experiments on NbC coated NERVA fuel indicate that fuel lifetime is <10 minutes at temperatures $>2900^{\circ}\text{C}$. Failure results from melting of the coating due to interaction with UC_2 from the matrix and consequent exposure of the graphite matrix to hydrogen attack.

the uranium (i. e., migration resistant fuel particles, UC-MeC solid solution, etc.), the temperature capability will be improved and the eutectic melting point of the carbide coating materials would then be a major criterion for selection.

Neutron Cross-Section

For NERVA operation, it is desirable that the coating have a low thermal neutron absorption cross section. A comparison of the carbides indicate that the cross section of

$$\text{ZrC}(0.18) < \text{NbC}(1.1) < \text{TaC}(21.0)$$

Because of its high cross section, TaC is unsuitable for use as a coating on NERVA fuel elements. Of course, other reactor designs may not necessarily impose this limitation, thus permitting a wider latitude in material choice.

Density

Density can be an important consideration in choosing between alternate coating materials. Obviously, for a given volume of carbide per fuel element (thickness), the lowest density material is more desirable from the standpoint of lower overall weight. On this basis, the most preferable carbide is ZrC (6.7 g/cm^3) followed by NbC (7.8 g/cm^3) and TaC (14.5 g/cm^3).

However, a more important factor is the carbon density (product of carbide density and carbon weight fraction) in a given carbide material. The lower the carbon density, the less carbon is required to carburize the coating. Since in the present NERVA coating process*, all the carbon comes from the surface of the graphite matrix⁽⁶⁾, a reduction in the carbon requirement would be advantageous with respect to adherence. The ratio of the carbon densities for ZrC, NbC, and TaC are 1.00:1.15:1.16, respectively. Thus, ZrC requires about 15-16 per cent less matrix carbon to produce a given thickness coating than either NbC or TaC and should therefore be the most adherent material of the group.

* At present, WANL does not use methane in the vapor deposition process.

Metal Diffusivity in the Carbides

The diffusivity of the metal atoms in the carbides can influence selection of a particular carbide in the following ways:

(1) A high metal diffusivity is important with respect to coating adherence. An adherent bond requires that the carbide coating be in intimate contact with the graphite matrix. Since the carbon that is supplied to the coating comes nearly entirely from the graphite substrate surface⁽⁶⁾, the graphite-coating interface must recede with the subsequent formation of a gap. However, if the metal diffusivity is sufficiently large, the metal atoms can diffuse to the MeC-graphite interface where they react with the carbon. The coating at this interface can then grow inwards toward the graphite matrix, tending to reduce the gap size and thereby producing a more adherent bond.

(2) A low metal diffusivity is desirable to minimize interbonding of contacting carbide surfaces. In current NERVA design, the carbide coated hot end faces of the fuel elements are in contact with the carbide coated support blocks. Under operational conditions (high temperature and pressure), the coatings can bond or weld to each other. Upon cooldown, this can result in the removal or stripping of the coatings from the graphite matrix thereby restricting restart capabilities.

In the absence of any meaningful data, we can only estimate the relative metal diffusivities in the carbides. It is expected that the diffusivities would be related to the metal vapor pressure over the carbides. That is, the metal atom diffusion coefficient in $ZrC > NbC > TaC$.

Discussion

It is now possible, based on the discussion of the properties of TaC, ZrC, and NbC in this report, to evaluate materials which best meet the requirements that make for an effective coating for fueled graphite elements. From the standpoint of the important criteria of protection of the matrix from hydrogen corrosion and the eutectic melting point, TaC is the most promising material. However, its large neutron cross section makes it unsuitable for current NERVA use. ZrC would be an effective coating material in that it is

highly resistant to hydrogen attack, has a low cross section and should be more adherent to the graphite substrate than the other carbides. The major liability of ZrC, however, lies in its low eutectic melting point ($2890^{\circ} \pm 50^{\circ}\text{C}$). Although this temperature may be adequate for current NERVA applications, it should be noted that the employment of ZrC coatings would place unnecessarily low temperature limits on the future development of graphite fuel elements. NbC coatings offer a reasonable compromise with respect to the properties of the three carbides under consideration. NbC does not have the serious liabilities of high neutron cross section or low eutectic melting point as does TaC or ZrC, and although it may be somewhat less protective to the graphite substrate, its effectiveness in inhibiting high temperature hydrogen corrosion was clearly demonstrated by the success of KIWI-B4E, NRX-A2, and NRX-A3 reactor tests.

From the above comparison of TaC, ZrC, and NbC it can be seen that they all have deficiencies which make them somewhat less than ideal as coating materials for severe NERVA applications. An approach which can conceivably overcome the limitations of the individual carbides and result in a coating material with optimum properties may involve the use of a mixed alloy carbide system. Little information is available on these systems other than that they exhibit complete miscibility. However, it might therefore be expected that the properties of such alloy carbide systems would be intermediate to the parent carbides. Because of nuclear considerations (high neutron cross section of TaC), a mixed ZrC-NbC alloy would be most desirable for NERVA applications. Hopefully, a composition could be obtained which would retain the protective properties of ZrC without unduly sacrificing the high carbon-eutectic temperature of NbC. It is clear, however, that further intensive investigations are required into the properties of the mixed carbides to determine if they are of sufficient interest to justify the difficult development of methods to coat them on graphite substrates.

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