Some Observations on Uranium Carbide Alloy/Tungsten Compatibility

W. M. Phillips
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Details of illustrations in this document may be better studied on microfiche

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

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PREFACE

The work described in this report was performed by the Propulsion Division of the Jet Propulsion Laboratory.
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Chemical compatibility tests between both pure tungsten and thoriaed tungsten were run at 1800°C for up to 3300 hours with uranium carbide alloys. Alloijing with zirconium carbide appeared to widen the homogeneity range of uranium carbide, making additional carbon available for reaction with the tungsten. Reaction layers were formed both by vapor phase reaction and by physical contact, producing either or both UWC$_2$ and W$_2$C dependent upon the phases present in the starting fuel alloy. Formation of UWC$_2$ results in slow growth of the reaction layer with time, while W$_2$C reaction layers grow rapidly allowing equilibrium to be reached in less than 2500 hours at 1800°C. The presence of a thermal gradient had no effect on the reactions observed nor did the presence of thoria in the tungsten clad.
INTRODUCTION

Both uranium dioxide and uranium carbide alloys have been investigated as possible nuclear fuels for in-core thermionics applications in the U. S. The utilization of uranium carbide as a nuclear fuel in thermionic converters is complicated by the narrow range of homogeneity of UC at room temperature, less than 0.05 wt.% carbon. Departure from stoichiometry has been shown to have an adverse effect on behavior of this fuel. Excess carbon results in carburization of the clad material [1-3], while experimental results have indicated that excess uranium results in poor irradiation swelling behavior [4]. Gross interaction effects of uranium carbide alloys with clad materials were evaluated in early compatibility work [5]. Zirconium carbide alloy additions produced a reduction of weight loss by vaporization in unclad carbides and was retained as an alloy addition in clad fuels since the reduced vapor pressure is indicative of reduced surface activity.
Bare work function determined by vacuum emission of tungsten clad fuels has been used as a criteria for long term fuel clad thermionic stability [6-10]. The emphasis on electron emission properties arose from the fact that the presence of a fraction of a monolayer of absorbed impurity atoms affects electron emission characteristics of the tungsten surface and, consequently, thermionic performance. A flux of either uranium or carbon through tungsten has been observed for uranium carbide fuels [11]. Typical flux data are shown in Fig. 1, with its effect on the bare work function of tungsten clad. Even in those cases where the work function is constant, an effect on thermionic performance can be produced by vaporization of the diffusing species from the emitter and, subsequently, its condensation on the collector. In those cases where an effect on emitter work function is produced, the diffusing species (uranium) is arriving at the emitting surface more rapidly than it is evaporating.

Electron emission studies indicated that excess carbon is needed in uranium/zirconium carbide alloys to minimize uranium diffusion through tungsten cladding and, thusly, to produce a stable tungsten clad (emitter) work function. The amount of excess carbon needed was observed to decrease as the zirconium carbide content increased [11]. Among the possible causes of this behavior are: (1) the improved oxidation resistance imparted to the alloy by increased amounts of zirconium carbide, or (2) the wide range of ZrC homogeneity which exists in the zirconium/carbon system. This wide homogeneity range allows the ZrC to act as a carbon source, which effectively lowers the uranium activity in the fuel system.

Recent tests on thoriated tungsten indicate a high vacuum work function for this material [12]. Thoriated tungsten as an emitter material with UO₂ fuel produces good thermionic performance at a low optimum cesium pressure, indicating oxygen enhanced performance [13]. Thermodynamic calculations indicate the feasibility of using uranium carbide fuel with a thoriated tungsten clad. The stability of ThO results in the prediction that an equilibrium pressure of CO will build up, dependent upon the activity of carbon in the uranium carbide fuel. This indicates the possibility of using thoriated tungsten as a diffusion barrier for carbon. In addition, the cubic structure of ThO could act as a stabilizer for UO, resulting in diffusion barrier behavior for uranium metal also.

Previously reported work [14] investigated the effects of zirconium carbide additions to uranium carbide/tungsten alloys on chemical compatibility of these fuel alloys with pure tungsten.

The work presented in this paper was undertaken: (1) to determine the effects of fuel composition variations, particularly carbon content, on tungsten/uranium carbide alloy compatibility, (2) to evaluate effects of thermal gradient on carbide fuel stability, and (3) to experimentally verify the thermodynamic calculations for the thoriated tungsten/uranium carbide alloy system.

TEST MATERIALS AND METHODS

Two types of tungsten were used as clad materials in the experiments, chemically vapor deposited tungsten from the fluoride and powder metallurgy tungsten/2% thoria. The uranium carbide fuel alloys used in the tests were also prepared by two process, arc casting and cold pressing followed by sintering. All fuel materials were prepared from the pure elements. The arc cast alloys were hot-drop cast into a graphite mold. The castings were stress relieved in vacuum two hours at 1600°C. The powder metallurgy fuel was pressed
from ground arc cast material and sintered at 2200°C. Composition of the fuel alloys is shown in Fig. 2.

The cylindrical fuel slugs were ground to provide an interference fit of approximately 0.05 mm (0.002 in.) within a tubular tungsten clad at test temperature. The fuel was sealed in the tungsten tubes by electron beam welding. Testing was done in a vac-ion pumped furnace with a tungsten hot zone in the 10^-8 to 10^-9 torr range.

Pretest metallographic examination of the arc cast fuel alloys, Fig. 3, indicated the presence of free tungsten metal, while the excess carbon was present as UC. In addition, UWC was present in the matrix of UC or (U,Zr)C. Existing phase diagram data [15], Fig. 4, indicate that the equilibrium phases should be UC or (U,Zr)C with the excess carbon present as UWC and U$_2$C$_3$. Thus, the two-hour anneal at 1600°C was insufficient to eliminate the metastable structure produced by the relatively rapid cooling cycle from the arc casting temperature. The binary phase diagram for the uranium/carbon system [16], indicates that U$_2$C$_3$ is stable only below 1880°C, thus a longer anneal at a temperature below 1880°C is needed to produce an equilibrium structure.

RESULTS AND DISCUSSION

Isothermal Compatibility Tests

The carbon levels present in the fuel alloys were sufficient to place the composition in the UC, UWC$_2$, U$_2$C$_3$ three-phase region of the phase diagram. Thus, it can be predicted that the U$_2$C$_3$ would react with the tungsten clad to produce UWC while eliminating the U$_2$C$_3$ from the fuel alloy.

If all the excess carbon did react in this manner, a reaction layer of UWC$_2$ would be predicted to form on the tungsten clad to a thickness of 0.025 mm (0.001 in.). Reaction layer thickness observed with pure tungsten varied from 0.01 mm to 0.025 mm after 1000 hours at 1800°C and from 0.025 mm to 0.05 mm after 2500 hours at 1800°C. A typical UWC$_2$ reaction layer 0.04 mm thick is shown in Fig. 5. No obvious correlation was observed between layer thickness and test time. So the variation in layer thickness appears to be attributable to differences in carbon in the test samples. Thus, 1000 hours at 1800°C appears sufficient to establish equilibrium in the U-W-C system.

Using this 1000-hour time at 1800°C to reach equilibrium and the following approximation:

\[
\frac{x}{D \tau} = 1, \quad \text{where } x = \text{diffusion distance} = 6.4 \text{ mm} \\
t = \text{time} = 1000 \text{ h} = 3.6 \times 10^6 \text{ sec}
\]

the diffusion coefficient (D) is calculated to be $1 \times 10^{-7}$ cm$^2$/sec. This coefficient is reasonable for interstitial diffusion of carbon in UC at 1800°C.

A material balance calculation based on the reaction layer thickness indicates that very limited, if any, substoichiometry exists in the UC alloy in contact with tungsten after 2500 hours at 1800°C. The microstructure of a typical UC/W fuel alloy after test is shown in Fig. 6. The structure appears to be two phase, UWC$_2$ in a matrix of stoichiometric UC conforming to the expected behavior of the system.

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Isothermal compatibility tests of the UC/W fuel alloy with thoriated tungsten resulted in very similar thicknesses of UWC$_2$ reaction layers as the test of UC/W with pure tungsten. A typical UWC$_2$ reaction layer with thoriated tungsten is shown in Fig. 7.

Greater amounts of excess carbon were present in the initial (U,Zr)C/W alloys than in the UC/W alloys. These arc cast alloys also had free tungsten, Fig. 3, indicating the structure to be metastable.

The amount of excess carbon in these (U,Zr)C/W alloys can be calculated to produce a UWC$_2$ reaction layer 0.41 mm (0.010 in.) thick if the U$_2$C$_3$ is reduced to UC and the zirconium is present as ZrC. Several of the samples tested displayed reaction layers of UWC$_2$ approximately 0.01 mm (0.0005 in.) thick at the fuel/clad contact area, Fig. 8. This is considerably less than the thickness which could be formed based on available carbon and approximately equal or slightly less than that formed with the UC/W alloys. Thus, some reduction in surface activity is apparently produced by the alloy addition ZrC. The presence of excess carbon in the fuel alloy after test also indicates that the UWC$_2$ reaction layer is a diffusion barrier for carbon and uranium. This reaction layer can thus be expected to grow in thickness with increased time and temperature as long as carbon is available in the fuel for reaction. In addition to the UWC$_2$ type reaction layer, microprobe analysis, etching characteristics, and hardness measurements identified W$_2$C reaction layers in several samples. The rate of formation of W$_2$C was much more rapid than UWC$_2$, allowing equilibrium to be reached within the 2500-hour test period. Measurements of the W$_2$C reaction layer thickness coupled with literature data on the solubility of tungsten in UC allows calculation of a material balance within the test sample. This results in the conclusion that the (U,Zr)C/W fuel alloy has a carbon-to-metal atom ratio C/(U + Zr) of 0.95.

Substoichiometry of this type has been produced in the (U,Zr)C alloy in contact with uranium and zirconium [17]. The degree of substoichiometry was considerably greater (carbon-to-metal atom ratio was 0.9) than that observed above.

Metallographic examination of the fuel after test, Fig. 9, indicated the presence of a finely divided third phase in addition to the (U,Zr)C matrix and UWC$_2$. It can be postulated that this third phase is uranium/tungsten/zirconium metal precipitated during cooling because of the widened homogeneity range of the carbide phase at elevated temperatures.

In addition to the formation of UWC$_2$ and W$_2$C at the contact area between the fuel and clad, both types of reaction layers were found in areas not directly in contact with the fuel. The reaction layer of W$_2$C, Fig. 10, is typical of those produced by vapor phase reaction.

To verify this vapor phase reaction mechanism, a capsule was run vented to the vacuum chamber (10$^{-8}$ torr). This sample did not display the typical reaction layers after 2500 hours at 1800°C, Fig. 11. The reactions produced in this sample were: (1) solution of tungsten into the fuel, and (2) production of a second phase containing uranium in the clad to a depth of 0.1 mm (0.004 in.). Microprobe analysis identified uranium in this second phase which did not appear to be associated with the thoria particles. Size and distribution of the parti-
cles prevented definite identification of the phase.

The fuel after test also displayed a composition variation from areas adjacent to the clad to areas near the centerline of the fuel, Fig. 12. The areas of the fuel near the clad appeared to be a (U,Zr)C matrix containing UWC$_2$. The core of the fuel appeared to be a (U,Zr)C matrix with UWC$_2$ and UC$_3$ or U$_2$C$_3$ phases. Thus, the vacuum exposure appeared to inhibit reduction of the higher-carbide by reaction with the tungsten clad.

The use of thoriated tungsten clad did not result in any observable change in the type of reaction layer produced, as compared with pure tungsten. The UWC$_2$ and W$_2$C phases observed were produced in the contact areas between the fuel and clad as well as by vapor phase reactions.

**Thermal Gradient Tests**

Powder metallurgy fuel (UC$_{1.04}$/W) was tested under thermal gradient conditions. The capsule after test is shown in Fig. 13. This sample was heated by electron bombardment of a small tungsten crucible at the centerline. Nominal capsule size was 25 mm diameter by 75 mm length. A thermal input power of 400 watts was maintained for 3300 hours with the outer tungsten clad temperature of 1650°C.

A UWC$_2$ reaction layer less than 0.01 mm thick was produced at the fuel/clad contact area. In addition, a vapor phase reaction layer approximately 0.1 mm (0.004 in.) thick was formed on the top end cap (Fig. 14). The thickness of this layer varied as a function of temperature. The thickest layer was at the outside diameter of the end cap, a calculated temperature of 1725°C. The thickness decreased as temperature increased, becoming zero at the electron beam heated centerline crucible, approximately 1775°C. No reaction layer was present on the centerline tungsten crucible although evidence of vaporization loss of tungsten was present, Fig. 15.

**SUMMARY AND CONCLUSIONS**

Reaction between tungsten clad and hyperstoichiometric uranium carbide follows either of two diffusion paths, one producing UWC$_2$ and the other producing W$_2$C. The diffusion rate of carbon is rapid in W$_2$C and as a consequence equilibrium is reached within 2500 hours at 1800°C when this reaction occurs. The UWC$_2$ reaction layer acts as a diffusion barrier for carbon and, as a consequence, layer growth is slowed to the order of 0.025 mm in 2500 hours.

The presence of a thermal gradient in the fuel had no observable effect on chemical compatibility of the fuel with tungsten clad.

Zirconium carbide additions to uranium carbide appear to widen the homogeneity range of the monocarbide, resulting in additional carbon being available for reaction with tungsten cladding. At the same carbon level, the tungsten buffered UC, without ZrC, is more compatible with tungsten clad since there is less carbon available for reaction. Similar behavior may be achievable with the (U,Zr)C/W alloy at lower carbon contents but at the risk of producing free uranium because of thermal cycling.

For thermionic applications, because of the high temperatures and associated rapid reaction rates, the fuel should contain excess tungsten to combine with the additional carbon which becomes available from the fuel as the homogeneity range narrows.
of the increases with temperature. The existence of vapor phase reactions at thermionic temperatures also indicates the need for additional tungsten in the fuel to decrease carbon activity.

Thus, compositional control of the fuel must be maintained in the three phase region UC or (U,Zr)C + UWC$_2$ + W (reduced carbon contents increased tungsten content, or both) to minimize both uranium and carbon activity, diffusion, and associated thermionic performance degradation. The above fuel may produce acceptable long term levels of thermionic performance stability with pure tungsten clad. The use of thoriated tungsten clad could provide a complete diffusion barrier as well as enhanced thermionic performance through oxygen additive effects. Additional testing of the proposed carbide fuel with both tungsten and thoriated tungsten emitters in thermionic converters is needed to verify the above tentative conclusions.

REFERENCES


<table>
<thead>
<tr>
<th>Cladding Thickness (mil)</th>
<th>Temperature (deg K)</th>
<th>Time (h)</th>
<th>$\phi$ of Tungsten Cladding</th>
<th>Average Uranium Flux g/(cm$^2$ h)</th>
<th>Average Carbon Flux g/(cm$^2$ h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 (0.5 mm)</td>
<td>2223</td>
<td>820</td>
<td>Stayed at 4.7 to 4.8 eV for 770 h, then decreased rapidly to 4.2 eV</td>
<td>$2.5 \times 10^{-7}$</td>
<td>-</td>
</tr>
<tr>
<td>20 (0.5 mm)</td>
<td>2173</td>
<td>1000</td>
<td>Stable at 4.8 eV</td>
<td>$1.4 \times 10^{-7}$</td>
<td>-</td>
</tr>
<tr>
<td>40 (1.0 mm)</td>
<td>2073</td>
<td>8600</td>
<td>Stable at 4.75 eV</td>
<td>$1.1 \times 10^{-8a}$</td>
<td>$1.9 \times 10^{-9a}$</td>
</tr>
</tbody>
</table>

$^a$Determined at 7070 h.


Fig. 1 Summary of some diffusion-emission results and fuel-component transport rates through fluoride vapor deposited tungsten cladding from (U$_{0.9}$Zr$_{0.1}$)$_{1.02}$
<table>
<thead>
<tr>
<th></th>
<th>A/O U</th>
<th>A/O W</th>
<th>A/O C</th>
<th>A/O Zr</th>
<th>C/U Ratio*</th>
</tr>
</thead>
<tbody>
<tr>
<td>UC/W Arc Cast</td>
<td>45.05</td>
<td>4.85</td>
<td>50.10</td>
<td>—</td>
<td>1.02</td>
</tr>
<tr>
<td>(U,Zr)C Arc Cast</td>
<td>38.2</td>
<td>4.85</td>
<td>51.35</td>
<td>4.98</td>
<td>1.12</td>
</tr>
<tr>
<td>UC/W Powder Metallurgy</td>
<td>47.08</td>
<td>2.64</td>
<td>51.28</td>
<td></td>
<td>1.05</td>
</tr>
</tbody>
</table>

*Assuming 0.85 A/O W in solution, UC$_2$ and ZrC$_{0.0}$

Fig. 2  Chemical analysis of fuel alloys
(a) UC/W alloy, arc cast, annealed 2 h at 1600°C
Etch: $90\text{H}_2\text{O}_2-10\text{H}_2\text{SO}_4$

(b) (U,Zr)C/W alloy, arc cast, annealed 2 h at 1600°C
Etch: $90\text{H}_2\text{O}_2-10\text{H}_2\text{SO}_4$

(c) UC/W alloy, arc cast, annealed 2 h at 1600°C
Etch: Modified Murakamis

(d) (U,Zr)C/W alloy, arc cast, annealed 2 h at 1600°C
Etch: Modified Murakamis

Fig. 3 Microstructures of starting fuel alloys
Fig. 4  Uranium, carbon, tungsten phase diagram isotherm at 1500°C

Fig. 5  Typical UWC₂ reaction layer formed on Fluoride Tungsten by UC/W alloy reaction

Fig. 6  Typical UC/W fuel alloy after test, UC matrix with UWC₂ precipitate

Fig. 7  Typical UWC₂ reaction layer formed on thoriated tungsten by UC/W reaction at 1800°C after 2500 h
Fig. 8 Typical UWC₂ reaction layer formed on Fluoride Tungsten by (U,Zr)C/W alloy reaction

Fig. 9 Typical (U,Zr)C/W fuel alloy after test, (U,Zr)C matrix with UWC₂ precipitate and possible U/W third phase

Fig. 10 Typical W₂C reaction layer formed on thoriated tungsten by vapor phase reaction with (U,Zr)C after 2500 h at 1800°C

Fig. 11 Typical interaction between thoriated tungsten and UC/W under vacuum conditions after 2500 h at 1800°C
Fig. 12 UC/W fuel after 2500 h at 1800°C in thoriated tungsten clad, vented to vacuum

Fig. 13 Fluoride deposited tungsten thermal gradient test capsule with UC/W after 3300 h at 1800°C
Fig. 14 Top end cap area of fluoride tungsten thermal gradient capsule containing UC+w after 2500 h at 1800°C

Fig. 15 Centerline crucible from thermal gradient test capsule