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IDENTIFICATION OF THE MODIFIER

IN

SNAP FUEL

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AEC Research and Development Report

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IDENTIFICATION OF THE MODIFIER

IN

SNAP FUEL

(Title Unclassified)

By:
H. TAKETANI
L. SILVERMAN
W.L. KORST

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ABSTRACT

Stoichiometric zirconium carbide powder is added to SNAP fuel during the melting of the zirconium-uranium alloy, in order to prevent cracking of the fuel element during the subsequent hydriding process. During melting, zirconium carbide reacts with zirconium to form substoichiometric zirconium carbide. This reaction probably continues while the alloy is maintained at high temperature during the hydriding process. The major portion of the substoichiometric zirconium carbide, ZrC_{1-y} , reacts with hydrogen during the hydriding process to form a ternary compound with the approximate stoichiometry of $ZrC \cdot ZrH_x$, where x can approach 2.

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I. INTRODUCTION

Zirconium carbide powder (-325 mesh) is added to SNAP fuels during the arc-melting operation. This is done in order to prevent cracking⁽¹⁾ during the subsequent hydriding process. The carbide has limited solubility in the zirconium-uranium system, and consequently acts as a grain refiner during hydriding.

Measurements⁽²⁻⁴⁾ made on these fuel materials indicated that the equilibrium dissociation pressure was greater than would be predicted if the carbon were associated with zirconium on a 1:1 atomic basis. In addition, analytical chemical separation and quantitative metallographic examination⁽⁵⁾ of the carbide precipitate revealed an anomalous behavior, insofar as the carbon content was concerned. This report attempts to interpret these results by exploring the possible existence of a hydrided compound, $ZrC \cdot ZrH_x$, as an explanation.

The problem was examined, using three techniques:

- a) Chemical reagents were employed to separate carbide precipitates selectively from the ZrH_x matrix.
- b) X-ray diffraction patterns were employed to identify the phases present.
- c) Metallographic sections were examined to disclose the morphology and structure of the precipitate phases.

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II. EXPERIMENTAL PROCEDURES

A. CHEMICAL ANALYSIS

Carefully weighed U-Zr hydride fuel element samples, of about 15 mg, were used. Each sample was placed in a 250-ml Erlenmeyer flask, and 50 ml of acetonitrile was added. The flask was fitted with a condenser and set in an ice bath. After ice temperature was attained, 10 ml of liquid bromine, in small portions, were poured into the condenser, and the mixture was allowed to react overnight (16-hr minimum). The liquid was filtered successively through 1.5-, 0.5-, and 0.05- μ polyethylene filters in a Millipore apparatus, and the residue was washed with an acetonitrile-bromine mixture. The filter and residue were dried in an oven at 90 to 105°C for 2 to 3 min, cooled, and weighed. X-ray diffraction studies were then conducted on the powdered residue.

As an additional test with some of the first samples treated in the program, the powder residue was transferred to a small crucible and carefully heated. No colored vapors or fumes formed, which is indicative of the absence of brominated organic polymers.

B. X-RAY DIFFRACTION

X-ray diffraction patterns were obtained, using Ni-filtered Cu radiation (λ for Cu $K\alpha$ = 1.5418 Å, λ for Cu $K\alpha_1$ = 1.54051 Å). Diffractometer patterns were prepared, using a Norelco diffractometer. X-ray powder photographs were made in a 114.6-mm diameter Straumanis-type camera, with the powdered samples contained in thin-walled glass capillaries. Corrections were made for film shrinkage. In some cases, lattice constants were calculated according to a least-squares method described by Mueller, Heaton, and Miller,⁽⁶⁾ using the Nelson-Riley correction function. A program for this calculation is on file at Atomics International, and is described in a report by Korst, Tannenbaum, and Miller.⁽⁷⁾

C. METALLOGRAPHY

The metallographic procedure for preparing hydride fuel samples for optical and electron microscopy studies has been described elsewhere.⁽⁵⁾ The only significant departure in the replication procedure was the use of Faxfilm

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(cellulose acetate) to remove the fine debris. Faxfilm was applied and stripped off twice before a direct replica was made.

In an attempt to concentrate the ternary compound for X-ray diffraction purposes, several techniques were attempted. These were: (1) matrix masking, (2) Ultrasonic Jack Hammer, and (3) extraction replication.

Matrix masking consists of the application of a coating of epoxy resin over the ternary compound in situ (i. e., when the ternary compound is present as a second-phase precipitate within the hydride matrix); this is followed by plating the matrix with a 0.5-mil layer of nickel, and then dissolving the epoxy resin. In this manner, the matrix is masked, leaving the precipitates exposed. An X-ray diffractometer pattern would then only show peaks of the ternary compound and of nickel, making it easy to decide whether the ternary were present.

The Ultrasonic Jack Hammer is a mechanical method of removing inclusions from a matrix. It consists of a pointed stylus oscillating at ultrasonic frequencies. A miniature "vacuum cleaner" system was used, in place of the micro-manipulator, for gathering up the inclusion debris after it was dislodged by the "jack hammer."

A standard extraction replication technique was used. This consisted of applying Faxfilm to the surface of the sample, and subsequently under-etching the matrix away from the Faxfilm. Hopefully, a sufficiently large number of precipitate particles would adhere to the Faxfilm for X-ray diffraction purposes.

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III. RESULTS

A. CHEMICAL ANALYSIS

In the development of a procedure for determining the amount of zirconium carbide in SNAP fuel elements, a solution of bromine in acetonitrile was chosen. Such a solution does not react with zirconium carbide, but does destroy the zirconium hydride-uranium matrix. This was confirmed by treating (1) pure zirconium carbide and (2) a mixture of zirconium carbide and zirconium hydride and uranium, with the solution and weighing the residue. In both cases, complete recovery of zirconium carbide was obtained.

However, in the bromine treatment of a fuel element which contained zirconium carbide, the recovery of zirconium carbide was found to be incomplete. This was true, even though a $0.05\text{-}\mu$ filter was used, which was an unexpected result; since an optical photomicrograph (Figure 1) of fuel containing 0.15 wt % C shows the average particle size of what is presumed to be the carbide phase to be of the order of 4 to 6μ .

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Figure 1. Ternary Compound in SNAP Fuel

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Further confirmation of this incomplete recovery of zirconium carbide was obtained by comparing the amount of carbon recovered from the bromine treatment (expressed as a percentage of the original weight before treatment) with the amount found by using combustion analysis. The results are given in Table 1.

TABLE 1
CARBON RECOVERIES

Sample Number	Combustion Analysis (wt % C)	Bromine Treatment (wt % C)
1	0.02	<0.01
2	0.09	0.02
3	0.40	0.04
4	0.50	0.12

The incomplete recovery of zirconium carbide from the bromine treatment was unexpected. However, a logical explanation of this anomalous behavior would be that the zirconium carbide was no longer present as such, but very likely was hydriding to form the recently reported ternary compound, $\text{ZrC} \cdot \text{ZrH}_x$.⁽⁸⁾ The fact that this ternary compound does react with bromine substantiated the explanation. Consequently, increased recovery could be obtained by processing a dehydrided rod; since the ternary compound would revert to ZrC_{1-y} , which does not react with bromine.⁽⁹⁾ This was the case. A hydrided rod was cut in half, and one half was dehydrided by heating it at 900°C in a dynamic vacuum. Both halves of the rod were then processed in the same manner, using the bromine dissolution and filtration technique. Analyses of recovered material showed an 85% recovery of zirconium carbide for the dehydrided rod, whereas the hydrided rod showed only a 20% recovery. Thus, for the same material, an increase in carbide recovery (from 20 to 85%) was obtained simply by dehydriding the material, demonstrating that hydriding and dehydriding of the ZrC_{1-y} was taking place.

A recovery of 85%, instead of 100%, for the dehydrided fuel element is probably due to either the experimental limitations of our technique or to the possibility that hydriding and dehydriding reduces some of the particles to sizes

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smaller than 0.05μ . The recovery of 20% from the hydrided fuel reflects incomplete hydriding (i.e., some of the ZrC_{1-y} is still unreacted). This is explained in greater detail in Section III-B. The important point is that dehydriding does raise the recovery of ZrC_{1-y} .

B. X-RAY DIFFRACTION

Unhydrided, hydrided, and dehydrided fuels were examined by X-ray diffraction. In addition, the residues from the bromine treatment of them were studied. For greater clarity, the results are given in three sections: alloys prior to hydriding, hydrided alloys, and dehydrided alloys.

1. Alloys Prior to Hydriding

Diffraction and film patterns for the Zr - 10 wt % U alloy, prior to hydriding, revealed:

- a) A strong pattern for α -Zr
- b) A weak pattern for γ -U, Zr
- c) A weak zirconium carbide pattern with $a_0 = 4.688 \text{ \AA}$
- d) Unidentified lines.

No conclusion could be drawn as to whether stoichiometric or sub-stoichiometric zirconium carbide was present, since accurate cell constants for zirconium carbide could not be obtained. Because of this, the sample was heated in vacuum at 1000°C for 2 days, in order to equilibrate the reaction for the formation of substoichiometric zirconium carbide. This treatment resulted in a greatly improved X-ray pattern. It showed:

- a) A strong pattern for α -Zr
- b) A weak pattern for γ -U, Zr with a_0 of $3.563 \text{ \AA}$
- c) A weak pattern for zirconium carbide, for which a_0 was calculated to be $4.673 \text{ \AA}$, indicating the phase to be $ZrC_{0.54}$
- d) Unidentified lines.

The heat-treated samples were then treated with bromine, in order to concentrate the insoluble precipitates. The residue was examined, and the results showed:

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- a) An excellent sharp pattern for ZrC_{1-y} with $a_o = 4.674 \text{ \AA}$
- b) A large number of unidentified lines which were indicative of a single unknown phase, due to their spacing regularity.

Thus, the diffraction studies of SNAP fuel, prior to hydriding, indicate the carbide phase to be carbon deficient. However, under our melting conditions, equilibrium is not attained; since the cell constants measured were between the values reported for zirconium carbide and $\text{ZrC}_{0.54}$. Heating the samples does convert the zirconium carbide phase to $\text{ZrC}_{0.54}$, as indicated by annealing and subsequent diffraction studies.

2. Hydrided Alloys

A hydrided fuel alloy was treated with bromine, and an X-ray diffraction photograph prepared from the residue showed:

- a) A strong pattern for UO_2 with $a_o = 5.470 \text{ \AA}$
- b) A medium pattern of ZrC_{1-y} with $a_o = 4.674 \text{ \AA}$.

Another hydrided fuel sample which was an isochore specimen was treated with bromine. This material had been exposed to hydrogen for many hours (~200 hr) during dissociation pressure measurements. The X-ray pattern showed:

- a) A very sharp and distinct UO_2 pattern with $a_o = 5.470 \text{ \AA}$
- b) A few unidentified lines
- c) No positive indication of substoichiometric ZrC_{1-y} .

Since bromine dissolves the ternary compound, its diffraction pattern did not appear. The ZrC_{1-y} remaining, for the first sample described here, probably represents that portion of the zirconium carbide that had not reacted with hydrogen to form the ternary compound, $\text{ZrC} \cdot \text{ZrH}_x$. The absence of ZrC_{1-y} in the residue of the second sample is probably the result of its complete reaction with hydrogen, to form the ternary compound, during the long period of time in which the dissociation pressure measurements were made.

Because zirconium carbide addition to SNAP fuel only results in a maximum formation of about 3 wt % $\text{ZrC} \cdot \text{ZrH}_x$, which is rather low for identification by X-ray diffraction, several techniques for its separation and concentration were applied. These techniques, described in Section II-C, were

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TABLE 2
X-RAY DIFFRACTION PATTERN FOR HYDRIDED
FUEL ELEMENT ALLOY

Samples		ZrH ₂			α-U			ZrC·ZrH _x		
I	1/d ²	hkl	I	1/d ²	hkl	I	1/d ²	hkl	I	1/d ²
vvw--	0.10131									
vvw--	0.10841	111 β		0.13296						
vs	0.13237	111	vvs+	0.13151				002	32	0.13316
vvw--	0.13769									
w	0.15328				110	70	0.15129	101	100	0.15320
vw	0.15861				021	100	0.15747			
m	0.16358	200	vs	0.16184	002	55	0.16259			
vvw--	0.18495									
vvw	0.19416				111	60	0.19237			
vw	0.20342	002	m	0.20236						
vvw	0.25306							102	23	0.25306
vw	0.31638				112	45	0.31456			
m	0.32434	220	s	0.32368						
vvw	0.35877							110	20	0.35973
s	0.36499	202	vs	0.36526						
vvw	0.41950							103	18	0.41950
vvw	0.42653				131	30	0.42496			
vs	0.45615	311	vvs	0.45519						
vvw--	0.48334				023	16	0.48225	200	3	0.47964
vvw-	0.49134				200	6	0.49108	112	18	0.49289
vvw--	0.51084				113	10	0.51757	201	15	0.51293
m	0.52632	222	m+	0.52604						
m-	0.53590	113	m+	0.53623				004	2	0.53264
w, d	0.65045	400	vw	0.64736	$\begin{Bmatrix} 221 \\ 004 \\ 202 \end{Bmatrix}$	$\begin{matrix} 14 \\ 12 \\ 10 \end{matrix}$	$\begin{matrix} 0.64827 \\ 0.65141 \\ 0.65352 \end{matrix}$	104	3	0.65255
?	0.72854									
vvw	0.75262				133	12	0.75091			
w+	0.77753	331	m	0.77887				203	7	0.77925
w	0.80837	$\begin{Bmatrix} 420 \\ 004 \end{Bmatrix}$	m-	$\begin{Bmatrix} 0.80920 \\ 0.80944 \end{Bmatrix}$						
vw	0.84734	402	w	0.84972	150	4	0.84946			
w+	0.85984	313	m+	0.85991						
vvw--	0.89070							114	7	0.89237
vvw---	0.92880									
vvw--	0.94853							105	3	0.95211
w, d	0.96922	204	w	0.97128	223	8	0.97258	212	2	0.97253
m, d	1.01156	422	m+	1.01156	152	6	1.01211	204	2	1.01228
w, d	1.10255	511	m-	1.10255						
w, d	1.13132	224	w	1.13312				213	7	1.13898
w, d	1.18311	333	w+	1.18311						
vw, d	1.29353	440	vvw	1.29472						
vw	1.34248	115	w	1.34567						
m	1.42479	531	m	1.42623						
w	1.45290	$\begin{Bmatrix} 600 \\ 004 \end{Bmatrix}$	w	$\begin{Bmatrix} 1.45656 \\ 1.45680 \end{Bmatrix}$						
band	1.49972	$\begin{Bmatrix} 442 \\ 513 \end{Bmatrix}$	m	$\begin{Bmatrix} 1.49708 \\ 1.50727 \end{Bmatrix}$						
band	1.61330	$\begin{Bmatrix} 620 \\ 424 \end{Bmatrix}$	s	$\begin{Bmatrix} 1.61840 \\ 1.61864 \end{Bmatrix}$						
d	1.66502	$\begin{Bmatrix} 602 \\ 315 \end{Bmatrix}$	w	$\begin{Bmatrix} 1.65892 \\ 1.66935 \end{Bmatrix}$						

- 1) Columns 1 and 2 list the observed intensities (I) and 1/d² values (v = very, w = weak, s = strong, m = medium, d = diffuse, + = stronger, - = weaker).
- 2) The ZrH₂ I-values are for comparison here. They are taken from a Debye-Scherrer pattern for a commercial sample of zirconium hydride. The 1/d² values for ZrH₂ were calculated, using the observed (511) and (333) lines as standards. Cell constants obtained from these lines are: a₀ = 4 971 Å, c₀ = 4 446 Å, c₀/a₀ = 0 894. These values correspond approximately to those for ZrH_{1.9}.
- 3) All values in the α uranium columns are taken from Card 11-628 in the X Ray Powder Data File.
- 4) The 1/d² values for ZrC·ZrH_x were calculated, using the (102) and (103) lines as standards. The intensities are taken from a pattern for a previous preparation of this compound. The cell constants obtained here are: a₀ = 3 335 Å, c₀ = 5 481 Å. In a previous preparation, we had found 3 344 and 5 491 Å, while Rexer and Peterson report 3 347 and 5 469 Å.⁽⁸⁾
- 5) The line at 1/d² = 0 10131 is the strongest line for UO₂ and for ZrO₂. Lines at 0 13769, 0 18495, and 0 92880 are believed to be due to zirconium carbide.

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not successful. They consisted of matrix masking, Ultrasonic Jack Hammer, and extraction replication.

Matrix masking requires a micro-manipulator with indexing capabilities, for accurate application of the coating to the precipitates. This equipment was not available, and attempts at coating precipitates manually were unsuccessful.

The Ultrasonic Jack Hammer offered the best potential for concentrating the precipitate. Unfortunately, due to the small size of the precipitates (~ 4 to 6μ), the process was time consuming and tedious. Though several days were spent at this operation, the quantity of debris extracted was insufficient for identification purposes.

Extraction replication was unsuccessful, since it fell heir to the same phenomenon that first gave clue to the compound's true identity (i.e., the chemical reagent dissolved the ternary compound, leaving only unreacted sub-stoichiometric zirconium carbide).

Since separation and concentration techniques were unsuccessful, fuel containing 8 wt % $\text{ZrC} \cdot \text{ZrH}_x$ was examined directly with X-ray diffraction. Though background effects of α uranium and ϵ zirconium hydride were present, strong X-ray diffraction evidence for the presence of the ternary compound, $\text{ZrC} \cdot \text{ZrH}_x$, was found. Data taken from a Debye-Scherrer pattern for this sample are presented in Table 2.

The arguments for the presence of the ternary compound, based on Table 2, can be summarized as follows:

- a) The α -U lines at $1/d^2 = 0.15328$ and 0.15861 are reversed in intensity from that expected. This reversal is attributed to the coincidence of the strong $(101) \text{ZrC} \cdot \text{ZrH}_x$ line with the $(110) \alpha$ -U line.
- b) The (102) , (110) , (103) , (114) , and (105) lines for $\text{ZrC} \cdot \text{ZrH}_x$ all appear, noncoincident with other lines in the pattern. Other lines expected to be seen for this compound all coincide with ZrH_2 or α -U lines.

In addition, other types of X-ray patterns, obtained using this sample, support the conclusions drawn in the preceding paragraph, although not all of the same lines are discernible.

A diffractometer pattern showed:

- a) The (100) line for $\text{ZrC} \cdot \text{ZrH}_x$
- b) The intensity reversal of the (110) and (021) α -U lines
- c) The presence of the (102), (103), and (200) $\text{ZrC} \cdot \text{ZrH}_x$ lines.

A Guinier pattern showed:

- a) The (100) $\text{ZrC} \cdot \text{ZrH}_x$ line
- b) The intensity reversal of the (110) and (021) α -U lines
- c) The presence of the (102), (110), and (103) $\text{ZrC} \cdot \text{ZrH}_x$ lines; the limit of the lines read was at $1/d^2 = 0.65102$.

3. Dehydrated Alloys

A sample was dehydrated by heating in a dynamic vacuum for two days at approximately 1000°C . X-ray photographs showed:

- a) A strong pattern for α -Zr with cell constants of $a_o = 3.231 \text{ \AA}$, $c_o = 5.154 \text{ \AA}$, and $c_o/a_o = 1.595$
- b) A weak γ -U, Zr pattern with $a_o = 3.563 \text{ \AA}$
- c) A weak ZrC_{1-y} pattern with $a_o = 4.670 \text{ \AA}$
- d) Unidentified lines.

Another dehydrated sample was treated with bromine, and the diffractometer pattern obtained from the residue showed:

- a) A very strong ZrC_{1-y} pattern with $a_o \sim 4.680 \text{ \AA}$
- b) Unidentified lines.

A film pattern for the same sample showed:

- a) A strong ZrC_{1-y} pattern with $a_o = 4.675 \text{ \AA}$; this value, using a least-squares Nelson-Riley extrapolation, is considered to be more accurate than the value ($4.680 \text{ \AA}$) obtained from the diffractometer pattern
- b) Unidentified lines.

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Thus, X-ray diffraction studies of dehydrided fuel showed the ternary compound to have disappeared. Presumably, it had reverted to the substoichiometric compound, ZrC_{1-y} .

C. METALLOGRAPHY

Electron microscopy studies were conducted on hydrided and dehydrided fuel, to see if any morphology differences could be detected and attributed to the dehydriding of the ternary compound. Examination of Figure 2 did not reveal any significant differences in the morphology of the ternary compound or in the interface between compound and matrix.

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a. Hydrided

Photographed at 6000X
Enlarged to 7200X

7568-51400

b. Dehydrided

Photographed to 2500X
Enlarged to 3000X

7568-51401

Figure 2. Electron Micrographs of Ternary Compounds

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IV. CONCLUSION

SNAP fuel rods, prior to hydriding, contain α -Zr, γ -U, Zr, and carbon-deficient zirconium carbide. However, the deficiency does not correspond to $\text{ZrC}_{0.54}$, the composition in equilibrium with α -Zr.⁽¹⁰⁾ This was determined by lattice constant measurements. A value of 4.688 Å was found for the carbide phase, which is intermediate between the values of 4.699 Å found for zirconium carbide and 4.673 Å found for $\text{ZrC}_{0.54}$. However, annealing the sample does lead to $\text{ZrC}_{0.54}$, as indicated by the smaller lattice constant found.

Kieffer and Benesovsky⁽¹⁰⁾ report 4.693 Å for zirconium carbide and 4.675 Å for $\text{ZrC}_{0.54}$. A more recent report, by Storms,⁽¹¹⁾ who used very pure samples, lists lattice constants of 4.691 Å for $\text{ZrC}_{0.55}$ and 4.6983 Å for $\text{ZrC}_{0.95}$. The difference in lattice constants from those reported previously is attributed to the presence of oxygen or nitrogen in the earlier studies. Since our fuel contains 1000 ppm oxygen and our lattice constants are close to those reported by Kieffer and Benesovsky,⁽¹⁰⁾ it was concluded that approximate compositions of zirconium carbide and $\text{ZrC}_{0.54}$ correspond to the lattice constants of 4.699 Å and 4.673 Å, respectively.

During the hydriding process, annealing of the alloy takes place, and all of the carbide phase is converted to $\text{ZrC}_{0.54}$, which subsequently hydrides to form $\text{ZrC} \cdot \text{ZrH}_x$. However, complete hydriding does not take place. Dissolution techniques conducted on hydrided fuel revealed the presence of some $\text{ZrC}_{0.54}$ material. A possible explanation is that hydriding of the carbide phase is a diffusion process; and, under our conditions, equilibrium is not achieved. Careful examination of the photomicrograph in Figure 1 illustrates a cored structure for the carbide phase, indicating that hydriding is taking place at the periphery of each precipitate and is moving inward, with the core being unreacted. However, if samples are held for many hours (~200 hr) at elevated temperatures, reaction does go to completion. This was demonstrated by analyzing isochore samples. These samples had undergone many tests that involved heating to elevated temperatures under a hydrogen atmosphere, and diffraction patterns of the residue of this material from the bromine treatment revealed the absence of the $\text{ZrC}_{0.54}$ phase.

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It is interesting to note that stoichiometric zirconium carbide does not hydride. Zirconium carbide powders, in a hydrogen atmosphere, have been held at 1000°C for three weeks, and no hydride compounds were formed. Hitherto, investigators of pressure-composition-temperature relationships for SNAP fuel materials have assumed that the effect of the addition of zirconium carbide on these relationships has been only that of a diluent. What was not taken into consideration was that substoichiometric zirconium carbide formed during melting, and that this compound does hydride. However, the hydriding rate relative to that of zirconium is slow, and complete hydriding of the substoichiometric ZrC_{1-y} phase does not take place under our conditions.

The variances in reported values for dissociation pressure measurements can now be explained. The differences are caused by:

- a) ZrC_{1-y} forming from zirconium carbide
- b) ZrC_{1-y} hydriding to form $ZrC \cdot ZrH_x$
- c) $ZrC \cdot ZrH_x$ having a finite dissociation pressure.

Pressure measurements on modified fuel thus involve pressure measurements of two phases (ZrH_x and $ZrC \cdot ZrH_x$), and not a single phase, as assumed by previous studies.

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