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Report No. SCNC-266

Metallurgy and Ceramics

DISPERSION-TYPE MATERIALS FOR FUEL ELEMENTS

PART I. URANIUM MONONITRIDE AND URANIUM

SILICIDE DISPERSION MATERIALS

by

I. Sheinhart and J. L. Zambrow

AEC RESEARCH AND DEVELOPMENT REPORT

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I. Sheinhartz and J.L. Zambrow

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- 2 -

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- 3 -

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- 4 -

Report SCNC-266

TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT	5
I. INTRODUCTION	6
II. SELECTION OF RAW MATERIALS	6
III. PREPARATION OF RAW MATERIALS	8
IV. URANIUM NITRIDE DISPERSIONS	9
V. URANIUM SILICIDE DISPERSIONS	10
VI. CORROSION TESTS	10
VII. DISCUSSION	11
VIII. FUTURE WORK	11

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- 5 -

ABSTRACT

This report describes the basic requirements for dispersion-type fuel elements and the basis for the selection of the components, i.e., melting temperature, density and uranium-content of the uranium compounds, and melting temperature and absorption cross section of the matrix materials. Two types of dispersions are investigated: uranium nitride and uranium silicide. Their reactions with Zircaloy-2 and other matrix materials, such as molybdenum, niobium, Nichrome-V, Ti-Nb alloys, or vanadium, are shown in some characteristic photomicrographs. The corrosion rate of some of these dispersion-type materials in 600°C water is briefly discussed.

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I. INTRODUCTION

The basic requirements for dispersion-type fuel elements may be formulated as follows:

- a) Discrete particles of fuel material are to be uniformly distributed in a continuous, corrosion-resistant matrix in order to prevent a catastrophic failure in the event of a localized opening in the fuel cladding;
- b) The dispersion should contain a high percentage of uranium and be of high density in order to have the fuel concentrated in a minimum volume.
- c) The dispersion should be compatible with the matrix at both fabricating and operating temperatures.
- d) Both the dispersant and the matrix should be of low nuclear cross section.
- e) The transfer of heat from the dispersant to the outside should occur with a minimum thermal gradient.

II. SELECTION OF RAW MATERIALS

Based on the above requirements, an investigation has been made with some uranium compounds and some metallic matrix materials selected from Tables I and II. Table I shows the melting temperatures, densities and uranium content of seven uranium compounds. From these data one would conclude that UO_2 is a very desirable dispersant on account of the high melting temperature. It is, however, considerably less desirable for its low density and small amount of uranium in the compound. U_3Si would be an excellent dispersant with respect to high amount of uranium, but the melting temperature of this compound is rather low.

The most desirable dispersants seem to be UN, U_3Si_2 , UC and US, which have fairly high melting temperatures, relatively high densities, and high amounts of uranium in the compound. This report deals with UN and U_3Si_2 as dispersants. UN contains 94.4 w/o uranium and U_3Si_2 contains 92.7 w/o uranium. For the studies to be described below, the dispersant was used in the amount of 30 volume per cent in the mixture, with the metallic matrix.

Table II contains a list of various metals to be considered as matrix materials, their melting points, and nuclear cross sections. For the investigation to be described below, aluminum, Zircaloy-2, molybdenum, niobium, Nichrome-V, 40% Ti-Nb alloy and vanadium were used. The 30 volume per cent of the dispersant resulted in an approximately 40-70 w/o mixture depending on the densities of the dispersant and matrix materials. The matrix materials were mainly selected with respect to low neutron cross section, and satisfactory corrosion behavior in 600°C water. Some of them, however, were also considered for their high-temperature properties.

TABLE I

MELTING TEMPERATURE, DENSITY AND RELATIVE AMOUNT OF URANIUM
OF VARIOUS URANIUM COMPOUNDS

<u>Uranium compound</u>	<u>Melting temp., °C</u>	<u>Density, g/cc</u>	<u>Uranium content in vol. percent of metallic U</u>	<u>w/o U</u>
<u>U</u>	<u>1120</u>	<u>18.9</u>	<u>100</u>	
UO ₂	2800	10.96	53	88.1
✓ UN	2630	14.3	71	94.4
U ₃ Si	930	15.6	77	96.2
✓ U ₃ Si ₂	1665	12.2	59	92.7
UC	2270	13.6	69	95.2
UC ₂	2400	11.7	56	90.8
UBe ₁₃	2000	4.37	15	91.0
✓ US	> 2000	10.9	-	88.1

TABLE II

VARIOUS MATRIX METALS, THEIR MELTING TEMPERATURES AND
NEUTRON CROSS SECTIONS

<u>Matrix metal</u>	<u>Melting temp., °C</u>	<u>Absorption cross section, barns</u>
Al	660	0.22
Fe	1539	2.4
Mg	651	0.059
Mo	2625	2.4
Nb	2415	1.1
Ni	1455	4.5
Ti	1670	5.8
V	1900	4.7
Zr	1852	0.18

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- 8 -

III. PREPARATION OF RAW MATERIALS

Uranium mononitride was prepared by nitriding 1/4"-thick uranium wafers at 850°C, followed by a vacuum-decomposition of the higher nitrides (U_2N_3 and UN_2) into UN, at 1300°C. The nitride was formed as a powder, and no pulverizing was necessary. Chemical analysis indicated a stoichiometric composition corresponding to UN.

U_3Si would be a desirable dispersant, in spite of the low melting temperature, because of its high uranium content and its corrosion resistance. Attempts to make substantial amounts of it as a powder, however, have not been very successful; it is too ductile to be pulverized, even at low temperatures, and it decomposes when hydrided. U_3Si_2 is readily made by arc melting, and does not require any special heat treatment; it is brittle, and can be readily pulverized into a powder. Furthermore, it is apparently quite resistant to corrosion and the powder indicates no reaction with boiling water.

Since there was some doubt in the literature as to the exact composition of this phase, a series of arc melted buttons were made ranging from 6.2-7.8% silicon, the balance uranium. Metallographic examination of these buttons indicated a single phase material for the composition corresponding to U_3Si_2 , without any subsequent heat treatment. The other compositions showed two or more phases.

Since Zircaloy-2 was being considered as a matrix material because of its low cross section and high corrosion resistance, a series of tests were started to determine whether the material made by powder metallurgical techniques was comparable to the wrought material. Zircaloy-2 samples fabricated by the following methods were corrosion-tested simultaneously in an autoclave at 750°C:

1. Wrought Zircaloy-2 (density, 6.48 g/cc)
2. Hot pressed Zircaloy-2 made by vacuum hot pressing Zircaloy hydride powder at 2 tsi and 1200°C (density, 6.40 g/cc)
3. Zircaloy-2 made by hot pressing, followed by a hot rolling operation. The material in item (2) was reduced 60% by hot rolling at 800°C (density, 6.48g/cc)
4. Sintered Zircaloy-2 made by compacting the powder at 40 tsi, followed by vacuum sintering for four hours at 1200°C (density, 6.36 g/cc)

The corrosion rate for items (2) and (3) was comparable to the wrought material; however, since all of the samples showed a decrease in weight after testing, the test will be repeated. The sintered material, which was slightly porous, corroded at a more rapid rate than any of the other materials, as was to be expected.

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The results of the metallographic investigations on the above Zircaloy-2 materials are shown in Figs. 1 to 5. The original wrought material is shown in Fig. 1. Fig. 2 shows the structure of a sample made by vacuum-hot-pressing of the hydride powder at 1200°C. Its structure is entirely different than that of the wrought material from which the powder was made. Fig. 3 indicates that the hot pressed material started to recrystallize during the hot rolling operation. The resulting grains are much smaller than those of the original wrought material. Fig. 4 shows the hot pressed and hot rolled material after being annealed for four hours at 1500°C. The material has completely recrystallized and has a structure similar to that of the original wrought material, except for the slightly smaller grain size, which is rather favorable for processing. Fig. 5 indicates that the vacuum sintered material had a structure that was very similar to the wrought, except for the presence of approximately 2% porosity.

IV. URANIUM NITRIDE DISPERSIONS

Thirty volume percent (70 w/o) UN was mixed with a -325 mesh aluminum powder and compacted at room temperature into a core which was then assembled in an aluminum picture frame. The assembly was given a 3-1 reduction by hot rolling at 600°C. A section of such an element is shown in the photomicrograph, Fig. 6. It indicates that there was no reaction between UN and aluminum during fabrication at 600°C. There was no reaction after holding for seventy-five hours at 500°C, but there was some swelling of the core after 24 hours at 600°C, indicating some reaction between the two powders. A 60-mil hole was drilled through the skin and core of a UN-Al section, which was then held for 168 hours in boiling water. Bubbles kept forming very slowly at the hole, but no distortion was observed. Examination of a cross section cut through the drilled hole, however, indicated no apparent reaction.

Picture-frame assemblies containing cores of 30 v/o (49 w/o) UN in Zircaloy-2 were hot rolled at 1500°F. A section of the core is shown in the photomicrograph, Fig. 7, and it indicates a very slight reaction between the UN and the Zircaloy during fabrication. There is also some stringering of the UN. Holding for twelve hours at 1500°F caused further reaction between the UN and the Zircaloy, and some distortion of the plate. This is shown in the photomicrograph, Fig. 8. The reaction between UN and Zircaloy-2 may possibly be eliminated by fabricating at lower temperatures.

A series of powder mixes containing 30 v/o UN in molybdenum, niobium, Nichrome-V, 40% titanium-niobium alloy, and vanadium were vacuum-hot-pressed at 1200°C. The resulting materials were quite porous. The dispersions were, therefore, made by cold compacting the powder mixture at 50 tsi, vacuum sintering for four hours at 1200°C, hot forging, and finally annealing, both latter operations at 1200°C. This resulted in a more dense material than was obtained by hot pressing. The sintered compacts were clad in stainless steel while being forged. The following table shows the densities obtained by the compacting-sintering-hot forging process:

<u>Dispersant</u>	<u>Matrix</u>	<u>Density, g/cc</u>	<u>Calculated porosity, %</u>
30 v/o UN	Molybdenum	10.4	9
30 v/o UN	Niobium	9.6	6
30 v/o UN	40% Ti-Nb alloy	9.1	0
30 v/o UN	Nichrome-V	partial melting during sintering	
30 v/o UN	Vanadium	8.0	8

Metallography of the above samples is shown in the photomicrographs, Figs. 9-12. The following has been observed after a total of approximately twelve hours' testing at 1200°C, during fabrication:

1. There is no reaction between UN and either molybdenum or niobium.
2. Apparently a slight reaction occurs between the UN and the vanadium.
3. There is a definite reaction of UN with Nichrome-V and Ti-Nb alloy.

V. URANIUM SILICIDE DISPERSIONS

A series of dispersion samples similar to those described above were made containing 30 v/o U_3Si_2 . These were also made by compacting, sintering, hot forging and annealing. The resulting densities are shown in the following table:

<u>Composition</u>	<u>Density, g/cc</u>	<u>Calculated porosity, %</u>
30 v/o U_3Si_2 -molybdenum	10.0	7.5
30 v/o U_3Si_2 -niobium	8.5	10.0
30 v/o U_3Si_2 -Nichrome-V	melted during sintering	
30 v/o U_3Si_2 -Ti-Nb alloy	melted during sintering	
30 v/o U_3Si_2 -vanadium	7.72	1.0

Metallography on the above samples is shown in the photomicrographs, Figs. 13-15. They indicate that there apparently is a reaction between the U_3Si_2 and all of the materials tested, at 1200°C.

VI. CORROSION TESTS

Some of the above core materials were tested for corrosion in 600°F water for three days. There was no protective cladding on these dispersions, and all of the surfaces were exposed. The results to date are shown in the following table:

<u>Material</u>	<u>Condition</u>	<u>Corrosion rate, 600°C water</u>
30 v/o UN-molybdenum	disintegrated	-
30 v/o UN-niobium	undamaged	+1.3 mg/cm ² /hr
30 v/o UN-vanadium	disintegrated	-
30 v/o UN-40 a/o Ti-Nb alloy	cracked	+0.9 mg/cm ² /hr
30 v/o U_3Si_2 -molybdenum	undamaged	+0.11 mg/cm ² /hr
30 v/o U_3Si_2 -niobium	undamaged	+0.1 mg/cm ² /hr
30 v/o U_3Si_2 -vanadium	severe cracking	-

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- 11 -

These results indicate that niobium in combination with either UN or U_3Si_2 is corrosion resistant. The molybdenum- U_3Si_2 mixture is also corrosion resistant, but apparently the molybdenum-UN is not. This may not necessarily be indicative of the material, but rather may be due to the manner in which this particular sample was fabricated.

VII. DISCUSSION

Zircaloy-2 hydride powder can apparently be fabricated by hot working techniques into fully dense Zircaloy-2 that is comparable to the wrought material from which the powder was made, in respect to purity, structure, corrosion and mechanical properties. This, however, is based on a very limited number of tests and will have to be confirmed.

Dispersions of UN in aluminum appear promising. Satisfactory dispersions containing at least 70 w/o UN can be made by conventional picture-frame cladding techniques. There is a very slow reaction at 600°C, but the elements could be fabricated before any significant amount of reaction occurs, and there is apparently no reaction at 500°C and lower.

At fabricating temperatures of 1500°F, there is a reaction between UN and Zircaloy-2. Two methods of eliminating this condition are being studied at the present time. One, by the application of powder metallurgical techniques, is to fabricate at temperatures low enough to prevent the reaction from occurring. The second concerns an apparatus which is being built for the vapor deposition of a metallic film on UN powder. This film would act as a barrier to prevent any reaction from occurring. Molybdenum, niobium and aluminum oxide films are being evaluated.

Thirty volume per cent UN is compatible with molybdenum and niobium, up to at least 1200°C. There apparently is a reaction with Nichrome-V, vanadium and 40 a/o titanium-niobium alloy at 1200°C. Corrosion tests indicate the UN-niobium to be the most promising combination.

Thirty volume per cent U_3Si_2 apparently reacts with all of the dispersants tested at 1200°C. It may be possible to fabricate dispersions of this material at lower temperatures.

VIII. FUTURE WORK

Uranium carbide and uranium sulfide will be evaluated as dispersants in the above matrix materials. A method of depositing a protective film on powder particles is being developed.

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- 12 -

Fig. 1 Wrought Zircaloy-2 from which the hydride powder was made.
Mag. 100X Polarized Plate 23263

Fig. 2 Zircaloy-2 made by hot pressing Zircaloy hydride powder
at 1200°C.
Mag. 100X Polarized Plate 18942

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Fig. 3 Zircaloy-2 made by hot pressing Zircaloy hydride powder at 1200°C and then hot rolling at 800°C. The structure has apparently started to recrystallize.
Mag. 100X Polarized Plate 18941

Fig. 4 Hot pressed and hot rolled material shown in Fig. 3, after being annealed 4 hrs at 800°C.
Mag. 100X Polarized Plate 18943

Fig. 5 Zircaloy-2 made by vacuum sintering compacted Zircaloy
hydride powder 4 hrs at 1200°C
Mag. 100X Polarized Plate 18940

Fig. 6 Core containing 30 v/o (70 w/o) UN in aluminum. Made by
hot rolling picture frame at 600°C
Mag. 500X Polarized Plate 18945

Fig. 7 Core containing 30 v/o UN in Zircaloy-2. It was made by hot rolling in a picture frame at 1500°C. There apparently is some reaction.
Mag. 500X

Plate 20091

Fig. 8 Material in Fig. 7 after 12 hours at 800°C. This is further reaction between UN and Zircaloy-2.
Mag. 500X

Plate 20098

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- 16 -

Fig. 9 30 volume per cent UN in molybdenum.
Mag. 500X

Plate 21306

Fig. 10 30 volume per cent UN in niobium.
Mag. 500X

Plate 21307

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- 17 -

Fig. 11 30 volume per cent UN in 40 a/o Ti-Nb alloy
Mag. 500X Plate 21308

Fig. 12 30 volume per cent UN in vanadium
Mag. 500X Plate 21309

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Fig. 13 30 volume per cent U_3Si_2 in molybdenum
Mag. 500X

Plate 21303

Fig. 14 30 volume per cent U_3Si_2 in niobium
Mag. 500X

Plate 21304

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- 19 -

Fig. 15 30 volume per cent U_3Si_2 in vanadium
Mag. 500X

Plate 21305

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