NMI-1183

METALLURGY AND CERAMICS

UNITED STATES ATOMIC ENERGY COMMISSION

**NIOBIUM-URANIUM ALLOYS AS CONTAINER
MATERIAL FOR MOLTEN URANIUM EUTECTIC
ALLOYS**

By
G. W. Powell

August 22, 1957

Nuclear Metals, Inc.
Cambridge, Massachusetts

Technical Information Service Extension, Oak Ridge, Tenn.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

This report has been reproduced directly from the best available copy.

Printed in USA. Price 75 cents. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

Niobium-Uranium Alloys as Container Material
for Molten Uranium Eutectic Alloys

G. W. Powell

August 22, 1957

Nuclear Metals, Inc.
Cambridge, Massachusetts

Contract No. AT(30-1)-1565

A. R. Kaufmann
Technical Director

ABSTRACT

A previous investigation concerned with liquid-core fuel elements and the materials from which they could be constructed revealed that an alloy of U - 5 ^w/o Nb had considerable promise as container material. Results are given from a further investigation of this alloy, as well as another containing 10 ^w/o Nb, to determine the time and temperature limits within which the oxide layer remains protective, the factors which hasten or delay the breakdown of the film, and the mechanism whereby the film deteriorates.

TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT	4
I. INTRODUCTION	7
II. EXPERIMENTAL METHODS	8
A. Preparation of Crucibles	8
B. Oxidation of Crucibles	8
C. Testing of Crucibles	8
D. Inspection of Crucibles	9
III. RESULTS AND DISCUSSIONS	9
A. Conditions of Oxidation	9
B. Testing Temperature	10
C. U - 11 ^W /o Ni Core Material	11
D. Thermal Cycling	11
E. Niobium Content	12
F. Metallographic Observations of Oxide Layer	13
IV. CONCLUSIONS	14

I. INTRODUCTION

In a previous report,* the concept of liquid-core fuel elements was set further, and some experimental results were presented relating to a scheme for their construction. Such an element, visualized essentially as a column of molten, enriched, uranium alloy surrounded by a solid skin of a depleted uranium alloy, has the advantage of eliminating the cracking and distortion originating from the build-up of insolubles such as krypton and xenon in the molten core; since the solid skin of the element is contemplated to be comparatively thin, the distortion of this portion would be practically uniform. The obvious problem to be solved before a fuel element of this type can be given any serious consideration is to find for the molten alloy a container material which will resist its attack at high temperatures for long periods of time. The initial approach to this problem, which yielded promising results, was to find a uranium alloy which, under appropriate conditions, could form a thin, tenacious oxide coating. The alloy, after fabrication into some suitable form such as a crucible, would be oxidized, and the coating thus formed would serve as a diffusion barrier between the crucible and the molten core. Briefly, the results of the previous investigation demonstrated that small oxidized crucibles (1-inch long x 0.375-inch OD), prepared from a binary uranium alloy containing U - 5 ^W/o Cr eutectic alloy, served for at least three weeks at 900°C (40°C above the melting point of U - 5 ^W/o Cr) without suffering any attack. At 1100°C, however, severe attack of the crucible occurred after 16 days.

Because the experimental results summarized above showed some signs of promise, a more detailed investigation has been made of the U - 5 ^W/o Nb alloy as well as an alloy with 10 ^W/o Nb. The objectives of this investigation were to determine: (1) the time and temperature limits within which the oxide layer remains protective, (2) the factors which hasten or delay the breakdown of the film, and (3) the mechanism whereby the film deteriorates. The results obtained are reported below.

- - - - -

*NMI-1154, G. W. Powell, June 12, 1956.

II. EXPERIMENTAL METHODS

A. Preparation of Crucibles

Ten-pound ingots were vacuum melted in graphite crucibles and extruded to rods from which the experimental crucibles were machined. All experiments were made with small crucibles, 0.375-inch OD x 1-inch long, prepared in this way. The cavity, 0.213-inch diameter x 3/4-inch long, was formed with a No. 3 carbide drill.

B. Oxidation of Crucibles

The crucibles were submerged to about 75% of their length in a bath of molten lead-cadmium eutectic. During the time the bath and crucibles were attaining thermal equilibrium and a specified temperature, the cavity of the crucible was purged with argon to prevent any reaction of the cavity surface with the oxygen in the air. When the bath and crucible had reached the desired temperature, the oxidation treatment was begun by passing oxygen into the crucible cavity after the flow of argon had been terminated. Prior to oxidation, each crucible was carefully cleaned to remove any dirt or grease.

The oxidation temperatures were approximately 270, 300, and 425°C; the oxidation time was ordinarily 5 min, but a time of 16 min was employed for the crucibles oxidized at 270°C.

C. Testing of Crucibles

After oxidation, each crucible was again carefully cleaned. The eutectic alloy and, in some cases, powdered UO_2 or U_3O_8 were then placed in the crucible. The U - 11 w/o Ni eutectic alloy has the disadvantage of being very brittle and it proved impossible to prepare an ingot of this alloy without the formation of large cracks during solidification. The crucible with its contents was wrapped in tantalum foil and sealed in quartz tubing. The quartz tubes were either evacuated or filled with helium before sealing.

Usually, the quartz tubes containing the crucibles were simply placed in a vertical furnace controlled at some temperature above the melting point of the eutectic alloy in the crucible and held at this temperature for a definite length of time. For some thermal cycling experiments, however, the power to the furnace was periodically shut off and the furnace allowed to cool from 900°C to approximately 200°C , when power to the furnace was again turned on. A complete cycle required about 8 hr.

D. Inspection of Crucibles

Following completion of a test, each crucible was sectioned longitudinally. One of the crucible halves was given a fine mechanical polish and a photograph taken at a magnification of 2X. The crucible halves were examined for evidence of bonding between the core and crucible and for the extent of diffusion, if any had occurred.

Attempts were made to dislodge the core from each of the crucible halves. If no attack of the crucible by the molten core had occurred during the test period, there would be no metallurgical bonding and the core should be easily separable from the crucible. If the test appeared to have been especially successful, that is, a test of some length during which the crucible was not attacked, the pieces of core material separated from the crucible halves were wrapped in tantalum, sealed in evacuated quartz tubes, and reheated to the temperature at which the test had been made to establish whether or not the core was molten at the end of the test.

III. RESULTS AND DISCUSSIONS

A. Conditions of Oxidation

Some crucibles were oxidized at 270, 300, and 425°C . At 300°C and 425°C , the oxidizing treatment lasted 5 min and, at 270°C , 16 min. These crucibles were then held at 900°C for 62 days. The results obtained are shown in Fig. 1. The crucibles oxidized at 270°C and 300°C were attacked by the molten core and bonding occurred. The crucibles oxidized

at 425°C, however, were not attacked; the contents of the two crucibles shown in Fig. 1 were easily dislodged from the crucible halves, and the cavity surface had remained smooth. A check was made to establish whether or not the core of one of the crucibles oxidized at 425°C was molten at the end of the run. The test proved that it was, and, in addition, a chemical analysis showed that no niobium was present in the U - 5 ^W/o Cr eutectic, thus giving further evidence that the crucible was not attacked.

It is believed that the greatly improved performance obtained by oxidizing the crucibles at 425°C is due to the greater thickness of oxide layer which is formed rather than to any constitutional difference in the layers.

B. Testing Temperature

To establish the temperature range within which the oxide layer remains protective, crucibles which had been oxidized at 425°C were held for 30 days at 900, 950, and 1022°C. U₃O₈ was added to the crucibles tested at 950°C and 1022°C, but, as will be shown below, this does not affect the comparison with the test made at 900°C. Photomicrographs of these crucibles are shown in Fig. 2. Attack did not occur at 900°C but did in one of the two crucibles tested at 950°C. Extensive attack resulted from testing at 1022°C.

The results above indicate that, for periods of time approaching one month, the useful temperature range of such crucibles used to contain molten U - 5 ^W/o Cr eutectic is from 860°C (the melting point of this eutectic) to 950°C. When application of this technique to liquid-core fuel elements is considered, this temperature range is very limited. For this reason, a series of tests was made with a U - 11 ^W/o Ni eutectic alloy which melts at 740°C.

C. U - 11 ^W/o Ni Core Material

Three U - 5 ^W/o Nb crucibles were oxidized at 425°C and filled with particles of the brittle U - 11 ^W/o Ni alloy. Photomacrographs of these crucibles after being held at 800°C for 67 days are shown in Fig. 3. It is apparent that all three crucibles were attacked, two of them very badly. Because good results had been obtained in some of the long-time tests at 900°C, and the stability of the oxide film would be greater at the lower temperature, the failure of these crucibles at 800°C was unexpected. These results, however, suggest that some of the success which has been achieved with the oxidized crucibles at 900°C may be due to the presence of the chromium in the U - 5 ^W/o Cr eutectic. Consequently, it appears that in order to broaden the useful temperature range of the crucibles, the molten uranium alloy which is to be contained must be a ternary alloy composed of uranium, chromium, and another element such as nickel or iron.

D. Thermal Cycling

If in reactor practice an oxide film were to be used to contain a molten uranium alloy, the oxide film would be subject to thermal cycling, and this would be expected to accelerate its breakdown. Consequently, some thermal cycling tests were made, the results of which appear in Fig. 4. Fine-powdered U₃O₈ was added to two of the four crucibles cycled in an attempt to saturate the molten chromium-uranium eutectic with oxygen from a source other than the oxide film on the crucible. It was hoped that if the oxygen content of the molten core could be maintained at the saturation level the system could be made self-healing; that is, if any discontinuities occurred in the oxide barrier as a result of thermal cycling, they might be sealed in the presence of the oxygen-saturated core. The four crucibles were cycled (900°C to 200°C to 900°C) eight times during the 30 day tests with a three or four day lapse between cycles.

Each of the four was slightly attacked. Although the core sections were metallurgically bonded to the crucible halves at a few points, they

were readily pried loose from one another. The U_3O_8 did not limit the attack by any noticeable amount. Although extensive attack did not occur in these tests, the results indicate that the oxide barrier would be impractical under more intense thermal cycling.

E. Niobium Content

Container alloys with niobium contents of 1.5, 3, and 5 ^{w/o} were investigated in previous work, in which longer crucible life was attained with higher alloy content. A fourth alloy containing 10 ^{w/o} Nb was prepared and tested in the present work to determine if additional improvement in crucible performance was possible. The results of tests with this alloy are shown in Fig. 5.

Of the four crucibles tested, three were attacked, and these were oxidized in the as-extruded condition. But the fourth crucible, which was not attacked and is shown in the upper right photograph of Fig. 5, was oxidized after water quenching from 1000°C. The core of this crucible was molten at the end of the run and chemical analysis failed to detect the presence of any niobium in the U - 5 ^{w/o} Cr eutectic. Similar tests were made with U - 5 ^{w/o} Nb crucibles water quenched from 1000°C and oxidized at 300°C but, in this case, crucible performance was not improved. The difference in behavior of the heat-treated U - 5 or 10 ^{w/o} Nb crucibles can be attributed to the fact that in the latter alloy the high-temperature gamma phase may be retained at room temperature by water quenching.* Consequently, when the heat-treated 10 ^{w/o} Nb crucible is oxidized, a layer with a higher concentration of niobium may be formed, since all the niobium is in solid solution in the retained gamma phase.

It appears that the 10 ^{w/o} Nb alloy offers no advantage over the 5 ^{w/o} alloy if the oxidation treatment is carried out on as-extruded material, but may under other conditions.

- - - - -
*USAEC Report WAPD-127, McGeary, R. K., p. 56, 1955.

F. Metallographic Observations of Oxide Layer

Four U - 5 W/o Nb crucibles, one of which served as a control specimen, were prepared and oxidized at 425°C for 5 min. Tests were made at 900°C for periods of 14, 31, and 44 days; slight attack occurred only in the latter test. Photomicrographs of the oxide layer on these crucibles are shown in Fig. 6.

In the as-oxidized condition [see Fig. 6(a)], the oxide layer is predominantly U_3O_8 with a small amount of UO_2 , detectable metallographically with polarized light, as translucent red particles. After 14 days at 900°C [Fig. 6(b)], the oxide layer is considerably reduced in thickness and is constituted entirely of UO_2 . As shown in Figs. 6(a), (b), and (c), the major changes in the oxide layer occurred during the initial 14 day period. As the UO_2 was formed on the surface of the oxide layer in contact with the molten alloy, it must have spalled off, because there is a large volume increase in the transformation of U_3O_8 to UO_2 and all the UO_2 which must have been formed cannot be accounted for in the photomicrographs of Fig. 6. It would appear that the entire layer of U_3O_8 was converted to UO_2 by the inward movement of the UO_2 - U_3O_8 interface from the oxide-molten core interface. Had reduction of the U_3O_8 occurred at the interface between the body of the crucible and the oxide layer while the layer was still relatively thick, it is conceivable that the entire protective layer would be separated from the crucible. It has been suggested by J. Miner of Hanford that the problems introduced by the reduction of U_3O_8 to UO_2 could be eliminated by carrying out the oxidation of the crucibles with CO_2 , which would cause a layer of UO_2 to form as a result of the lower oxygen pressure. Although discontinuities formed in the oxide layer after a period of 31 days [Fig. 6(c)], it was still protective, as evidenced by the lack of bonding between the core and crucible. The appearance of the crucible surface after 44 days at 900°C is shown in Fig. 6(d). The particular region shown is one which had undergone some attack and in which a second phase in massive form had precipitated and grown into the crucible; the periphery of the solidified core was lined with closely-spaced angular particles of UC.

A complete explanation of the experimental results of this work, based solely on the photomicrographs of Fig. 6, is obviously impossible. But it may be hypothesized that the decreased longevity of the U - 5 ^W/o Nb crucibles at temperatures of 950°C and higher is caused by a greater tendency for reduction of the U₃O₈ to UO₂ to occur at the interface between the crucible and the oxide layer and result in a complete separation of the protective film from the crucible. Furthermore, fundamental studies are necessary in order to determine the role played by the chromium and, also, the behavior of the oxide layer in the presence of the U - 11 ^W/o Ni eutectic alloy.

IV. CONCLUSIONS

Within the limits of the experimental conditions, this work has led to the following conclusions:

1. To obtain acceptable crucible life, the oxidizing treatment must be carried out at a temperature in the neighborhood of 400°C.
2. For periods of time approaching one month, the useful temperature range of oxidized U - 5 ^W/o Nb crucibles containing molten U - 5 ^W/o Cr is from 860°C to 950°C. If the oxidizing treatment were to be carried out so that the oxide layer is constituted wholly of UO₂ instead of U₃O₈, it is possible that the useful temperature range might be extended to higher temperatures or that the crucible life within the 860°C to 950°C interval might be increased.
3. The oxidized U - 5 ^W/o Nb crucibles are extensively attacked by the U - 11 ^W/o Ni eutectic at 800°C, leading to the conclusion that chromium may be an important and necessary constituent of the molten alloy in that it contributes in some manner to the stability and protectiveness of the oxide layer.
4. Thermal cycling will bring about a breakdown of the oxide layer.
5. A U - 10 ^W/o Nb crucible alloy offers no advantages over the 5 ^W/o Nb alloy when the oxidation treatment is carried out on as-extruded material, but may under other conditions.

5-17
RF 4131

Oxidized 16 min at 270°C.

5-18
RF 4132

5-2
RF 3113

Oxidized 5 min at 300°C.

5-6
RF 3114

5-10
RF 3497

Oxidized 5 min at 425°C.

5-36
RF 4653

Fig. 1 - Effect of oxidizing conditions on the resistance to attack of crucibles held for 62 days at 900°C. 2X magnification.

5-9 900°C RF 3411

RF 4546 950°C

RF 4547

5-8 1022°C RF 3412

Fig. 2 - Effect of testing temperature on the resistance to attack of crucibles oxidized at 425°C and held at the testing temperature for 30 days. 2X magnification.

RF 4653

RF 4653

RF 4653

Fig. 3 - Attack of U - 5^{W/o} Nb crucibles oxidized at 425°C by molten U - 11^{W/o} Ni eutectic alloy. Held for 67 days at 800°C. 2X magnification.

RF 4135

(a) Tested without U_3O_8 in crucible.

RF 4136

RF 4138

(b) Tested with U_3O_8 in crucible.

RF 4137

Fig. 4 - Effect of thermal cycling on the occurrence of bonding between the core and crucible of crucibles oxidized at 425°C . Crucibles cycled 8 times during 30 day test at 900°C . 2X magnification.

RF 4542

(a) Oxidized at 300°C for 5 min,
 U_3O_8 added.

RF 3500

RF 3499

(b) Oxidized at 425°C for 5 min.

RF 3964

Fig. 5 - U - 10 ^{w/o} Nb crucibles held 60 days at 900°C. 2X magnification.

(a) As-oxidized.

A-1003-1b

(b) 14 days.

A-1003-2

(c) 31 days.

A-1032-a

(d) 44 days.

A-1044-c

Fig. 6 - Effect of time at 900°C on the structure and constitution of the oxide film. U - 5 w/o Nb crucibles oxidized at 425°C for 5 min. 500X magnification.