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COMPATIBILITY TESTS OF MOLTEN URANIUM WITH TUNGSTEN AND TUNGSTEN- 1.5 PERCENT HAFNIUM

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ABSTRACT

Isothermal compatibility tests were conducted on sealed tungsten (W) and tungsten - 1.5-weight-percent-hafnium (W-1.5Hf) capsules containing uranium (U) for 10 to 200 hours at 1200° and 1500° C. Extensive intergranular attack was observed in wrought W rod and in vapor-deposited W. Hafnium appeared to offer some promise in reducing intergranular attack on W. Single-crystal W appeared to be compatible with molten U although some evidence of mass transfer attack was found. In addition, U climbed up the sides of the single-crystal capsules and attacked grain boundaries in the closure weld. Cracks were formed in all the capsule walls during cooling after U had solidified.

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AND TUNGSTEN - 1.5 PERCENT HAFNIUM

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SUMMARY

A study was made of the corrosion problems associated with long term containment of molten uranium (U) at temperatures over 1200° C. Capsules were fabricated from single-crystal tungsten (W) and polycrystalline tungsten - 1.5-weight-percent-hafnium (W-1.5Hf) rods. Smaller polycrystalline W rods were partially coated with vapor-deposited W and then inserted into some of the single-crystal capsules. The capsules were then loaded with U, sealed, and heated to 1200° or 1500° C for 10 to 200 hours.

Both wrought W rod and vapor-deposited W exhibited extensive intergranular attack after only 10 hours at temperature. Additions of Hf to W showed some promise in reducing intergranular attack of W if areas of localized attack can be eliminated. However, the W-1.5Hf capsules exhibited some mass transfer of metal from the walls to dendrites which formed near the U meniscus.

Except for a small amount of mass transfer attack, single-crystal W appeared to be compatible with molten U. However, the excellent wetting between W and U resulted in U climbing up the capsule walls to attack grain boundaries in the closure weld and thereby penetrate through the weld.

Cracks were formed in all of the capsules during cooling after the U had solidified. These cracks apparently resulted from the difference in thermal expansivity and the strong bonding between U and W or W-1.5Hf. Thus, these metals cannot be used to contain molten U for more than one thermal cycle.

Based on these results, single-crystal W and possibly a polycrystalline W-Hf alloy can contain molten U for relatively long times at isothermal conditions. Corrosive attack on weld zones would probably be the limiting factor on containment time providing the containers are not thermally cycled.

INTRODUCTION

Molten uranium (U) has been considered as a fuel candidate for high-temperature (>1100° C) nuclear reactor concepts for space power generation. For example, molten U (melting point, 1132° C) has been considered for use in small liquid-metal-cooled Rankine cycle reactors and in thermionic reactors for space power systems.

Molten U has several advantages over solid ceramic fuels such as uranium oxide (UO_2), uranium carbide (UC), and uranium nitride (UN). The relatively high thermal conductivity of U plus convective flow of the liquid would reduce thermal gradients and thus result in a nearly isothermal heat source. Also, because the U density is higher than in solid ceramic fuels, smaller and lighter reactors are possible for space vehicles. In addition, fuel element swelling, a major problem with solid fuels, would be eliminated by using a molten fuel.

The use of molten U in reactors, however, does present several problem areas. Chief among these, from a materials standpoint, is containment of the liquid. Molten U and molten U alloys have been reported (refs. 1 and 2) to be extremely corrosive. Depending on the container material (type and purity) and reactor operating conditions (e. g. , temperature and temperature gradients), corrosion can occur by chemical reaction, alloying, integranular attack, and/or mass-transfer attack.

This study was undertaken to further evaluate the corrosion problems associated with containment of molten U in the temperature range of 1200° to 1500° C. Metals, rather than ceramics or ceramic-coated metals, were selected for study as containment materials for several reasons. Metals generally exhibit much better thermal conductivity and thermal shock resistance than ceramics. In addition, the fabricability and the probability of obtaining a defect-free container would be much better with a metal than with a ceramic or ceramic-coated metal. A previous corrosion study on metals (ref. 1) indicated that tungsten (W) resists U attack in short term (<10 hr) iosthermal (800° to 1500° C) tests to a greater extent than many other metals (including chromium, manganese, iron, cobalt, nickel, titanium, zirconium, vanadium, niobium, tantalum, molybdenum, iridium, rhenium, 18:10:1 stainless steel, Nimonic 80, and Inconel). Tungsten apparently exhibited the best U corrosion resistance because no eutectic or chemical compound forms between W and U, and because U and W exhibit low mutal solubilities at elevated temperatures (refs. 3 and 4). However, even W was reported (ref. 1) to exhibit some intergranular penetration by U at temperatures over 1300° C. Unfortunately, several of the properties which could affect the corrosion resistance of W were not reported in reference 1 - for example, the method of fabrication, the grain size, and the purity of the W. Therefore, it was decided to conduct further tests in the temperature range of 1200° to 1500° C on W capsules containing molten U.

The objectives of these tests were (1) to study the potential of W for long term (>10 000 hr) containment of liquid U and (2) to study the compatibility of U with several types of W. A corollary study between U and tungsten - 1. 5-weight-percent-hafnium (W-1. 5Hf) alloy also was undertaken. Hafnium was selected to be alloyed with W to determine whether this relatively strong oxygen getter could affect corrosion by tying up oxygen. Corrosion in other liquid metal systems has been reduced by tying up oxygen; for example, zirconium has been added to niobium to reduce intergranular attack by alkali metals (ref. 5).
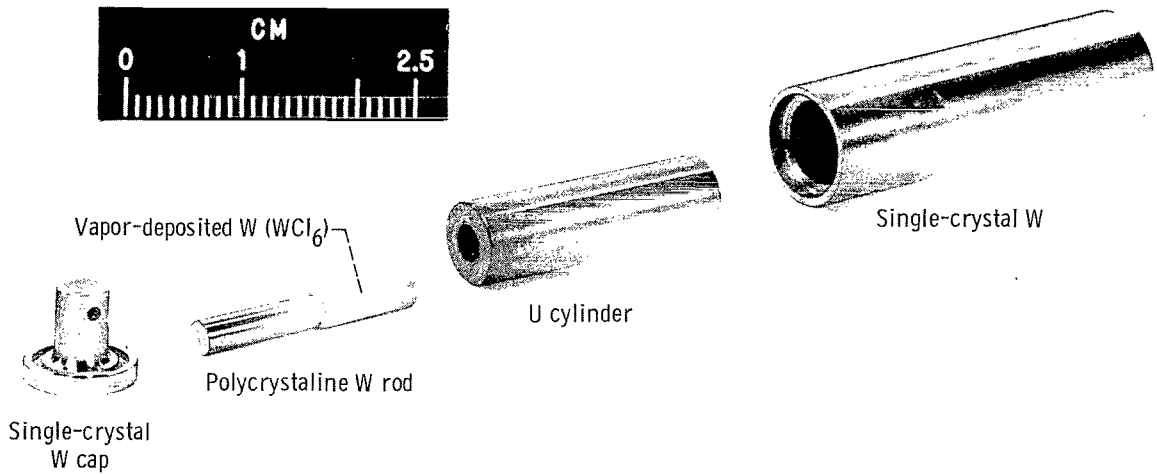
Test capsules were prepared from both single-crystal W and polycrystalline W-1. 5Hf rods. Single crystals of W were used to isolate the mode of corrosion in the absence of grain boundaries. Also, swaged polycrystalline W rods (partially clad with vapor-deposited W) were inserted into the single-crystal capsules to enable a comparison of the extent of grain boundary attack on two types of W.

The capsules were loaded with U, sealed by electron beam welding, and isothermally treated for 10 to 200 hours at 1200° or 1500° C in vacuum. After thermal treatments, the capsules were evaluated by metallographic, radiographic, autoradiographic, and visual observation. The results of these evaluations are presented in this report.
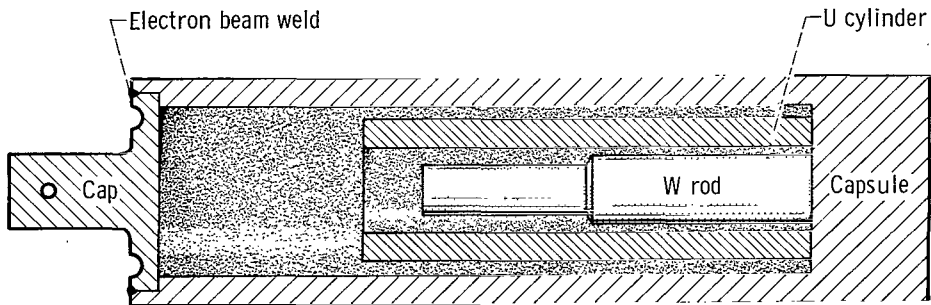
EXPERIMENTAL PROCEDURE

Test Capsule Components

Both W and W-1. 5Hf capsules were fabricated for compatibility tests with U. The W capsules were fabricated from 0. 50-inch- (1. 3-cm-) diameter single-crystal rods. And a 0. 125-inch- (0. 32-cm-) diameter polycrystalline W rod (partially clad with vapor-deposited W) was inserted into most of the W capsules along with a U cylinder (fig. 1). This configuration permitted comparison of U attack on two types of polycrystalline W as well as on single-crystal W. The W-1. 5Hf capsules were similar to the W capsule shown in figure 1 except that they were fabricated from wrought polycrystalline material because single crystals of this alloy were not available. Thus it was unnecessary to insert polycrystalline rods into the W-1. 5Hf capsules.

Vapor-deposited W (WCl$_6$)

Single-crystal W

U cylinder

Polycrystaline W rod

Single-crystal
W cap

(a) Exploded view.

Electron beam weld

U cylinder

Cap

W rod

Capsule

(b) Cross section of assembled view (not to scale).

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Figure 1. - Tungsten-uranium (W-U) capsule components.

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Fabrication of Capsule Components

The single-crystal W capsules were fabricated from a rod grown by a commercial vendor using the Arc-Verneuil technique ((111) was perpendicular to the rod axis). Laue X-ray patterns indicated that no grain boundaries were present in any of the capsules within a 2° tilt or rotation sensitivity limits. The W-1.5Hf capsules were fabricated from extruded (at 2200° C) and swaged (at 1700° C) arc-cast polycrystalline rod. The grains in these capsules (W-1.5Hf) were elongated in the direction of the axis and appeared highly worked (fig. 2(c)). An analysis of the chemical purity of both capsule metals is presented in table I along with analyses for the other capsule components.

The rods were machined into capsules and lids by (1) grinding the outside diameter of each rod to 0.50 inch (1.3 cm), (2) cutting the rods into proper lengths for capsules and capsule lids, and (3) machining a weld preparation groove into each lid (fig. 1(a)) and a blind hole into each rod by electric discharge machining (EDM) in oil. EDM was selected to reduce residual stresses left in the capsule walls and to reduce the frequency of fracturing of capsules during machining (compared to drilling and boring). However, EDM resulted in a roughened surface (fig. 2(a)) which was contaminated with carbon. The surface roughness and carbon contamination were eliminated by electropolishing a 0.005-inch- (0.13-mm-) thick layer of metal from the internal capsule surface. A typically smooth electropolished surface is illustrated in figure 2(b). Chemical analysis indicated that the carbon content in a W capsule was reduced from 17 to 2 ppm by electropolishing. These values correspond to a concentration of 400 to 500 ppm by weight of carbon in the 0.005-inch- (0.13-mm-) thick surface layer which was removed.

The polycrystalline W rods (which were inserted into the single-crystal capsules) were obtained from commercially available swaged rod. One-half of each polycrystalline rod was coated with a 0.005-inch- (0.13-mm-) thick layer of vapor-deposited W (produced by hydrogen reduction of tungsten-hexachloride gas). A typical microstructure of the W rod and coating is shown in figure 2(d).

The U cylinders were furnished by the Los Alamos Scientific Laboratory. Just prior to insertion into the capsules, the U cylinders were electropolished (in a solution of sulfuric acid saturated with chromic acid and diluted 25 percent with water) to remove surface oxides.

The capsule lids were sealed onto the capsules by electron beam welding in a vacuum of 10^{-6} torr. Each welded capsule was checked for defects by dye penetrant inspection and by helium pressurization followed by immersion in alcohol and inspection for gas bubbles. Finally, each capsule (except for capsule 5 in table II) was heated for 5 minutes at 1200° C to melt the U and freeze the capsule components in place for shipment to the Los Alamos Scientific Laboratory.
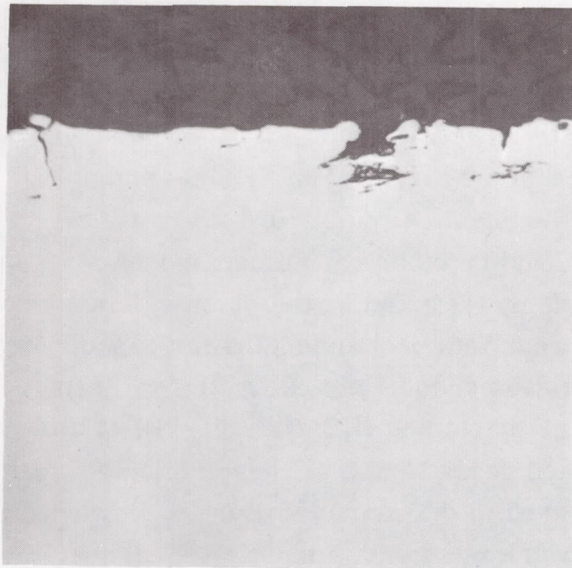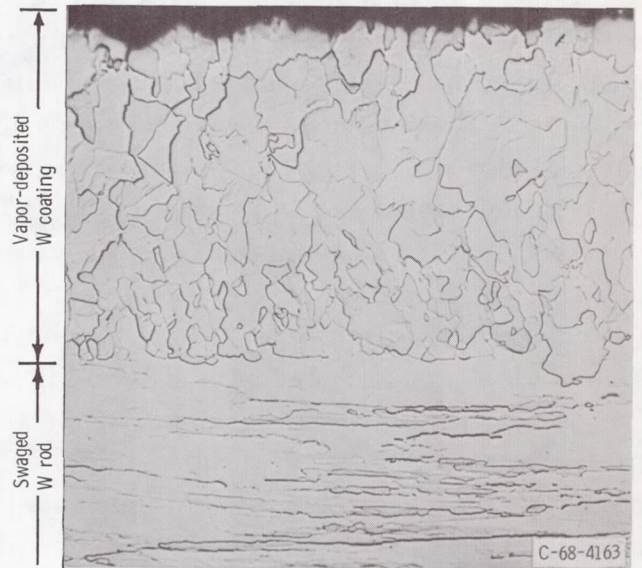
(a) Interior capsule surface after electric discharge machining.
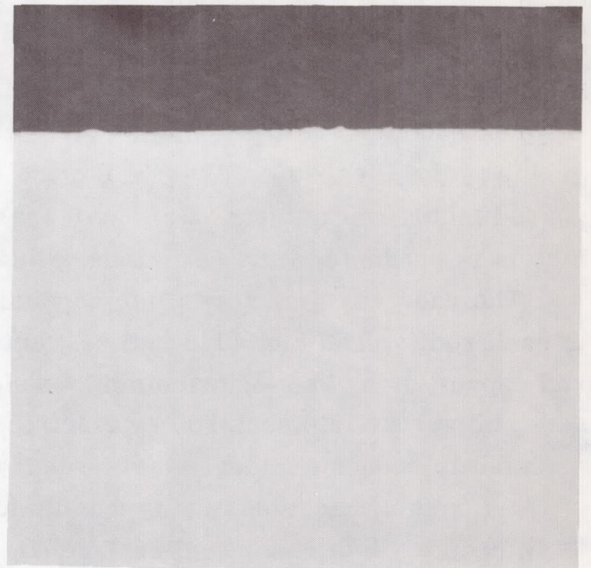
(b) Interior capsule surface after electropolishing.

(c) Swaged W-1.5Hf capsule. Murakami's etchant.

(d) Tungsten rod insert. Murakami's etchant.

Figure 2. - Photomicrographs of tungsten (W) and tungsten - 1.5-percent-hafnium (W-1.5Hf) capsules and inserts showing the interior capsule surfaces and the microstructures in the "as-fabricated" condition. 250X.

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TABLE I. - CHEMICAL ANALYSIS OF CAPSULE COMPONENTS

[Chemical analysis, ppm by weight (unless otherwise noted).]

Element	Single-crystal W rod	W-1.5Hf rod	Polycrystalline W rod	Vapor-deposited W (WCl$_6$ process)	U rod
Hf	[a]ND	1.45 wt.%	ND	ND	ND
C	4	8	9	3	400
Cl	15	<10	<10	20	<5
F	13	<5	<5	ND	2
H	1	2	1	3	1
N	5	13	<5	5	86
O	2	236	1	20	139
P	15	12	ND	ND	<15
S	27	<10	ND	ND	<10
Ag	<1	<1	<1	ND	ND
Al	<1	<1	<1	ND	30
B	<1	1	<1	ND	<1
Be	<1	<1	<1	ND	<10
Ca	<1	<1	<1	ND	<1
.Cd	<1	<1	<1	ND	<1
Co	<1	<1	<1	ND	<1
Cr	<1	3	<1	ND	<5
Cu	<1	<1	<1	ND	1
Fe	<1	3	7	ND	120
Mg	<1	1	<1	ND	<1
Mr	<1	1	<1	ND	20
Mo	ND	100	100	ND	700
Na	<1	<1	<1	ND	<1
Ni	<1	2	<1	ND	<5
Pb	ND	<1	<1	ND	<1
Si	<1	2	2	ND	250
Sn	<1	5	<1	ND	<5
Ti	<1	<1	<1	ND	<10
U	<10	<20	2	ND	ND
V	1	<1	<1	ND	<10
Zn	<10	<10	<10	ND	ND
Zr	ND	300	<1	ND	<10
K	<1	<1	<1	ND	<1
W	ND	ND	ND	ND	<13

[a]ND, not determined.

TABLE II. – SUMMARY OF CAPSULE TESTS AND RESULTS

Capsule	Capsule metal	Fabrication induced cracks	Test conditions - time, temperature, method of supporting capsule in furnace	Type of grain structure; extent of intergranular penetration by uranium	Single-crystal attack	Type and location of tungsten precipitate	Weld zone U in weld	Weld zone U through weld	Wetting contact angle,[a] deg	Estimated U loss, percent[b]
1	W	Small crack near weld; crack next to U	10 hr, 1200° C, pedestal	Worked structure; slight penetration but more in rod than in vapor-deposited W	None	None	No	No	7	80
2	W	Small crack near weld	100 hr, 1200° C, pedestal	Recrystallized structure; extensive penetration especially in rod	Slight dissolution	Fine precipitate at meniscus	Yes	No	10	5
3	W	None	100 hr, 1500° C, wire	Recrystallized; epitaxial grain growth; extensive penetration and some separation of grain from rod	Moderate dissolution; concentrated at meniscus	Dendrites near meniscus at the capsule walls	Yes	Yes	17	5
4	W	None	Two 100-hr cycles, 1500° C, MgO can on pedestal	Recrystallized; extensive penetration and partial disintegration due to grain separation	Mass transfer from one area near meniscus	Massive dendrites near meniscus and extending from walls	Yes	Yes	16	50
5	W	None	200 hr, 1500° C, wire	No polycrystalline W present	Moderate dissolution; most severe near meniscus	Fine precipitate at meniscus; dendrites near meniscus	Yes	No	18	0
6	W-1.5Hf	Small cracks near weld; longitudinal crack	10 hr, 1200° C, pedestal	Worked structure; some penetration in recrystallized zones	------------	Fine precipitate at meniscus and at bottom of capsule	Yes	Yes	5	30
7	W-1.5Hf	Small cracks near weld-crack next to U	Two 100-hr cycles, 1500° C, MgO can on pedestal	Recrystallized; extensive penetration localized areas	------------	Massive dendrites near meniscus and extending from rods	Yes	Yes	16	20

[a]Angle measured between U meniscus and capsule wall.

[b]Based on radiographs.

Capsule Furnace Treatments and Evaluation

Each capsule was furnace treated individually in continuous isothermal treatments at 1200° or 1500° C for 10, 100, or 200 hours. Except for capsule 5, which was furnace treated at the Lewis Research Center, the furnace treatments were performed at the Los Alamos Scientific Laboratory. Both furnaces always operated at pressures below 2×10^{-5} torr and generally below 4×10^{-6} torr.

The capsules were supported in the furnaces by various means (see table II). While some capsules were suspended in the furnace by a wire, the others were supported on a pedestal to (1) allow thermal conduction from both ends of the capsules and (2) prevent attack of the supporting wire by U. Several capsules were inserted into magnesium oxide (MgO) cans which were then placed on the pedestal. This was done to help contain the U in case of leakage and to reduce the heat conduction from the capsules.

The temperature gradient in the Los Alamos furnace was measured to be less than 5° C (at 1500° C) across a 9-inch- (22.9-cm-) long by 4-inch- (10.2-cm-) diameter heat zone. The gradient along the capsules is estimated to be less than 1° C by assuming a linear temperature gradient. The temperature gradient in the Lewis furnace was measured to be less than 8° C (at 1500° C) across a 1.5-inch- (3.8-cm-) long by 1.5-inch- (3.8-cm-) diameter heat zone. The gradient along the capsules in this furnace is estimated to be less than 3° C.

After furnace testing, the capsules were evaluated at the Lewis Research Center by visual, metallographic, autoradiographic, and radiographic examinations. In order to observe the microstructures, the W was etched with Murakami's etchant, and U was etched by heat tinting. Weight loss measurements were obscured because of the U which leaked out of capsules but remained on their external surfaces. However, an indication of the amount of U loss was obtained from radiographs of the capsules showing the height change of U in the capsules. None of the capsules exhibited any dimensional changes as a result of testing.

RESULTS OF CAPSULE TESTS

Seven W and W-1.5Hf capsules containing U were tested for various times at 1200° or 1500° C. The results of these tests are summarized in table II and are described in the next sections.

Tungsten Capsule Tests

1200° C for 10 hours. - The capsule tested at 1200° C for 10 hours (capsule 1 in table II) is shown in figure 3. The top of the capsule was broken (fig. 3(a)) after the test during attempts to separate the capsule from the tantalum (Ta) can used to hold the capsule in the furnace. The adhesion between the capsule and the Ta resulted from U leakage. About 80 percent of the U had leaked out of this capsule through fabrication-induced cracks; these cracks and the resultant U leaks were observed visually (fig. 3(a)).

As an interesting sidelight, figure 3(b-1) illustrates the relatively extensive intergranular penetration of U into the Ta can compared to the penetration of U into the W rod (fig. 3(b-2)). This supports other results (ref. 1) which indicate that Ta is less resistant than W to U intergranular attack.

Although most of the U leaked out of this capsule, enough was left to ensure that part of the W capsule and the rod insert were exposed to U for the total test time. After 10 hours, attack was not observed on the single-crystal capsule; that is, the wall edges appeared similar to the "as-fabricated" walls (fig. 2(b)). A small amount of intergranular penetration of U into the polycrystalline W rod insert (the shape of the insert resulted from the angle of sectioning) was observed (fig. 3(b-2)), but this penetration did not extend across the entire rod. As may be seen, the polycrystalline rod exhibited more U penetration than did the vapor-deposited coating.

1200° C for 100 hours. - A small amount of U leaked out of the capsule tested for 100 hours at 1200° C (capsule 2 in table II). The leakage from the capsule appeared to come from cracks which developed just below the U meniscus (i.e., gas-liquid interface). The U which had leaked out was observed on the external capsule surface in the form of either a thin film or as a blister (fig. 4(a)). Some of the cracks observed contained no U (fig. 4(b-1)), which indicated that they formed after the U solidified-that is, during cooling or metallographic preparation.

The polycrystalline W rod insert was recrystallized during the test (fig. 4(b-2)), and U was observed to have penetrated throughout the rod and its coating. The rod appeared to be attacked to a greater extent than the coating (compare figs. 4(b-3) and (b-4)). As may be seen in these figures, some W grains separated from the rod but not from the coating. Other than some surface dissolution (roughening of the surface), no corrosive attack by U on the single-crystal capsule was observed (fig. 4(b-5)).

An interesting phenomenon was observed at the U meniscus (fig. 4(b-1)). A relatively large number of small metallic-appearing crystals were found along the meniscus compared to the rest of the uranium melt. These crystals were identified as W by electron microprobe analysis.

1500° C for 100 hours. - Similar to the W capsule tested at 1200° C for 100 hours, the capsule tested at 1500° C for 100 hours (capsule 3 in table II) lost only a small
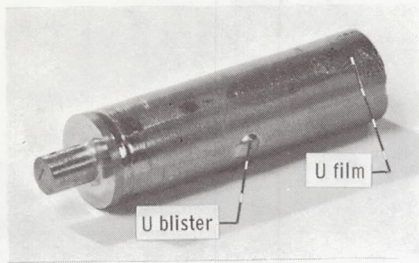
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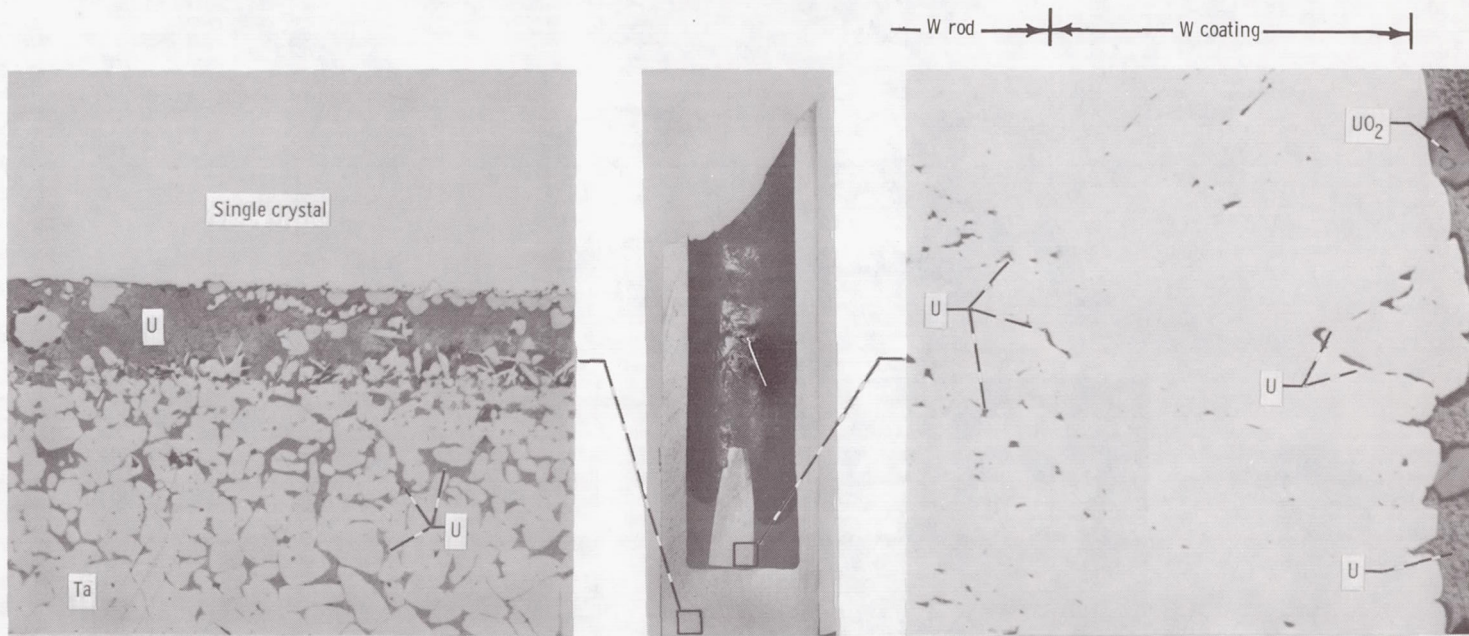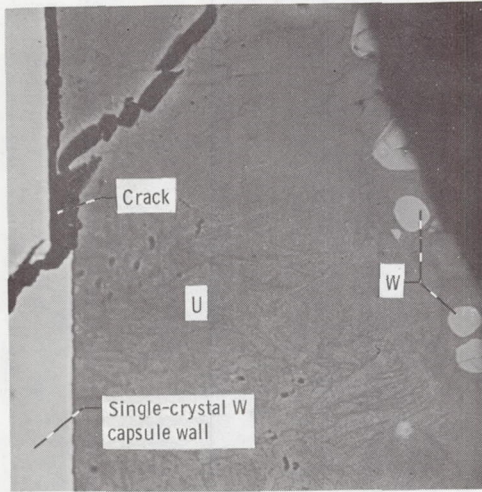
(a) Capsule.

(b-1) 250X.

(b-2) 500X.
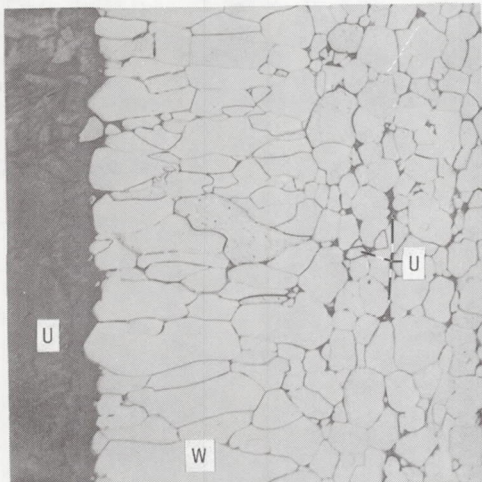
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(b) Photomicrographs of sectioned capsule.

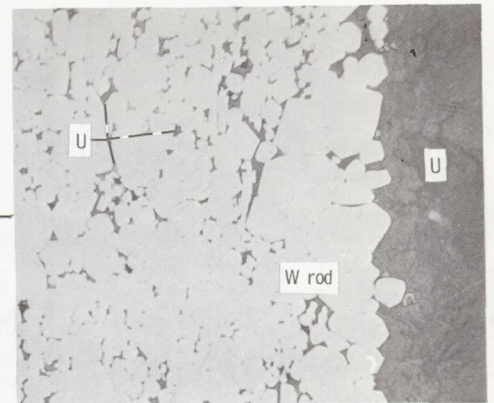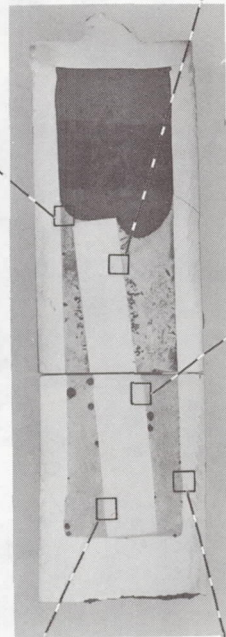Figure 3. - Tungsten (W) capsule tested for 10 hours at 1200° C.
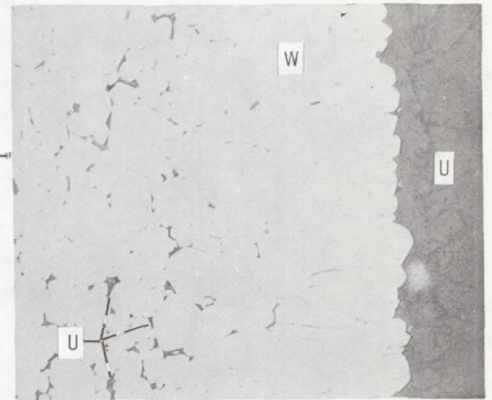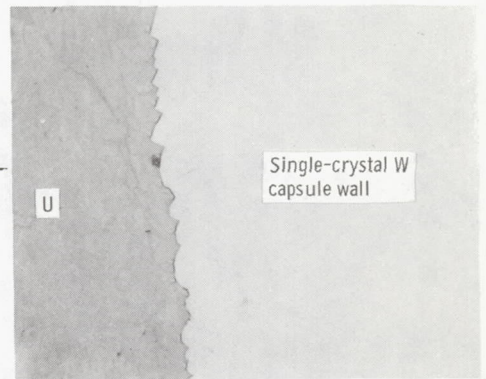
(a) Capsule.

(b-1).

(b-2) Murakami's etchant.

(b-3).

(b-4).

(b-5).

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(b) Photomicrographs of sectioned capsule. 250X.

Figure 4. - Tungsten (W) capsule tested for 100 hours at 1200° C.

amount of its U through cracks near the U meniscus (fig. 5). The dull appearance of this capsule (fig. 5(a)) resulted from a reaction between U and the Ta wire used to support the capsule in the furnace.
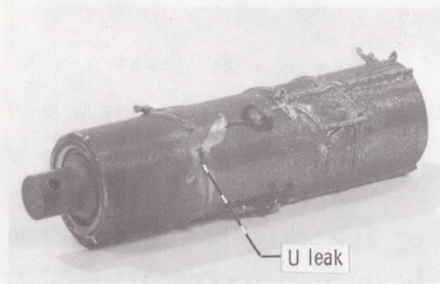
The autoradiograph shown in figure 5(b) (typical of those taken on other capsules) illustrates two points. First, the thin film of U (resulting from leaks) on most of the external capsule surface is indicative of the good wetting between U and W. And second, the figure indicates that a thin film of U is present on the internal capsule walls above the melt level. Some of the U depicted by the autoradiograph was also metallographically observed (fig. 5(c-1)). In addition, the latter figure illustrates intergranular penetration of U into, and through, the weld.

Both the single-crystal and polycrystalline W exhibited evidence of U attack. The single-crystal wall exhibited some dissolution below the U meniscus and appeared similar to figure 4(b-2). However, the single crystal was more extensively attacked near the meniscus. As shown in figure 5(c-2), the crystal wall exhibited considerable dissolution: this was greatest in regions near the meniscus. In addition, large W dendrites (identified by electron microprobe analysis) were observed along the capsule wall near the meniscus.
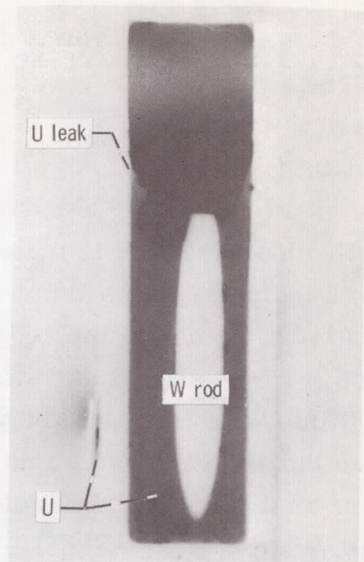
The W rod and vapor-deposited coating were recrystallized during the test, and epitaxial grain growth made it impossible to distinguish the W rod from its coating (fig. 5(c-3)). As illustrated in figure 5(c-4), the rod and coating exhibited extensive U intergranular penetration throughout. In addition, the surface of the rod exhibited considerable dissolution.

1500° C for two 100-hour cycles. - About half of the U was lost from the capsule tested at 1500° C for 200 hours (capsule 4 in table II). Most of this loss occurred during the second 100-hour cycle according to the radiographs (figs. 6(a) to (c)). However, formation of a large void (or gas bubble) and mass transfer from one side of the capsule wall began during the first 100-hour cycle. As can be seen in figures 6(d) and (e-1), the U leaked out of a crack located just below the original meniscus and in the vicinity of the large void. The source of this void, which was not observed in any other capsule, is unknown. Therefore, the results on this capsule should be considered anomalous. However, these results are presented herein because they may indicate a potential problem.
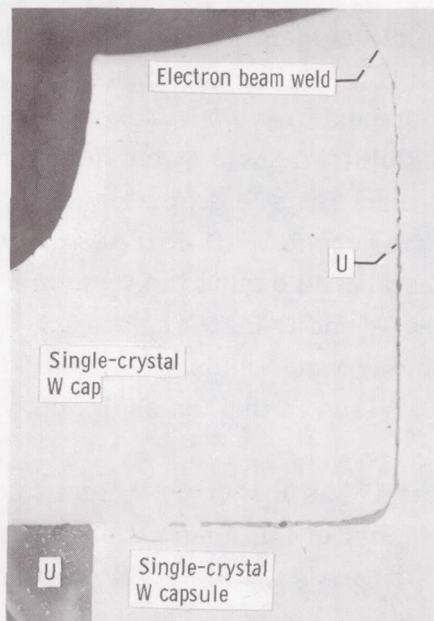
Uranium attack on the polycrystalline W is illustrated in figure 6(e-2). Similar to the capsule tested at 1500° C for 100 hours, U penetrated into grain boundaries throughout the W rod and coating. Part of the uncoated rod was disintegrated because grains separated from the rod. Also, some surface dissolution from both the rod and the capsule walls was observed. In addition, a layer of grains was formed along parts of the single-crystal capsule walls. This recrystallized layer is presumably due to insufficient removal of the EDM-damaged surface in localized areas. According to reference 6, EDM can convert a single-crystal surface into a cold-worked polycrystalline state.

(a) Capsule.

U leak

(b) Autoradiograph of sectioned capsule.

U leak

W rod

U

Electron beam weld

Weld area

U

Single-crystal
W cap

U

Single-crystal
W capsule

(c-1) 50X.

U

W

U

(c-3) 250X.

Single-crystal
W wall

W dendrite

U

(c-2) 250X.

U

U

W

U
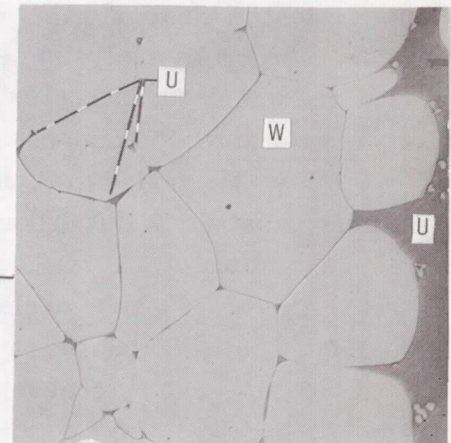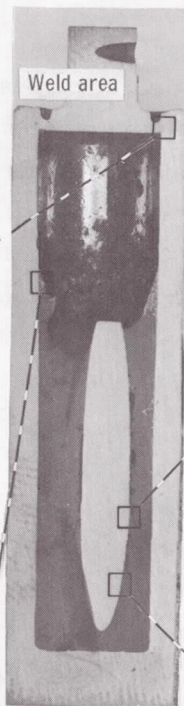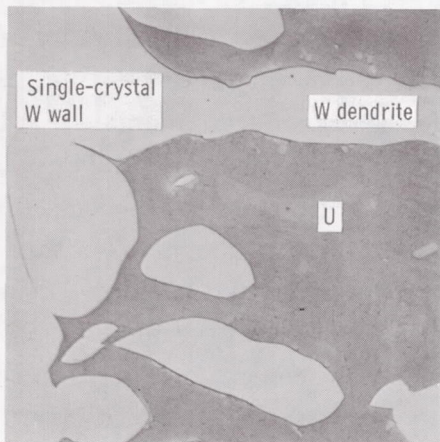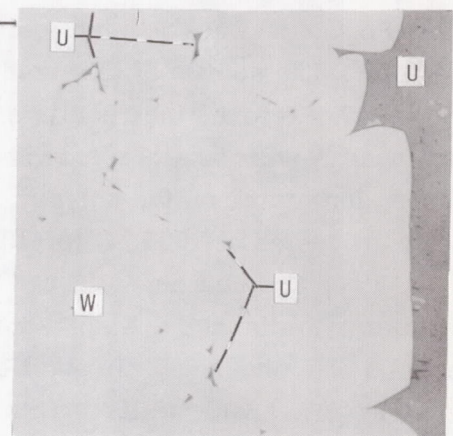
(c-4) 250X.

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(c) Photomicrographs of sectioned capsule.

Figure 5. – Tungsten (W) capsule tested for 100 hours at 1500° C.

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(a) Radiograph, as-fabricated condition.
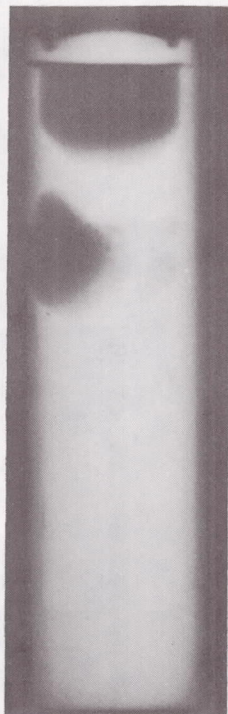
(b) Radiograph, after 100 hours.
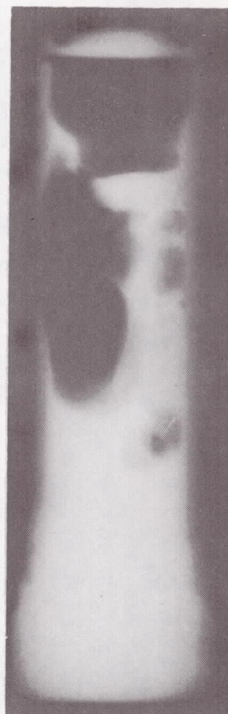
(c) Radiograph, after 200 hours.

(d) Autoradiograph, sectioned capsule after 200 hours.
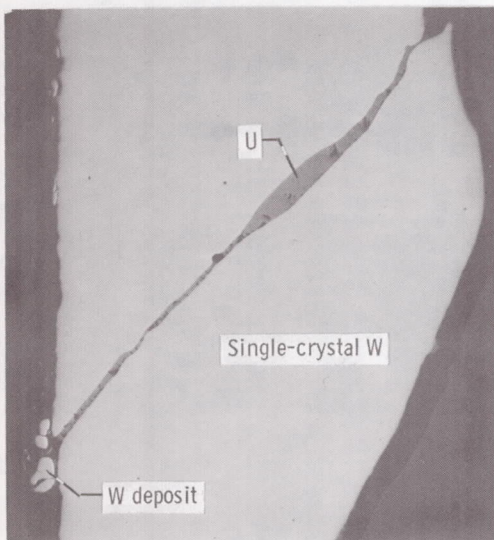
(e-1) 50X.
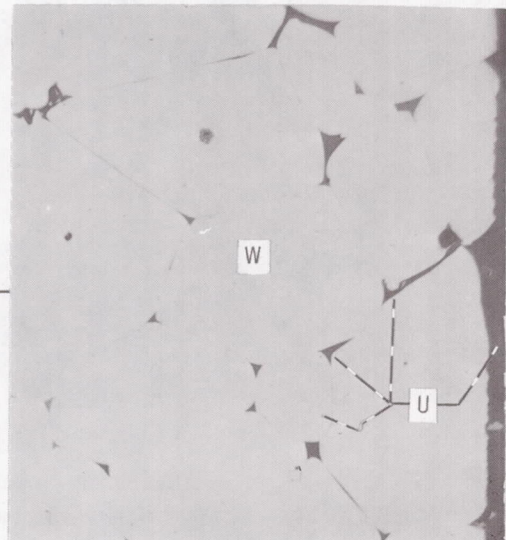
(e-2) 250X.

C-68-4167

(e) Photomicrographs of sectioned capsule.

Figure 6. – Tungsten (W) capsule tested for two 100-hour cycles at 1500° C.

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(a) Capsule.

(b-1).

(b-2).

(b-3).
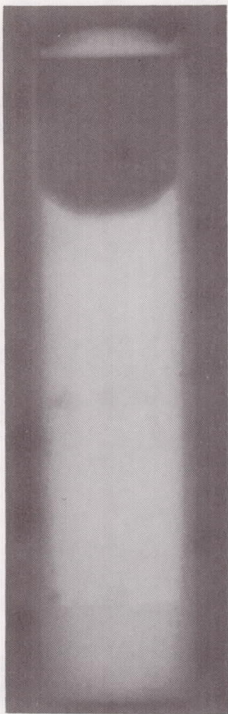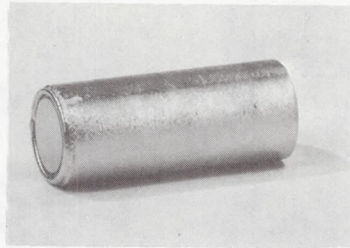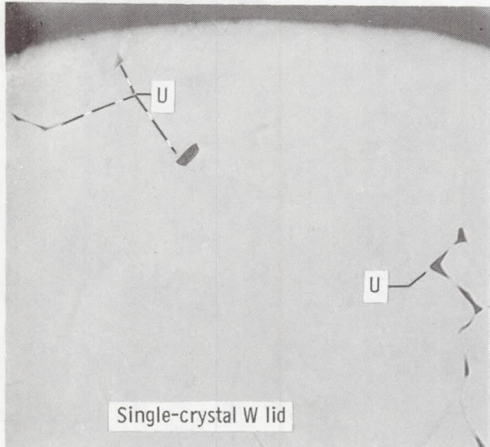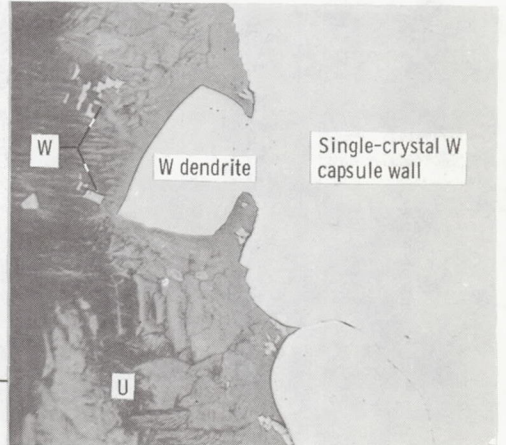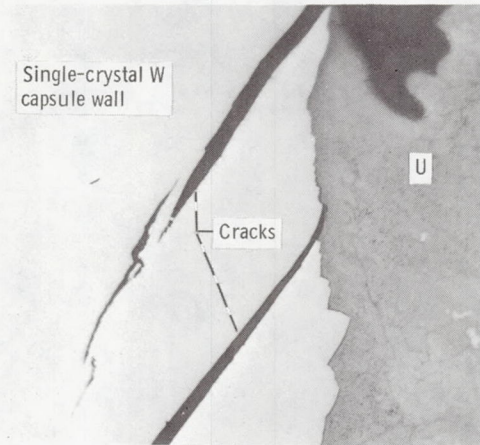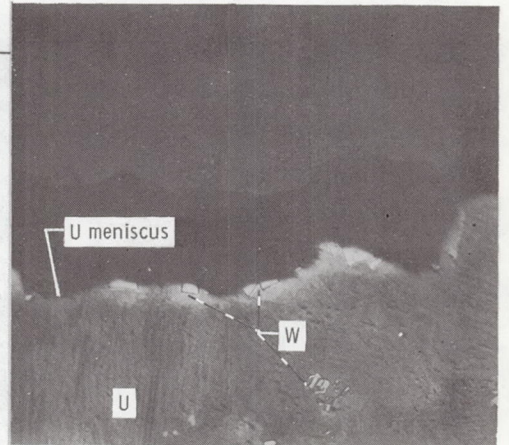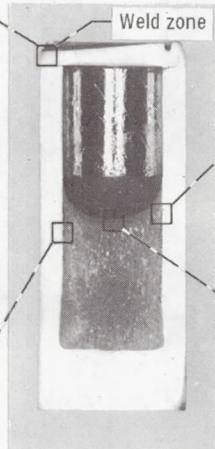
(b-4).

C-68-4168

(b) Photomicrographs of sectioned capsule. 250X.

Figure 7. – Tungsten (W) capsule tested for 200 hours at 1500° C.

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Massive W dendrites were observed just below the U meniscus similar to the 100-hour test. In addition, a dendritic structure (with U between the W dendrites) was observed to extend from the position of the original U meniscus to the final meniscus (fig. 6(e)). And this structure was located on the side of the capsule opposite to the location of the U leak and the area of mass transfer previously mentioned.

1500° C for 200 hours. - This test (capsule 5 in table II) was distinguished from the other single-crystal capsule tests in two ways. First, in order to better establish the effect of thermal cycling on the other capsules, this capsule was heated and cooled only once. And second, in order to determine whether polycrystalline W affected the corrosion of the other single-crystal capsules, no polycrystalline W rod was inserted into this capsule.

After 200 hours at 1500° C, no U loss from this capsule was detected by either weight loss measurements or by visual examination (see fig. 7(a)) in contrast to every other capsule tested. However, metallographic examination revealed that U had almost leaked out of the capsule by penetrating along grain boundaries in the weld zone (fig. 7(b-1)). In addition, metallographic examination revealed two cracks in the capsule wall (fig. 7(b-2)) which extended across three-fourths of the wall thickness. These cracks contained no U, indicating that they were formed after the U had finally solidified. It thus appears that if a capsule is not thermally cycled, the period of effective U containment by single-crystal W depends on the rate of U intergranular attack on the weld.

The extent of U corrosive attack on the single crystal was not significantly different than for any other capsule (except for the anomalous results on the capsule shown in fig. 6). The walls of the single crystal exhibited some dissolution and, for the most part, appeared similar to figure 7(b-2) without the cracks. However, the wall near the meniscus was more heavily corroded as shown in figure 7(b-3). This figure also illustrates the relatively small dendrites beginning to grow out from the wall. And, similar to the other capsules, figure 7(b-4) indicates a higher concentration of W precipitate at the U meniscus. The amount of dendrites and other W precipitates is significantly less than the other single crystal tested at 1500° C for 100 hours less time (fig. 5). This observation indicates that most of the W transferred to the meniscus and to dendrites near the meniscus in that capsule originated from the polycrystalline W.

Tungsten - 1. 5-Percent-Hafnium Capsule Tests

1200° C for 10 hours. - After only 10 hours, this W-1.5Hf capsule (capsule 6 in table II) lost over one-fourth of its U. However, much of this leakage probably resulted from radial cracks which originated during fabrication. Typical external cracks and U leaks are shown in figure 8(a). Internal longitudinal cracks in the capsule also were observed in areas adjacent to the U melt (fig. 8(b)). But these cracks did not contain any

(a) Capsule.
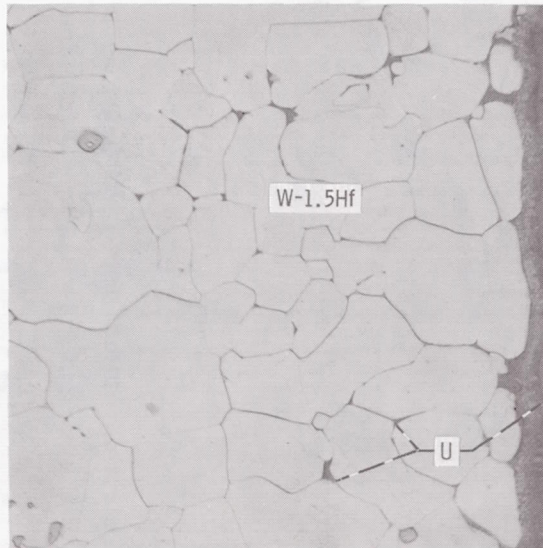
W-1.5Hf

U

HfO$_2$

(b-2).

W-1.5Hf

U

W-1.5Hf

Dendrites

Cracks

U

HfO$_2$

U

(b-1) Murakami's etchant.

(b-3).

C-68-4170

(b) Photomicrographs of sectioned capsule. 250X.

Figure 9. - Tungsten - 1.5-percent-hafnium (W-1.5Hf) capsule tested for two 100-hour cycles at 1500° C.

(a) Capsule.

(b-1) Murakami's etchant.
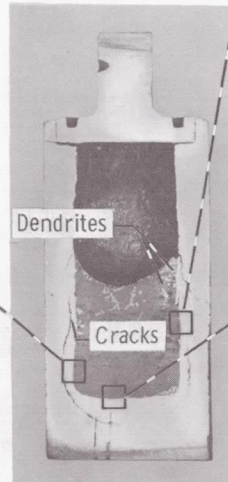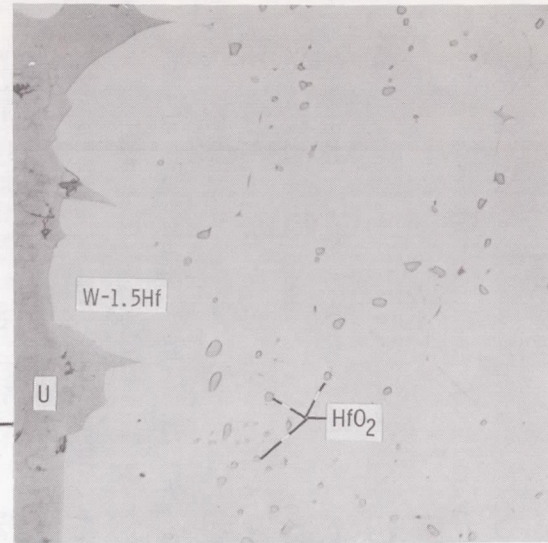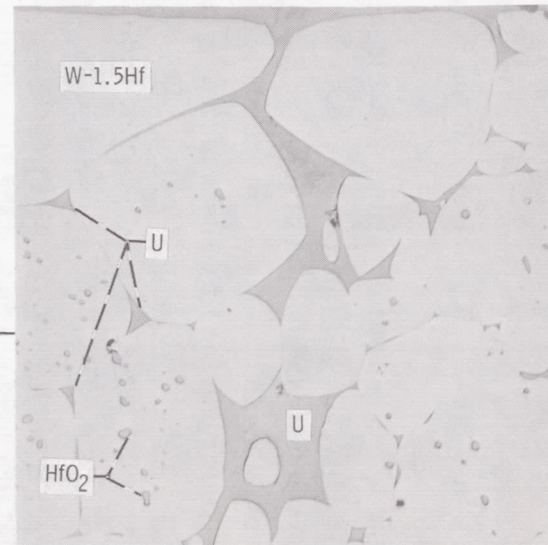
(b-2).

(b-3).

C-68-4170

(b) Photomicrographs of sectioned capsule. 250X.

Figure 9. - Tungsten - 1.5-percent-hafnium (W-1.5Hf) capsule tested for two 100-hour cycles at 1500° C.

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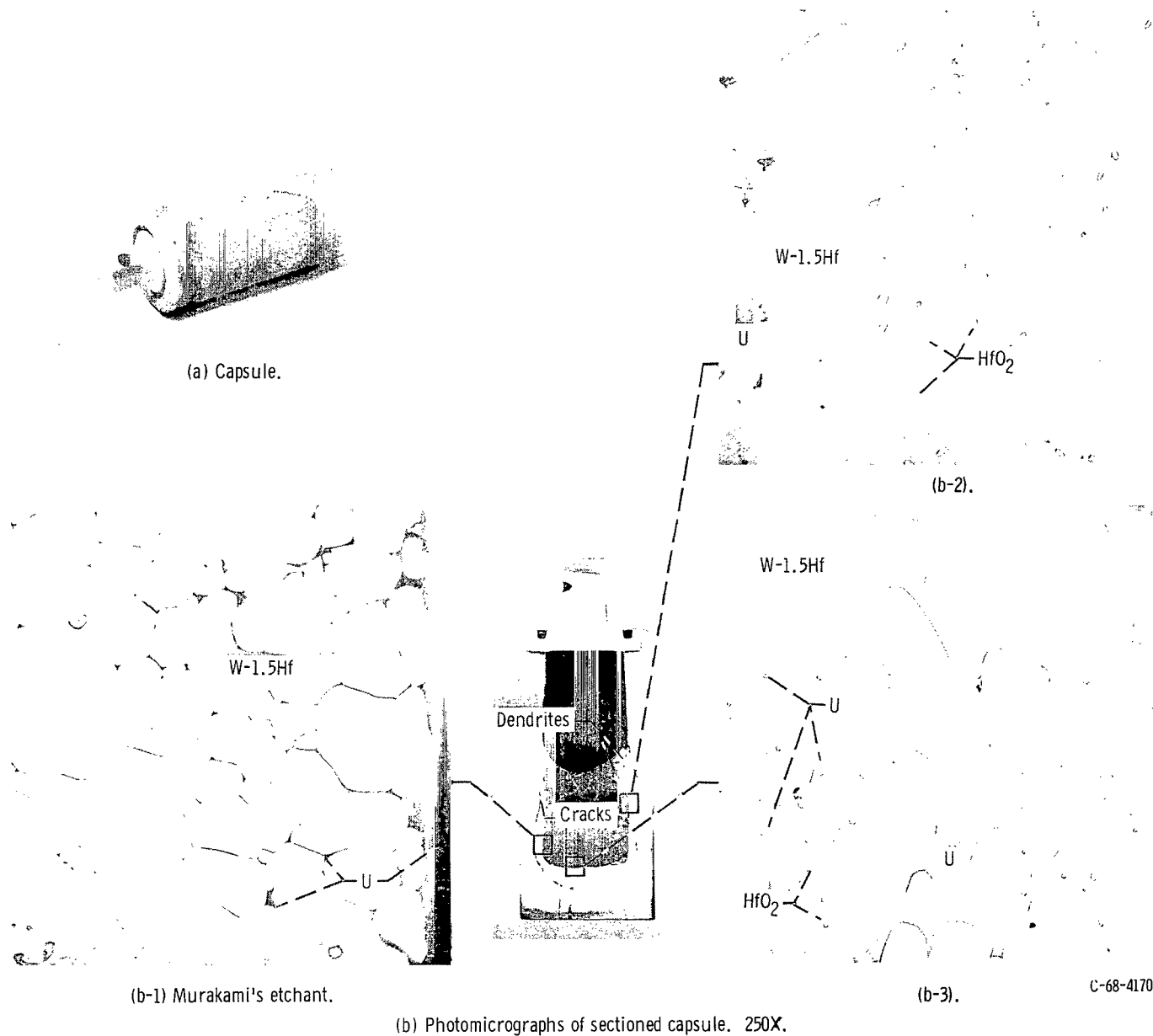
U and, therefore, formed after the U solidified.

In contrast to the polycrystalline W rod tested for 10 hours (fig. 3(b-2)), U was not observed to have penetrated into the worked grain structure of this capsule. However, U did penetrate into grain boundaries in the recrystallized weld zone. As may be observed in figure 8(b-1), U penetrated through grain boundaries in the weld zone to the external surface.

Similar to the W capsules, fine metallic-appearing crystals were observed near the U meniscus (fig. 8(b-2)). In addition, both fine crystals and larger cubical crystals were observed near the bottom of the U melt (fig. 8(b-3)). All of these crystals were identified as W by electron microprobe analysis (the microprobe was not sensitive enough to distinguish the Hf content in the crystals).

1500° C for two 100-hour cycles. - Less than one-fifth of the U leaked out of the W-1.5Hf capsule tested for two 100-hour cycles (capsule 7 in table II). The dull appearance of the capsule (fig. 9(a)) is due to a surface reaction with the magnesium oxide (MgO) holder can. Similar to the W-1.5Hf capsule tested for 10 hours, this capsule exhibited longitudinal cracks surrounding the U melt (fig. 9(b)). Although most of these cracks contained no U some cracks did contain U according to autoradiographs. This observation indicates that some of the cracks were formed before, and some after, the last U meltdown, that is, the second 100-hour thermal treatment.

The initial worked structure of the capsule was completely recrystallized during the test (fig. 9(b-1)). Some areas of the capsule exhibited little or no U intergranular penetration (fig. 9(b-2)) while other areas, especially in the vicinity of the weld or capsule cracks (fig. 9(b-3)), exhibited extensive intergranular attack. The small, nearly spherical phase distributed throughout the microstructure was not identified but is believed to be hafnium oxide (HfO_2). This phase was grey-colored and did not tarnish during heat tinting as U does.

Similar to the W capsules at 1500° C, fine crystals and massive dendrites (see fig. 9(b)) of W were observed in the U melt near the meniscus. And dissolution of the capsule surface by U (i.e., the roughened walls) also is evident in figure 9(b).

DISCUSSION OF RESULTS

As previously stated, this investigation was performed not solely to study the containment of U by W but also to study the compatibility of U with several types of unalloyed W and a W-1.5Hf alloy. Thus, even though U leaked out of most of the capsules during testing, the main objective was satisfied as long as some U remained in the capsule for the test duration. These leaks might have affected compatibility results by permitting impurities in the external atmosphere to enter into the capsules. But I believe that they did not have a significant effect for two reasons. First, attack on the wall of

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the capsule which did not leak (capsule 5 in table II) was similar to the attack on those capsules which did leak U. And second, the U vapor pressure at test temperatures was slightly higher than the external vacuum pressure; this higher internal pressure would tend to inhibit any flow of gaseous impurities from the external atmosphere into the capsules.

Intergranular Attack

One study (ref. 7) has indicated that it may be possible to fabricate and weld single-crystal W without recrystallization. But the difficulties and expense in producing single crystals would probably require the use of polycrystalline W in any practical reactor concept. Therefore, the extent of intergranular attack by U on polycrystalline containment materials is of particular importance to reactor applications.

The mechanism of intergranular attack by liquid metals on solid metal is complex and depends on several variables. In general, attack is believed to concentrate at grain boundaries because they are at a higher energy level than the grains and because they often contain a higher concentration of impurities than the grains. Factors which have been observed to enhance grain boundary attack include the following: (1) reactive impurities (e.g., oxygen, nitrogen, and carbon) in either the liquid metal or the solid containment metal, (2) selective removal of a constituent from an alloy, (3) large grain size, (4) low surface tension between the liquid and solid metal, (5) solubility between the liquid and solid metal, and (6) high temperatures (refs. 1, 5, and 8).

In this study, intergranular penetration of U into W was observed after only 10 hours at 1200° C. And the extent of penetration increased with both temperature and time. Thus, neither vapor-deposited nor wrought W rod appears to be a suitable container material for molten U.

It is interesting to make a comparison of the amounts of U intergranular penetration in the vapor-deposited W and the wrought W rod. At 1500° C, epitaxial grain growth across the coating-rod interface resulted in a microstructure with equal penetration of U into the coating and the rod. However, at 1200° C, epitaxial grain growth did not occur. And the amount of U penetration was significantly less in the coating than in the rod (fig. 4(b-4)). Although the average interstitial impurity levels in the two types of polycrystalline W were similarly low according to chemical analysis (table I), possible localized high concentrations of impurities at grain boundaries could have affected the degree of penetration. The rate of penetration into the rod could also be higher than in the coating because the residual energy in the rod (due to swaging) would be higher than that in the vapor-deposited coating.

Polycrystalline W-1.5Hf capsules were tested to determine the effect of Hf on intergranular attack of W by molten U. Hafnium could potentially reduce the amount of attack

if, for example, oxygen is involved in the penetration mechanism. This is possible because HfO_2 is slightly more stable than UO_2 from 1200° to 1500° C (ref. 9) and, therefore, Hf could tie up oxygen. In other words, the liquid metal attack in this system might be analogous to the system in which niobium is alloyed with a small amount of zirconium to tie up oxygen to prevent intergranular penetration by liquid alkali metals (ref. 5).

The U intergranular attack on the W-1.5Hf capsules was localized and generally concentrated in the vicinity of welds and cracks. I believe this localized attack resulted from inhomogeneities in the Hf content in the alloy and/or highly stressed regions in the alloy. This belief is based on several observations. For example, intergranular attack was always found in weld zones. During welding, Hf was probably depleted from the weld zone because of the higher vapor pressure of Hf than W. This would indicate that Hf does inhibit intergranular attack on W by U. Intergranular attack also was observed to concentrate near cracks. These cracks are indicative of regions of high stress and thus, high residual energy. As previously mentioned, corrosion tends to concentrate in regions of higher energy. The occurrence of intergranular attack near cracks is therefore not surprising. To conclude, it may be possible for W-Hf alloys to resist intergranular attack by U providing regions of either Hf inhomogeneity or of high stress are eliminated.

Mass Transfer Attack

Because the tests conducted in this study were isothermal and the capsules were monometallic, no significant mass transfer of capsule metal was expected. However, the results of the tests indicate some evidence of mass transfer. All of the capsules exhibited surface dissolution which resulted from the solubility of W in U (0.5 percent at 1200° C and 1.5 percent at 1500° C (refs. 3 and 4). In addition, the U in the capsules exhibited a larger amount of capsule metal near its meniscus than elsewhere. Relatively large dendrites were observed in the U near the meniscus in the capsules tested at 1500° C. And the walls of these capsules appeared to be more severely attacked near the meniscus. Several factors could possibly contribute to the mass transfer observed. They include thermal gradients, localized high-impurity concentrations, U leakage, and a higher solubility of W in U at the meniscus than in the bulk U. Each of these factors is discussed briefly in the following paragraphs.

Thermal gradients in the U melt could cause mass transfer because of the increasing solubility of W in U with temperature. However, the contribution of thermal gradients to the mass transfer observed in these tests was not significant because (1) the temperature gradient was measured to be less than 5° (and based on linear interpolation is less

than 1° across the capsule), (2) the solubility of W in U varies only about 0.003 percent per degree of temperature gradient at the test temperatures (refs. 3 and 4), and (3) the W dendrites were formed near the U meniscus regardless of whether heat was conducted away from the capsules through the pedestal at the bottom of some capsules or through the wire at the top of other capsules.

The preferential volatilization and loss of U from the capsules through defects also could contribute to the formation of W dendrites. That is, the loss of U from the melt which contains a small amount of dissolved W would result in a supersaturated solution and subsequent precipitation of W. But it is difficult to see how this mechanism could account for the large amount of W precipitate in the melt since U can contain only 1.5 percent W at equilibrium at 1500° C. Furthermore, a W deposit was observed on the external capsule surface at the end of a defect (fig. 6(e-1)). This deposit indicates that the U was preferentially volatilized at the external surface. Therefore, a liquid solution of U and W, not U vapor alone, must have leaked out of the capsule.

The only evidence of a W concentration gradient in the U was a higher concentration of W precipitate near the meniscus. Similar phenomena have been observed in other liquid metal systems (ref. 10) and have been attributed to a surface chemistry phenomenon known as "Gibbs' adsorption." According to Gibbs (ref. 11), if the surface tension of a liquid is lowered by a solute, then the solute is adsorbed at the interface according to

$$\tau = - \left(\frac{a}{RT}\right)\left(\frac{d\gamma}{da}\right)$$

where

τ solute surface excess per unit area

a   activity of solute

γ surface tension

T   temperature

R   gas constant

Thus, the concentration of fine W crystals observed at the meniscus in figures 4 and 8 could have resulted from W precipitation from the W-rich surface layer during cooling. However, the number and size of dendritic crystals in other capsules (figs. 5, 6, and 9) are probably too large to result merely from cooling the Gibbs' layer. It is more likely that these dendrites were built up during the test as W (1) dissolved from the capsule walls and the W rod inserts into the U, (2) transferred through the melt to the Gibbs' surface layer, and (3) precipitated out of this layer on impurities near the meniscus and on capsule walls. However, in order for Gibbs' adsorption to have caused con-

tinuous transfer of W from capsule walls and W rods to dendritic crystals during the test, some driving force had to cause continued precipitation and continued dissolution of the capsule walls and rod inserts in preference to the precipitated crystals.

Several mechanisms could conceivably cause the Gibb's W-rich surface layer to precipitate W during the test and thus cause mass transfer. For example, the density of the W-rich surface layer (W is more dense than U) may have caused it to drop into the U melt and, hence, precipitate W. More W would then be required to again supersaturate the surface layer. But in order for additional W to be dissolved from the capsule walls or rod inserts rather than from the precipitated crystals, these crystals must be at a lower energy level than the capsule or rod metal. This explanation for the preferential dissolution of capsules and rod inserts seems plausible for polycrystalline W-1.5Hf and W. These metals would be at a higher energy state in the polycrystalline condition than as precipitated single crystals. And this explanation accounts for the relatively small amount of W transfer in the single-crystal capsule containing no polycrystalline W insert.

The reasons for the anomalous localized mass transfer from the wall of the capsule tested for 200 hours at 1500° C (fig. 6) are not completely understood. The radiographs in this figure indicate that localized mass transfer was present after 100 hours of testing. In contrast, no such localized attack occurred in other capsules tested for 100 to 200 hours at 1500° C (figs. 5, 7, and 9). Perhaps the localized attack resulted from a flaw (defect) in the single-crystal capsule wall. If this flaw resulted in disturbed (e. g., worked) metal at a high energy level relative to the rest of the capsule, preferential dissolution of metal from this area might result. Although no flaws were observed in this capsule before testing, an internal flaw could have been present (e. g., an EDM-damaged surface, an internal crack, or a low angle ($<2^\circ$) grain boundary).

Wettability Between Uranium and Tungsten

The extremely good wettability between U and W is perhaps best illustrated on the external surfaces of capsules from which U escaped (fig. 4(a)). In general, the U spread out over the surface, indicating a zero degree contact wetting angle. The few U "blisters" observed on the external surfaces contained some UO_2 and probably resulted from oxidation of U by oxygen impurities originally on the capsule surface or from oxygen in the furnace vacuum.

The contact angle between the U and the internal capsule walls was measured to range from 5° to 10° in the capsules tested at 1200° C (table II). These values probably represent the contact angle at the solidification temperatures of U (1130° C). The higher contact angles (16° to 18°) observed in the capsules tested at 1500° C were probably dis-

torted from their true values by the W dendrites which formed near the meniscus and the capsule walls.

Uranium was also observed microscopically to have climbed part way up the capsule walls. This film of U was too thin to be observed metallographically, but the autoradiographs indicate such a film by revealing the outline of the internal walls above the U melt. Therefore, it is likely that the U observed in the weld zones of the capsules (figs. 5 and 8) resulted from U which climbed up the capsule walls above the melt. The only other possibility of getting U in the welds is by vaporization and condensation. This possibility is remote in view of (1) the very slight thermal gradient in the furnaces and (2) the observation of U in the top enclosure welds of capsules positioned in the furnace on pedestals even though this positioning would tend to keep the bottoms of capsules cooler than their tops.

The observation of U intergranular attack on weld zones is quite important. For even if single crystals of W are used to contain U, the problems of preventing U attack on the final closure welds exist even though the welds may not be in direct contact with the U.

Containment of Uranium for Long Times

In order to use molten U in space power reactors, the U must be contained for extended periods of time (over 10 000 hr). In this study, problems in both chemical compatibility and capsule crack generation were found to limit the period of effective containment of U. As previously mentioned, U intergranular and mass transfer attack on W appear to present the major compatibility problems. Hafnium alloying additions to W appear to offer promise in reducing intergranular attack. And single-crystal W appears to be more resistant to both intergranular and mass transfer attack than either of the polycrystalline materials.

Unfortunately, two other phenomena limit the period of effective U containment by W. First, weld zones are particularly subject to intergranular attack even with single crystals, and second, cracks developed in the capsules as a result of thermal cycling. The following paragraphs describe the nature and probable causes of cracks which resulted in U leaks from capsules tested in this study.

In this study, most of the capsules lost U through cracks which developed during thermal testing; a few capsules lost U through fabrication-induced cracks. Considerable difficulty was encountered in preventing cracks from developing during welding. As stated in table II, small cracks were observed near the welds (above the U melt) in four of the capsules, but very little U was lost through these cracks. However, the two capsules (capsules 1 and 6 in table II) which exhibited fabrication cracks adjacent to the U

melt lost an inordinate amount of U during thermal cycling.

Cracks which developed during thermal testing represent a much more serious problem than the fabrication-induced cracks which could be detected prior to use in a reactor application. In the single-crystal W capsules, the test-induced cracks extended radially from the U meniscus; in the W-1.5Hf capsules, these cracks extended longitudinally from the U meniscus and surrounded the U melt. The absence of U in many of these cracks (in spite of the excellent wetting demonstrated between U and W or W-1.5Hf), indicates that they were formed after the U had solidified. And the consistently similar locations of the cracks indicates that they were formed as a result of stresses developed during furnace cooling rather than during metallographic preparation.

I believe that cracks formed during capsule cooling because of the difference in contraction between U and W or W-1.5Hf on cooling coupled with the strong bonding between U and W or W-1.5Hf. After U solidifies at 1130° C, its density increases (and volume decreases) over 5 percent during cooling to room temperature because of thermal contraction and allotropic transformations; for example, the density of U has been reported to increase from 18.06 to 19.04 grams per cubic centimeter during cooling from 805° to 25° C (ref. 12). Tungsten, on the other hand, exhibits a relatively minor thermal contraction when cooled from 1130° C. Thus, the shrinking U can cause stresses in the capsule walls which, if the capsule-U bond is strong enough, can be relieved by forming cracks in the walls. A good example of such a capsule crack, and the displacement of the wall below the crack (which is in contact with the U melt) towards the capsule axis, is shown in figure 4(b-1). Tungsten and W-1.5Hf capsules should be especially subject to cracking at temperatures below their ductile-brittle transition temperature.

The implications of crack formation as a result of cooling are important. For if liquid U fuel elements were used in a nuclear reactor, reactor shutdown or cyclic operation at temperatures below the melting point of U could result in container cracks and in subsequent fuel losses.

CONCLUDING REMARKS

The problems of containing molten U at temperatures of 1200° to 1500° C for 10 000 hours or more in nuclear reactors are formidable. In this study, several potential problem areas associated with U containment by W and W-1.5Hf were demonstrated. First, the relatively extensive intergranular attack by U on W after times as short as 10 hours appears to rule out the use of polycrystalline W. Alloying additions of Hf to W appeared to show promise as a method of reducing this intergranular attack. However, even the Hf alloy exhibited some localized intergranular attack.

Mass transfer of both W and W-1.5Hf by molten U is a second potential problem associated with long term containment of U. The results of this study indicate that mass transfer is more severe with polycrystalline than single-crystal metals. But even single-crystal W (which is probably impractical for a reactor application) exhibited some evidence of mass transfer attack after exposure under nearly isothermal conditions. And this mass transfer attack would be expected to become more pronounced in an actual reactor application because of larger thermal gradients.

In addition to corrosion problems, two other potential problems of containing molten U in a reactor were suggested by the results of this study. First, even if a single crystal were used to contain U, the excellent wetting between U and W results in U climbing the container walls above the melt. This U then attacks grain boundaries in the closure weld. Second, thermal cycling a reactor below the melting point of U can initiate container cracks and subsequent U leakage. The cracks probably result from the difference in thermal expansivity and the strong bonding between U and W or W-1.5Hf.

Much more work is needed to characterize and perhaps remedy the problems associated with containing U at elevated temperatures. But based on compatibility considerations, it may be possible to contain molten U with properly selected W alloys. For example, the alloy could contain some Hf to resist intergranular attack by U and some Re to give the alloy reasonable ductility. Also, some recent work (ref. 13) indicates that yttrium may adequately contain U up to 1300° C under short-time isothermal conditions.

Alternatively, a ceramic or ceramic-coated metal capsule could possibly contain molten U. A ceramic-coated capsule would be preferable because of thermal conductivity considerations. Such a coating would have to be compatible with both U and the capsule metal, and the thermal expansion of the coating would have to be nearly the same as that of the capsule metal. Based on considerations of thermal expansion, thermal conductivity, and free energies of reaction, such ceramics as hafnium carbide, titanium carbide, or tungsten boride may successfully protect W from attack by molten U. To successfully protect W, however, these coatings would have to be highly reliable and defect free. In addition, the containment material would have to resist weld attack and thermal-cyclic-induced cracking. These requirements may be very difficult to meet.

CONCLUSIONS

Single-crystal tungsten (W) and polycrystalline tungsten - 1.5-percent-hafnium (W-1.5Hf) capsules were loaded with uranium (U), sealed, and isothermally tested for varying times at 1200° and 1500° C. Some of the single-crystal capsules also contained

polycrystalline W inserts. Based on these tests, the following conclusions are made:

1. Other than minor dissolution of capsule surfaces, molten U appears to be compatible with single-crystal W. However, there was some evidence of mass transfer from the single crystal to dendrites which formed near the U meniscus.

2. Polycrystalline W is incompatible with molten U because of intergranular attack. Wrought W rod was more rapidly attacked than vapor-deposited W. But both kinds of W exhibited considerable attack after only 10 hours at temperature.

3. Hafnium alloying additions to W offer some promise in reducing U attack on W. The polycrystalline W-1.5Hf capsules exhibited less intergranular attack than polycrystalline W but more mass transfer attack than the single-crystal W capsules.

4. Molten U wets both W and W-1.5Hf very well. This good wettability resulted in the climb of U up capsule walls above the melt and the eventual penetration into and through the lid closure welds by means of grain boundaries.

5. Uranium cannot be contained in either W or W-1.5Hf capsules for more than one thermal cycle because of crack formation in capsule walls. These cracks apparently formed during cooling after U had solidified because of the difference in thermal expansivity and the strong bonding between U and W or W-1.5Hf.

Lewis Research Center,
  National Aeronautics and Space Administration,
    Cleveland, Ohio, November 20, 1968
      120-27-04-06-22.

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