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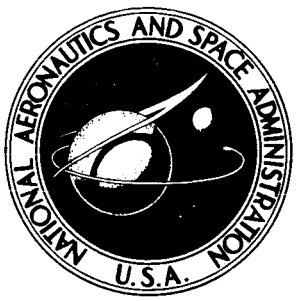

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COMPATIBILITY TESTS OF MATERIALS FOR A LITHIUM-COOLED SPACE POWER REACTOR CONCEPT

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16. Abstract

Materials for a lithium-cooled space power reactor concept must be chemically compatible for up to 50 000 hr at high temperature (about 1000° C, 1830° F). Capsule tests at 1040° C (1900° F) have been made of material combinations of prime interest: T-111 (tantalum - 8 percent tungsten - 2 percent hafnium) in direct contact with uranium mononitride (UN), UN in vacuum separated from T-111 by tungsten wire, UN with various oxygen impurity levels (ranging between approximately 800 and 2300 ppm by weight) enclosed in tungsten wire in lithium-filled T-111 capsules, and TZM (molybdenum - 0.5 percent titanium - 0.08 percent zirconium - 0.03 percent carbon) and lithium together in T-111 capsules. All combinations were compatible for over 2800 hr except for T-111 in direct contact with UN.

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SUMMARY

Materials for a lithium-cooled space power reactor concept must be compatible for times up to 50 000 hours at about 1000° C (1830° F). Chemical compatibility tests were made for the following combinations of materials: T-111 (tantalum - 8 percent tungsten - 2 percent hafnium) in direct contact with UN (uranium mononitride) fuel containing approximately 100 ppm by weight oxygen impurity; T-111 capsules containing tungsten-wire-wound UN fuel pellets of three different oxygen levels to test for interaction of UN and T-111 through vapor transport; T-111 capsules containing lithium and tungsten-wire-wound UN fuel pellets of three oxygen levels ranging between about 800 and 2300 ppm by weight to test for the effect of oxygen impurity in UN on the compatibility of UN with lithium (tungsten wire used to prevent direct contact between UN and T-111); and T-111 capsules containing lithium and TZM (molybdenum - 0.5 percent titanium - 0.08 percent zirconium - 0.03 percent carbon), a potential structural and reflector material, to test for bimetallic corrosion effects. The initial oxygen content of the lithium used in these tests was approximately 70 ppm by weight. All combinations were compatible at 1040° C (1900° F) for over 2800 hours except for T-111 in direct contact with UN. It was concluded that no major compatibility problems are evident in the fuel-pin or structural components for this reactor concept.

INTRODUCTION

Materials and design concepts potentially suitable for a liquid-metal-cooled, fast-spectrum reactor (ref. 1) for space power use are being studied at the Lewis Research Center. Selection of materials for this use is discussed in reference 2. The goals for this reactor are a life of 50 000 hours at an operating temperature of about 980° C (1800° F). These conditions place severe demands on the materials of construction.

The materials of chief interest include T-111 (tantalum (Ta) - 8 percent tungsten (W) - 2 percent hafnium (Hf)) for most structural components and for fuel cladding; uranium mononitride (UN) as the nuclear fuel; lithium as the coolant; and TZM (molybdenum (Mo) - 0.5 percent titanium (Ti) - 0.08 percent zirconium (Zr) - 0.03 carbon (C)) for some structural components and the reflectors. Other potential materials (not discussed in this report) are bearing materials such as hafnium carbide (HfC) and hafnium nitride (HfN); poison control materials such as boron carbide (B_4C), tantalum diboride (TaB_2), zirconium diboride (ZrB_2), and hafnium diboride (HfB_2); fission products; and other potential cladding and structural materials such as niobium (Nb) - 1 percent zirconium.

The purpose of the work described in this report was to determine if there are major chemical compatibility problems among the various materials proposed for fuel, cladding, coolant, and structural components of the reactor. That is, this study was intended to determine the feasibility of using these materials from a chemical compatibility viewpoint. This study utilized isothermal capsule tests as a relatively inexpensive method of screening for possible problem areas. The tests were done as a prelude to more complex tests such as pumped-liquid-metal loop tests. A test temperature of 1040° C (1900° F) was used for the tests. This temperature was selected to be a little above the 980° C (1800° F) reactor operating temperature currently planned to allow a safety margin for hot spots or temperature excursions in the reactor.

Potential compatibility problems associated with fuel pins are probably of the greatest concern. The fuel-pin concept is pictured in figure 1. There is a thin tungsten liner between the UN fuel and T-111 cladding to prevent possible reactions between the UN and T-111. It would be simpler and less expensive to make fuel pins if this liner could be eliminated. Hence, a question to be answered was whether this tungsten liner is really needed. Because tantalum and hafnium form nitrides of greater stability than uranium nitride (ref. 2), UN and T-111 were not expected to be compatible in direct contact with each other at reactor operating temperatures. Therefore, tungsten, which forms less stable nitrides than UN, is used to separate them. Diffusion rate calculations suggest that a tungsten liner 0.013 centimeter (0.005 in.) thick would prevent significant diffusion of tantalum or hafnium from T-111 to the tungsten-UN interface for 50 000 hours at a temperature of 1260° C (2300° F) or less (ref. 2).

But, if the reaction between UN and T-111 is slow enough at reactor operating temperatures, the tungsten barrier may not be required. Hence, it is important to know the extent of reaction between UN and T-111 in direct contact with each other at reactor temperature.

In addition, impurity levels of constituents (such as oxygen level of the UN) may well affect the reaction of UN and T-111. Recently, it has been possible to prepare UN with an oxygen content of about 100 ppm (in contrast to the 1500 to 2000 ppm level found a few years ago (ref. 3). Therefore, a UN compact with an oxygen content of about

100 ppm was tested in contact with polished T-111 surfaces for 2862 hours at 1040° C to determine if high-purity UN can be used in direct contact with T-111.

If a crack occurred in the tungsten liner of a T-111 clad UN fuel pin, vapor transport might occur between the fuel and cladding. For example, UN will undergo thermal dissociation to uranium and nitrogen (N_2). Or, if the UN has partially reacted with oxygen at lower temperatures (e.g., 900° C or less), uranium sesquinitride (U_2N_3) may be present and, if so, will dissociate readily to form UN and N_2 (refs. 3 and 4). Over a long period of time nitrogen may react with the cladding and possibly embrittle it (ref. 5). Therefore, to help answer the question of whether a cracked tungsten liner is as effective as an uncracked one in preventing unwanted reactions between UN and T-111, a group of three T-111 capsules containing only tungsten-wire-wound UN pellets of three oxygen levels (250, 800, and 1950 ppm) was tested at 1040° C in a vacuum of 10^{-7} newton per square meter (10^{-9} torr) for 2862 hours to determine if any evidence of change in T-111 composition or change in the UN due to vapor transport could be detected. The amount of nitrogen transported is expected to be small under these conditions (ref. 2).

The compatibility of UN and lithium would be an important concern if a crack were to occur in a fuel-pin cladding. Since lithium is known to be very reactive with oxygen, it is necessary to determine the upper limit of oxygen that can be tolerated in UN fuel without creating a compatibility problem among fuel, cladding, and coolant. Most of the oxygen in UN fuel will be found in the form of uranium dioxide (UO_2). Lithium might intrude through the crack and reduce the UO_2 to form lithium oxide (Li_2O) and free uranium. Then it is possible that the free uranium would penetrate the T-111 grain boundaries (at temperatures above the melting point of uranium (1132° C, 2070° F), or that the Li_2O in the lithium stream might lead to accelerated corrosion or might deposit in cooler regions of the primary loop. The effect of oxygen content in UN on the corrosion of T-111 was studied by heating T-111 capsules containing tungsten-wire-wound UN pellets of three oxygen levels (800 to 2300 ppm) and lithium for 1000 hours at 1040° C.

In one reactor concept, T-111 and TZM reactor structural components are both contacted by flowing lithium in the reactor vessel. The answer sought by this capsule screening test program was whether lithium would cause mass transfer between TZM and T-111. Such a reaction might be expected, and it has previously been found that carbon is transported from TZM to Nb - 1 percent-Zr in a bimetallic lithium loop (ref. 6). Carbon transport from TZM to T-111 might increase the ductile-to-brittle transition temperature of the T-111 reactor tubing to an unacceptable level. A carbon contamination level of about 500 ppm might embrittle T-111 (ref. 7). Hence, TZM (with an initial carbon level of 0.0155 percent) was tested in a lithium-filled T-111 capsule for 2862 hours to look for transport between TZM and T-111.

The conclusions drawn from these tests were largely based on comparison and interpretation of chemical and metallographic analyses of the pretest and post-test reactor materials.

MATERIALS, APPARATUS, AND PROCEDURE

T-111 Test Capsules

The T-111 capsules for these tests were made from 1.27-centimeter- (1/2-in.-) diameter tubing with a 8.1×10^{-2}-centimeter (0.032-in.) wall thickness machined into 5.08-centimeter (2-in.) lengths. Capsule bottoms were stamped from 5.1×10^{-2}-centimeter- (0.020-in.-) thick T-111 sheet. Capsule tops were machined from 1.43-centimeter- (9/16-in.-) diameter cold-worked T-111 rod. Chemical analyses of these materials are presented in table I.

Prior to assembly, the separate capsule parts were cleaned ultrasonically in a fluorinated hydrocarbon (Freon Precision Cleaning Agent) and then in a mild commercial detergent (Alconox). After this cleaning, the parts were etched in a solution with the following composition in weight percent: concentrated HF, 15; nitric acid (HNO_3), 20; sulfuric acid (H_2SO_4), 10; and distilled water, 55. Rinsing in distilled water and drying in an oven followed. The cleaned and etched parts were heat-treated at 1315° C (2400° F) for 1 hour in a vacuum of approximately 10^{-4} newton per square meter (10^{-6} torr). Bottom parts were then electron-beam welded to one end of each piece of tubing. The resulting capsules were checked for leaks, recleaned as before, and vacuum heat-treated for 1 hour at 1315° C (2400° F). This heat treatment is a standard postweld anneal for T-111 components to combine any oxygen in the weld zones with hafnium to prevent rapid penetration by lithium during testing (ref. 6).

Uranium Nitride Pellets

Several lots of UN were used because oxygen impurity level in UN was a variable being investigated. The oxygen content of these UN lots varied from about 100 to 2300 ppm. There were problems in quantitative analyses of the oxygen levels of the UN pellets used in these tests both in respect to interlaboratory agreement and (occasionally) intralaboratory reproducibility (tables II to IV). A short discussion of this problem is found in the section Large Variations Found in Chemical Analysis of Uranium Nitride. For convenience in discussion, the vendor's initial oxygen levels are used for UN lot identification in this report. Photomicrographs of as-received UN are presented in figure 2. Second-phase particles (presumed to be UO_2), which are often seen in high-

oxygen-content UN fuel, can be observed in figure 2(c). Some UO_2 was also observed in the UN shown in figures 2(d) and (e), although particles are not apparent in these figures.

Lithium Filling and Capsule Assembly

Molten lithium with an oxygen content of approximately 70 ppm was added to the appropriate capsules in the vacuum chamber of an electron-beam welding facility. The quantity of lithium added was measured by counting the drops added to the capsules and rechecked by weighing the filled capsules after they were sealed by electron-beam welding. The objective was to add enough lithium to a capsule so that at test temperature the lithium plus any other specimens within the capsule would occupy about 90 percent of the capsule volume to ensure contact of lithium with the materials being tested. Because of the low density of lithium and its wetting and surface tension characteristics, there were difficulties in filling the capsules with lithium. Although the capsules were heated to approximately 230° C (450° F) while being filled (to lower the surface tension of the lithium), the lithium drops frequently clung to the capsule walls, bridged the space between the walls, formed a meniscus, and hung up near the capsule tops. This often prevented the addition of the desired amount of lithium. Post-test X-ray films of the capsules were examined with the aid of an image enhancer (ref. 8). This showed that the capsule contents were in contact with lithium.

All capsules tested, whether or not they contained lithium, were sealed by electron-beam welding. The completed test capsules were weighed; the lithium weights thus determined agreed closely with the weights calculated from the number of drops added.

Capsule Testing Procedures

Three types of test capsules were prepared to test the following material combinations:

(1) Uranium nitride fuel in direct contact with T-111; no lithium present

(2) Uranium nitride in a simulated cracked tungsten liner made of coiled tungsten wire with or without lithium, all in a T-111 capsule

(3) TZM and lithium in a T-111 capsule

Figure 3 shows X-ray radiographs of examples of these types of test capsules. Figure 3(a) shows a UN pellet sandwiched between two polished T-111 contact pieces. Above the top T-111 specimen is a T-111 weight and some dished springs made of T-111 to assure contact between the UN and T-111. Figure 3(b) shows a TZM tube inside a lithium-filled T-111 capsule. The lithium does not show up in this radiograph reproduction. Figure 3(c) shows a UN pellet inside a simulated cracked liner made of 0.4-millimeter-

(15-mil-) diameter tungsten wire. The wire serves to prevent direct contact between the UN and the T-111 capsule. This type of capsule was tested with or without the addition of lithium depending upon the objective of the test.

Testing was done in a vacuum furnace facility in which the temperature was maintained at $1040^{\circ} \pm 10^{\circ}$ C and the pressure between 4×10^{-8} and 4×10^{-7} newton per square meter (3×10^{-10} and 3×10^{-9} torr) during the 2862-hour test run. After testing, capsules for which oxygen content of the lithium was to be determined were placed in a vacuum distillation rig (ref. 9) and opened with a tubing cutter under vacuum. A temperature of 700° C (1290° F) maintained for 1 hour was then used to remove the lithium by evaporation. Any oxygen present remained in the capsules as Li_2O. Capsules containing residual Li_2O were removed from the vacuum chamber, and the Li_2O was dissolved in distilled water. The resulting lithium hydroxide solution was titrated with standard acid solution, and the post-test oxygen content of the lithium was calculated.

Results of testing were evaluated by means of metallographic examination, chemical analysis, optical spectroscopy, X-ray diffraction, X-radiography, electron microprobe analysis, scanning electron microscopy, visual observation, and weight change measurements as deemed appropriate.

The following etchants were used for the metallography presented in this report:

Material	Etchant
T-111	30 g ammonium bifluoride ($NH_4F \cdot HF$) 50 cm^3 nitric acid (HNO_3) 20 cm^3 distilled water
TZM	Murakami's solution
UN	60 cm^3 lactic acid ($CH_3 \cdot CH(OH) \cdot COOH$) 24 cm^3 nitric acid (HNO_3) 2 cm^3 hydrofluoric acid (HF)

RESULTS AND DISCUSSION

Applicability of Test Results to Reactor Operation

The objective of this work was to determine insofar as was possible from capsule screening tests the feasibility (from a chemical compatibility viewpoint) of using the

materials selected for testing in the reactor concept previously described. Specifically the answers to four questions were sought:

(1) Is the tungsten liner between UN fuel and T-111 cladding (as currently planned) really necessary?

(2) Should a tungsten fuel-pin liner crack, would it be as effective as an uncracked one in preventing harmful reactions between UN and T-111?

(3) What is the tolerable upper limit of oxygen in UN?

(4) Will lithium cause mass transfer between TZM (a material used as a reflector) and T-111?

Necessity of tungsten liner. - To determine if a tungsten liner is necessary, UN was tested in contact with T-111, as described in the section Capsule Testing Procedures. The test specimen is pictured in figure 3(a). Figure 4 presents a photograph (at a magnification of 3) of the contact surfaces. Areas of T-111 that were in contact with UN are easily identified. Photomicrographs illustrating the effect of heating UN and T-111 in direct contact with each other are shown in figure 5. The UN shows no signs of attack (compare figs. 5(e) and 2(a)).

Areas of T-111 that contacted UN show a second phase in some of the grains and at grain boundaries; this second phase material is found in the T-111 to a depth of 1.1 centimeter beyond the contact surface (figs. 5(a) and (c)). Areas of T-111 that did not contact UN are shown in figures 5(b) and (d). All T-111 areas shown in figure 5 are from the same specimen. The precipitates shown in figure 5(b), an area of T-111 that did not contact UN, are typical of those generally found in T-111 heat-treated at 980° to 1150° C and are presumed to be related to microinhomogeneities in the T-111. The chemical composition of this type of precipitate in T-111 has not been established. However, the precipitates within the grains of the areas of T-111 that contacted UN are presumed to be hafnium and/or tantalum nitride. It was concluded in reference 5 that T-111 doped uniformly with nitrogen to a level of much over 300 ppm might exhibit brittle behavior if stressed at room temperature. The precipitates produced by doping were identified as hafnium nitride (ref. 5). The assumption that the precipitates found in T-111 that contacted UN are nitrides is supported by the fact that the UN appeared to have lost a little nitrogen (table II), although not enough to result in the appearance of free uranium in the fuel. It is concluded that the extensive reaction zone found in T-111 that was in contact with UN for less than 3000 hours might result in embrittlement of a T-111 fuel-pin cladding if it were not separated from the fuel by a protective tungsten liner. These results will be amplified in the sections T-111 and Uranium Nitride in Direct Contact and Large Variations Found in Chemical Analysis of Uranium Nitride.

Effect of cracked liner. - The effect of a cracked fuel-pin liner on the ability of the tungsten liner to protect T-111 cladding from reaction with UN fuel was studied by heating a group of three T-111 capsules containing UN pellets of three oxygen levels

(approximately 250, 800, and 1950 ppm) for 2862 hours at 1040° C in a vacuum of approximately 10^{-7} newton per square meter (10^{-9} torr). The pellets were enclosed in coiled tungsten wire containers to prevent direct contact between fuel (UN) and T-111. The objectives were to observe any changes in T-111 due to reaction with vapor-transported materials (primarily nitrogen) from the UN and to determine whether the reactions were affected by the oxygen content of the UN.

The nitrogen level of the T-111 from all three capsules appeared to drop slightly during testing (table III). The magnitude of the drop in nitrogen content of the T-111 (from approximately 25 to 16 or 17 ppm) is about the same as that also observed for an empty control capsule (table III) and also for the T-111 direct-contact capsule (table II). This drop in nitrogen content of the T-111 capsule walls is not surprising. It is predicted in reference 2 that, even though the tungsten liner becomes cracked, if a gap is maintained between UN and T-111 so that any reaction will have to occur through the gas phase, the increase of nitrogen in a 0.15-centimeter-thick T-111 fuel-pin wall will be less than 1 ppm in 50 000 hours at 1040° C and only 5 ppm at 1140° C. It is assumed that molecular flow of nitrogen is rate controlling. This experiment tends to support these calculations. The drop in nitrogen content of the T-111 capsule walls found in these experiments occurred because the rate of nitrogen diffusion out of the T-111 was greater than the rate of nitrogen leaving the UN. This nitrogen diffusion out of the T-111 was eliminated by the vacuum system. Since in an actual fuel pin the fuel-cladding gap will contain helium (initially at a pressure of about 1 atmosphere and standard temperature) to enhance heat transfer, the actual transport of nitrogen from UN to T-111 will be even slower than if a vacuum atmosphere existed (as in this experiment).

Other changes in chemical composition of T-111 or UN resulting from testing and of sufficient magnitude to affect reactor operation did not occur, or the analyses were too varied to allow conclusions to be drawn. Post-test metallography of the fuel revealed no changes resulting from the 2862-hour test at 1040° C. Microstructural changes occurring in T-111 were all attributed to thermal aging effects (fig. 6). They are of the type commonly observed in T-111 annealed at this temperature (ref. 10).

It is apparent from these tests that the physical separation of UN and T-111 provided by the coiled tungsten separators was successful in preventing reactions such as those observed when T-111 and UN are heated in direct contact. Furthermore, the variations in oxygen content in the UN pellets appeared to have no appreciable effect on the results. The conclusion is that a cracked fuel-pin liner would be effective in preventing harmful reactions between UN and T-111 at 1040° C (providing direct contact of T-111 and UN is avoided).

Tolerable upper limit of oxygen in uranium nitride. - The third answer sought was concerned with the tolerable upper limit of oxygen in uranium nitride (UN). This becomes most important if a fuel element cladding becomes cracked. Should lithium contact the fuel, it will reduce any UO_2 it contacts in the UN. Free uranium and Li_2O will

be formed; the free uranium may then penetrate the T-111 at grain boundaries. To look for the possible effects of this lithium intrusion, tungsten-wire-wound UN pellets of 800-, 1490-, and 2300-ppm oxygen content were sealed with lithium in T-111 capsules. (Pellets of UN containing 260, 390, and 1950 ppm oxygen were also tested, but unfortunately these specimens were lost because of experimental difficulties.) A typical test specimen is pictured in figure 3(c).

Photomicrographs of various parts of the tested specimens are presented in figures 7 to 9; they show little or no attack of the T-111 capsule walls. Apparently no significant transport of free uranium to the T-111 capsule walls occurred through the lithium because no grain-boundary attack was seen. Precipitates and changes in grain structures observed can all be related to capsule fabrication techniques and subsequent thermal history of the specimens. The UN was not attacked in any manner that could be detected metallographically (compare fig. 8(a) with 2(d) and 9(a) with 2(e)). Surfaces of UN that contacted lithium are shown in figures 7(a), 8(a), and 9(a); they appear no different than did surfaces of untested UN.

Chemical analyses for this series of tests are presented in table IV. Oxygen analyses of UN appear to be somewhat uncertain and are discussed in the section Large Variations Found in Chemical Analysis of Uranium Nitride. Tested UN appears to have a carbon content slightly lower than that of the untested UN, but if carbon was actually lost from the UN, it was not picked up by the T-111. The most significant result found by chemical analyses was the large increase in the oxygen content of the lithium contained in the test capsules (from an initial level of 70 ppm to over 300 ppm in two capsules and to over 700 ppm in the third). A mass balance calculation showed that much of this oxygen had to come from the UN. Thus, the danger of free uranium production cannot be discounted, and the conclusion drawn is that the maximum oxygen level that can be tolerated lies somewhere below 800 ppm. The best choice for fuel would be UN with the lowest oxygen content possible. And since UN containing less than 300 ppm oxygen can now be produced without significantly increasing fuel fabrication costs, this fuel should be used.

Interaction among T-111, lithium, and TZM. - The last objective of this work was to determine if any mass transfer between T-111 and TZM (through lithium) could be detected by a capsule test. The test consisted of a T-111 capsule 1.27 centimeters (1/2 in.) in diameter and 5.1 centimeters (2 in.) long containing lithium and a TZM tube 6.3×10^{-1} centimeter (1/4 in.) in diameter and 1.9 centimeters (3/4 in.) long with a 3.8×10^{-2}-centimeter- (0.015-in.-) thick wall heated for 1000 hours at 1040° C in vacuum.

A view of a test specimen is shown in figure 3(b). Microstructures for this test are presented in figure 10. Neither the T-111 nor the TZM shows any evidence of attack, although the TZM underwent recrystallization and grain growth. The empty control capsule segment (fig. 10(b)) shows precipitates caused by fabrication and subsequent

thermal treatment, as discussed in the section Effect of cracked liner. Chemical analyses revealed that the carbon content of the TZM specimen decreased from an initial level of 155 to 105 ppm. Carbon was removed from the TZM, but table V shows no significant increase in the carbon level of the T-111. Since capsule testing is not a good way to test for mass transfer, no positive conclusions should be drawn concerning mass transfer between T-111 and TZM from this capsule test. In reference 11 a lithium-pumped-loop test is described and additional information about compatibility among T-111, Li, and TZM is reported. A test section of this loop contained T-111 clad fuel pins centered in the T-111 loop tubing by TZM spacers. This test section was heated to 1040° C for a total of 7500 hours. Lithium flow rate through the test section was 1.3 meters per second. After 2500 hours of loop operation, fuel pins were removed from the test section and their T-111 claddings were analyzed. The carbon levels of the claddings (originally 61 ppm) increased to about 70 ppm after 2500 hours of exposure (ref. 11).

Further information on this loop test was obtained from General Electric (unpublished data from work done under NASA contract NAS 3-6475). A segment of this same T-111 loop which had housed corrosion test specimens ran for the 7500 hours at about 960° C. The carbon level in the T-111 wall from this coolest segment of the loop was about 22 ppm at the start and 30 ppm at the end of the test. Since the TZM and fuel pins were both in the hot section of the loop, it might be expected that most of the carbon transported from the TZM through lithium would accumulate in the relatively cool corrosion test section of the loop. The carbon level increase found in the section of the loop that had run for 7500 hours at 960° C was about the same as the carbon level increase found in the fuel-pin claddings that had been in the 1040° C section of the loop for 2500 hours (about 8 or 9 ppm). These data suggest that carbon transport from TZM to T-111 should not be a problem during the life of the reactor. The magnitudes of other interstitial changes in this "cool" section of the loop were small. Thus, it is unlikely that any mass transfer problems due to the combination of T-111, Li, and TZM would occur in the reactor.

T-111 and Uranium Nitride in Direct Contact

An attempt was made to identify the precipitates that occurred in T-111 after it was in contact with UN. These are the precipitates shown in figures 5(a) and (c) which (unlike the precipitates shown in fig. 5(b)) are not attributable solely to the thermal history of the T-111.

The T-111 that was in contact with UN was studied by scanning electron microscopy using the energy dispersive X-ray analyzer. Areas examined were a precipitate-free grain, a grain with a large number of precipitate particles, a precipitate "needle," a

grain boundary between grains that contained a large number of precipitated particles, and a grain boundary between two precipitate-free grains. No differences in compositions of the areas studied were detected, and no constituents alien to T-111 were found. Electron-beam-microprobe analyses also did not help in the attempt to identify precipitates or grain-boundary contents of T-111 which had been in contact with UN.

Changes in chemical composition of T-111 and UN due to testing are presented in table II.

These are generally small enough to be within the accuracy limits of the analytical limits of the analytical techniques used or can be accounted for by inhomogeneities of the materials being tested. It is felt, however, that based on the accuracies reported (ref. 12) for the analytical method used, the drop in nitrogen level for T-111 is real. It probably resulted from diffusion of nitrogen out into the vacuum system during the 2862-hour test, as discussed in the section Effect of cracked liner. At any rate, even if nitrogen transport from fuel to cladding were appreciable, a buildup of nitrogen in the T-111 capsule wall would not occur and should not result in fuel-pin cladding embrittlement during the 50 000-hour life of a reactor.

Large Variations Found in Chemical Analysis of Uranium Nitride

The spread in individual elemental analyses for UN (both interlaboratory and intralaboratory) often made it difficult to make very positive statements about some of the testing. The wide variations found in the oxygen content of UN (table IV, for example) were especially worrisome. A possible explanation for the disagreement between vendor and NASA analyses for the oxygen content of untested UN used in tests 2 and 3 can be given. Vendor analysis was made after the UN compacts were hydraulically pressed and sintered; NASA analysis was made on segments of actual test pellets that had been machined from the vendor's specimens. Much material from the outer surface was removed during the machining operation. It is known that the oxygen level of a UN pellet can vary widely among different regions of the pellet (ref. 13). Lower concentrations of UO_2 are found in the center of the pellet than are found near the outer surface. Thus, a lower oxygen content for the machined pellets than for the pressed fuel specimens seems reasonable.

At the time these tests were made, analytical methods for the constituents of UN (i. e., U and N) and impurities found in UN (such as carbon and oxygen) were not perfected to the point that it was possible to make very positive statements about changes of the magnitude generally found in tables IV and V. Further research on analytical techniques has resulted in the achievement of greater accuracy and reproducibility (precision) for these analyses which can be applied to any further work.

CONCLUSIONS

Isothermal capsule compatibility tests of several combinations of interest for fuel pins and structural components of a liquid-metal-cooled fast-spectrum reactor were made at 1040° C (1900° F) for 2862 hours. No major compatibility problems are evident in the fuel pin or structural components for this reactor concept. Other conclusions drawn from test results are

1. It was confirmed that it is better not to use T-111 and uranium nitride (UN) (even of high purity) in direct contact for a reactor for long-term operation.

2. A tungsten separator (liner) between UN fuel and T-111 cladding, even if it becomes cracked, is sufficient to prevent reaction between UN and T-111 at 1040° C. Such a separator is effective in the presence of lithium as well as in a vacuum.

3. When tungsten-wire wrapped UN fuel (containing up to 2300 ppm oxygen) was heated in T-111 capsules containing lithium (to simulate leakage of lithium into a fuel pin) for 2862 hours at 1040° C, there was no attack of T-111 or of UN. But the lithium picked up from 250 to 650 ppm of oxygen during testing, some of which had to come from UO_2 in the UN. It was concluded that UN oxygen level should be kept to a value less than 800 ppm (and preferably much lower).

4. Carbon transport from TZM to T-111 components through lithium was not revealed by capsule testing. A pumped loop test is necessary to determine if mass transfer between TZM and T-111 would be a problem. Preliminary information from a pumped loop test indicates that mass transfer should not be a problem in the reactor.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 5, 1973,
503-25.

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TABLE I. - CHEMICAL COMPOSITIONS OF MATERIALS USED FOR T-111 CAPSULES

T-111 form (capsule component)	Analysis source	Concentration										
		Tungsten, percent	Hafnium, percent	Oxygen, ppm	Hydrogen, ppm	Nitrogen, ppm	Carbon, ppm	Molybdenum, ppm	Niobium, ppm	Vanadium, ppm	Zirconium, ppm	Tantalum
Tubing (wall)	NASA	----	----	42.5	3.2	25	50	---	---	---	---	-------
	Vendor	7.30	1.93	[a]24	[a]12	[a]22	[a]6	15	500	<5	500	Balance
Rod (cap)	NASA	7.83	1.96	28	1	55	56	---	---	---	---	-------
	Vendor	7.2	2.06	[a]11	[a].7	[a]25	---	120	188	2	312	Balance
Sheet (bottom)	Vendor	8.5	2.0	[a]120	[a]2.9	[a]15	[a]<50	<10	470	<10	590	Balance

[a]Single analysis; others are averages of two to four determinations.

TABLE II. - CHEMICAL ANALYSES OF T-111 AND URANIUM NITRIDE USED IN DIRECT-CONTACT COMPATIBILITY TESTS

[Test temperature, 1040° C (1900° F); time, 2862 hr.]

Material condition	Uranium nitride				T-111 capsule wall[a]			
	Concentration							
	Oxygen, ppm	Nitrogen,[b] percent	Carbon, ppm	Uranium, percent	Oxygen, ppm	Hydrogen, ppm	Nitrogen, ppm	Carbon, ppm
Untested	[c]100 400 42 64	5.33 5.51	750 347	94.4	43	3.2	25	50
Tested	96	5.08	694	(d)	57 56	0.7 .6	19 13	66 59
Tested[e]	----	----	---	----	47 45	1.5 .8	18 17	38 46

[a]Sampled opposite uranium nitride pellet location.

[b]Theoretical nitrogen content of uranium nitride is 5.56 percent.

[c]Vendor's oxygen analyses were 130 and 110 ppm.

[d]Insufficient material for this analysis.

[e]Empty control capsule.

TABLE III. - CHEMICAL ANALYSIS FOR VAPOR TRANSPORT EFFECTS OF URANIUM NITRIDE ON T-111 WITH NO LITHIUM PRESENT

Material	Condition	Source of analysis	Low-oxygen uranium nitride				Medium-oxygen uranium nitride				High-oxygen uranium nitride			
			Concentration, ppm[a]											
			Oxygen	Hydrogen	Nitrogen	Carbon	Oxygen	Hydrogen	Nitrogen	Carbon	Oxygen	Hydrogen	Nitrogen	Carbon
Uranium nitride	As-received	Vendor	250	---	-----	----	800	---	-----	----	1950	---	-----	----
	As-received	NASA	240 230	---	5.30 percent	766	1050 870	---	(b)	1050	2180 2130	---	5.24 percent	1090
	After 2862 hr at 1040° C (1900° F)	NASA	173	---	5.46 percent	1270 1240	747	---	5.56 percent	3120	2280	---	5.26 percent	630 1170
T-111	As-received	NASA	43	3.2	25	50	43	3.2	25	50	43	3.2	25	50
	After 2862 hr at 1040° C (1900° F)	NASA	44 45	0.3 .5	16 16	55 65	42 40	0.4 .1	16 15	47 51	46 54	0.8 1.2	16 18	77 64
	After 2862 hr at 1040° C (1900° F)[c]	NASA	47 45	1.5 .8	18 17	38 46	----	---	-----	----	----	---	-----	----

[a]Concentrations given in ppm by weight unless otherwise noted.

[b]Insufficient sample for analysis.

[c]Empty control capsule.

TABLE IV. - CHEMICAL ANALYSES OF URANIUM NITRIDE, LITHIUM, AND T-111 USED IN CAPSULE TESTS

[Test temperature, 1040° C (1900° F); time, 2862 hr; vacuum of 10^{-7} N/m^2 (10^{-9} torr).]

Test	Material condition	T-111				Uranium nitride					Lithium
		Concentration									
		Oxygen, ppm	Hydrogen, ppm	Nitrogen, ppm	Carbon, ppm	Oxygen, ppm		Nitrogen, percent	Carbon, ppm	Uranium, percent	Oxygen, ppm
						Vendor	NASA				
0	Untested	43	3.2	25	50	----	----	----	---	-----	70
	Tested[a]	46	1.2	18	42	----	----	----	---	-----	---
1	Untested	--	---	---	--	800	960	(b)	(b)	(b)	---
	Tested	23	2.6	[c]29	22	----	780	(b)	596	(b)	302
2	Untested	--	---	---	--	1490	950	5.26	259	(b)	---
	Tested	39	3.3	56	50	----	1040	5.50	204	94.49	330
3	Untested	--	---	---	--	2300	1140 1780	5.24	311	(b)	---
	Tested	20	3.1	[c]23	52	----	1120	5.46	209	94.44	737

[a]Empty control capsule.

[b]Insufficient sample for analysis.

[c]Single analysis; others are averages of two or more determinations.

TABLE V. - INTERSTITIAL ANALYSES OF T-111 USED IN CAPSULE TEST FOR COMPATIBILITY AMONG T-111, LITHIUM, AND TZM

[Test temperature, 1040° C (1900° F); time, 2862 hr.]

Material	Concentration, ppm by weight			
	Oxygen	Hydrogen	Nitrogen	Carbon
Untested T-111 tubing	43	3.2	25	50
Tested empty T-111 capsule	46	1.2	18	42
Tested T-111 capsule containing TZM and lithium	30	.24	14	54

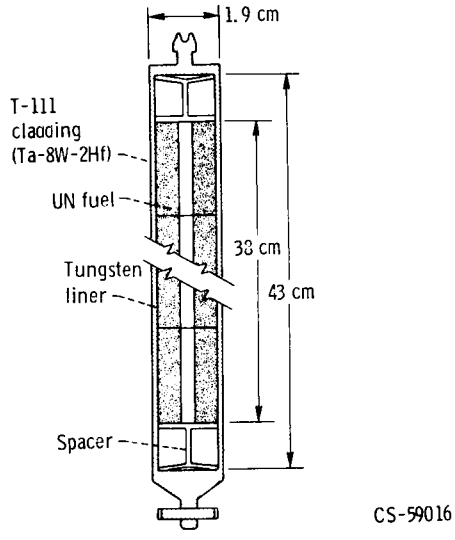
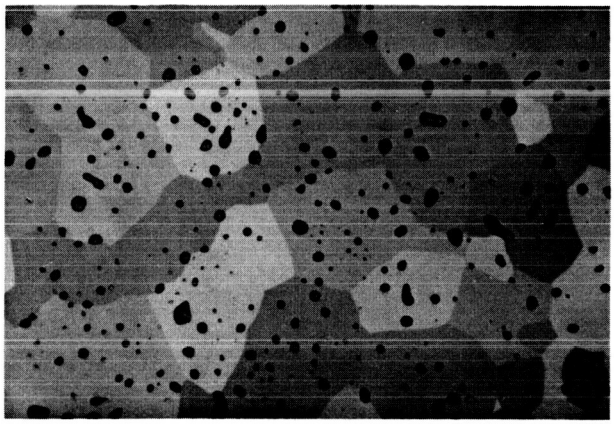
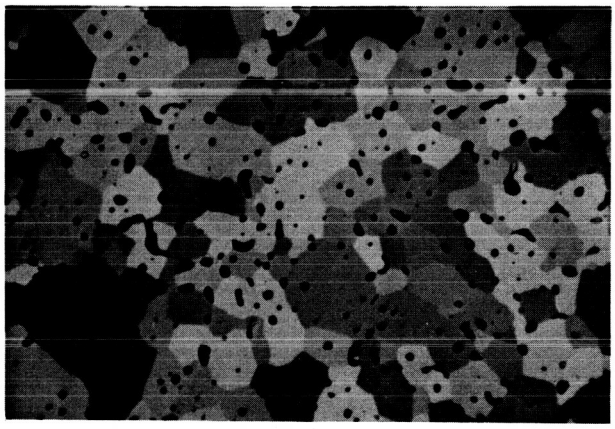


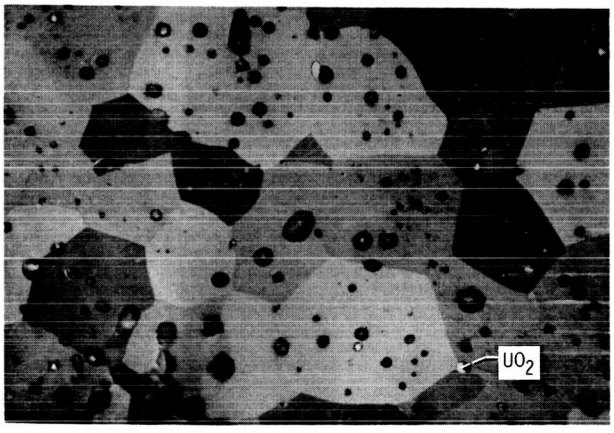
Figure 1. - Space power reactor fuel pin. Operating conditions for reactor: temperature, 930° C; time, 50 000 hours; coolant, lithium.



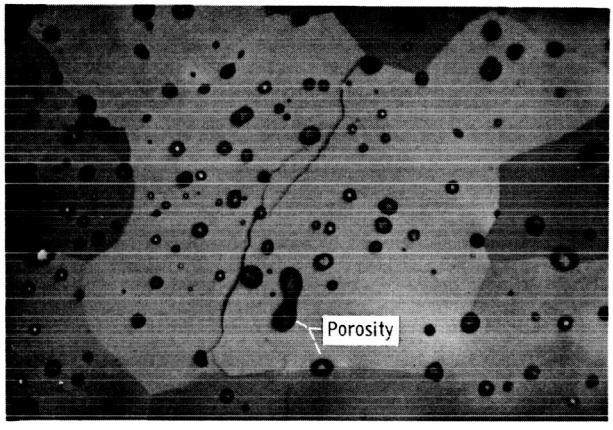
(a) Oxygen content, about 100 ppm.



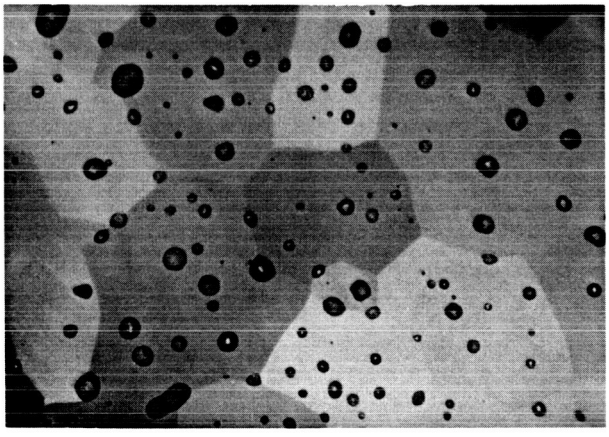
(b) Oxygen content, about 250 ppm.



(c) Oxygen content, about 1950 ppm.

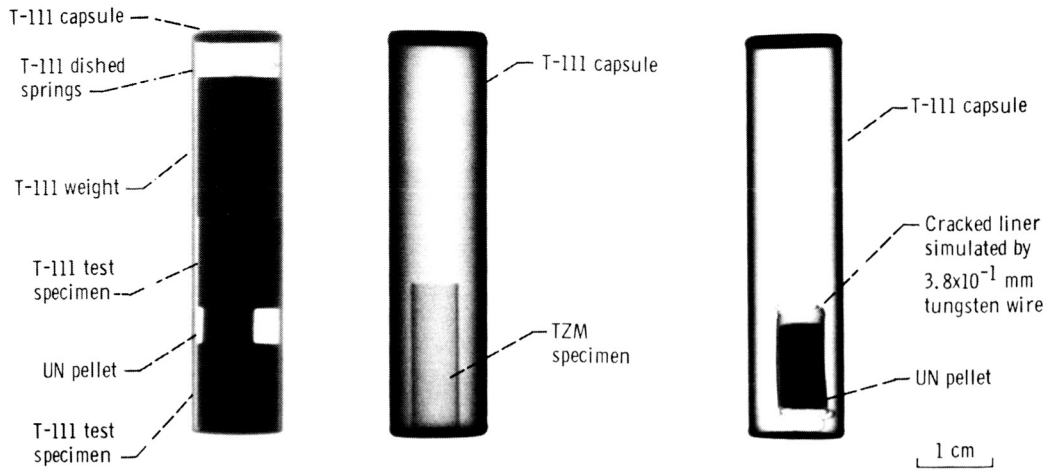


(d) Oxygen content, about 1490 ppm.



(e) Oxygen content, about 2300 ppm.

Figure 2. - Microstructures of various lots of uranium mononitride fuel in pretest condition. Etchant: 60 cubic centimeters of lactic acid, 24 cubic centimeters of nitric acid, and 2 cubic centimeters of hydrofluoric acid.



(a) T-111 and uranium nitride in direct contact, no lithium.

(b) T-111, lithium, and TZM.

(c) Uranium nitride in simulated cracked liner made of tungsten wire immersed in lithium within a T-111 capsule.

Figure 3. - X-ray radiographs showing types of compatibility tests made in T-111 capsules.

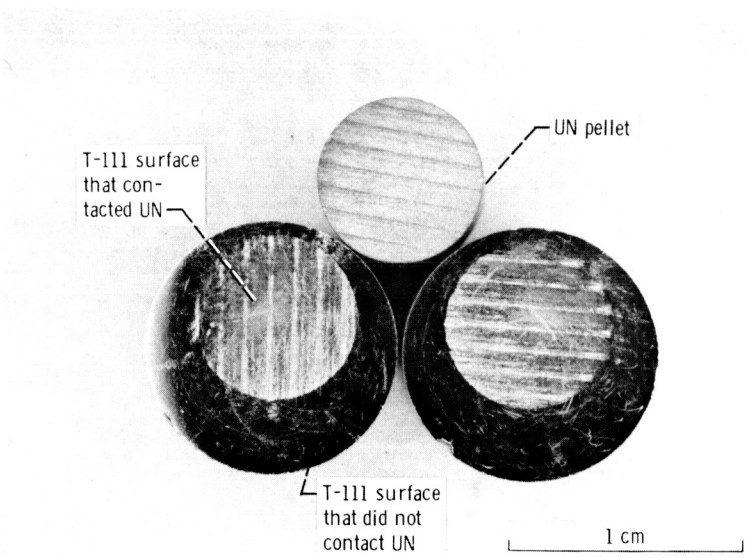
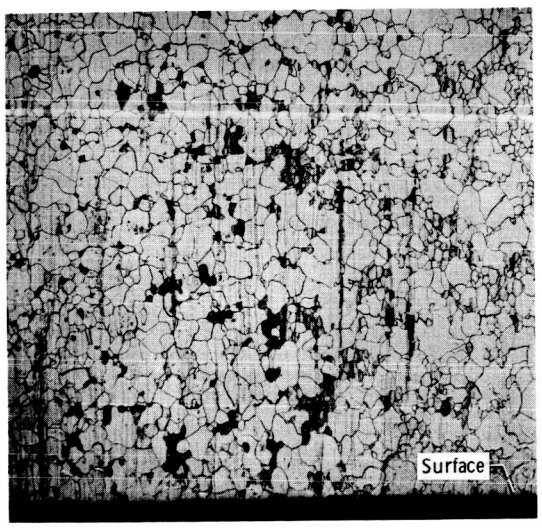
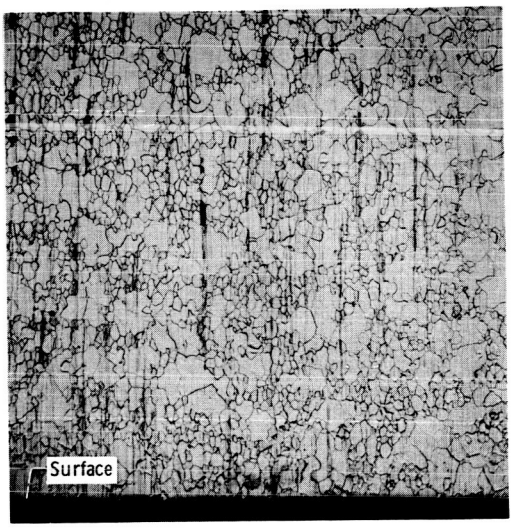


Figure 4. - Typical contact surfaces of T-111 and uranium nitride.

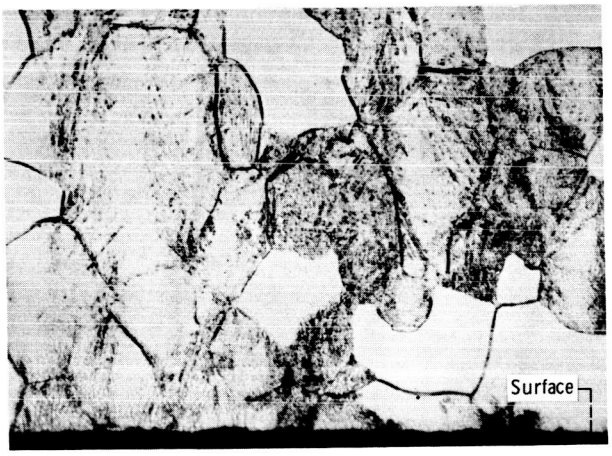


(a) T-111 contact surface. X60.

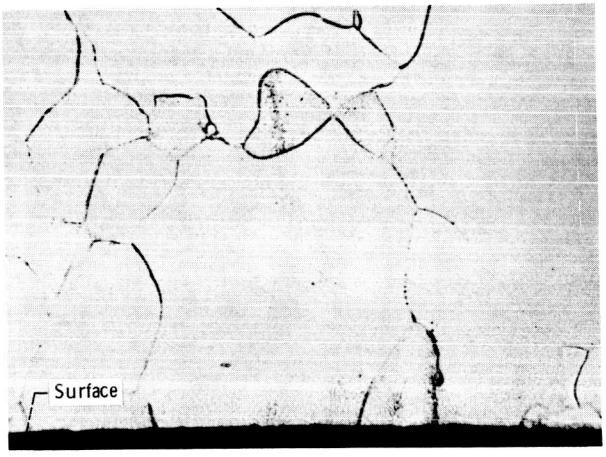


(b) T-111 surface not in contact with uranium nitride. X60.

100 μm

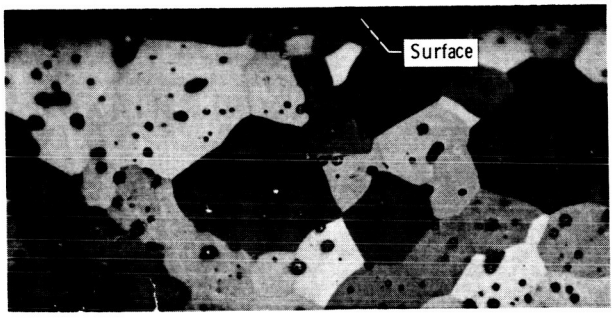


(c) T-111 contact surface. X500.



100 μm

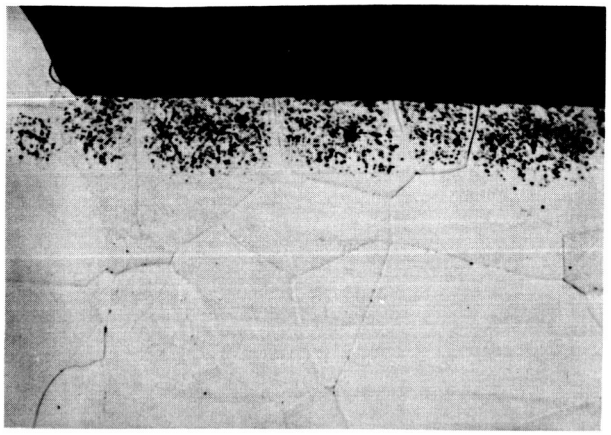
(d) T-111 surface not in contact with uranium nitride. X500.



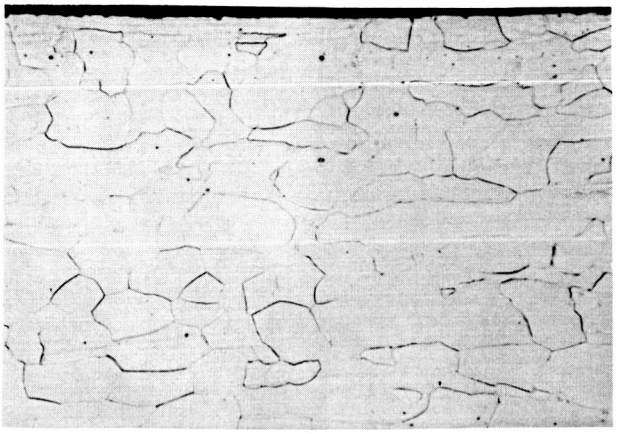
100 μm

(e) Uranium nitride contact surface. X500.

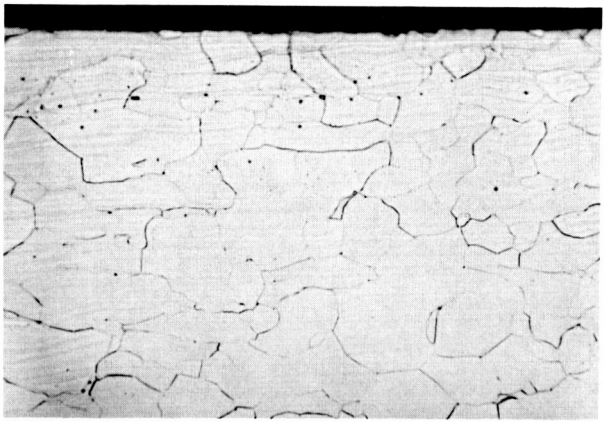
Figure 5. - Reaction surfaces of T-111 and uranium nitride that were in direct contact with each other at 1040° C for 2862 hours and areas of T-111 surface from same specimen that did not contact uranium nitride. T-111 etchant: 30 grams of ammonium bifluoride, 50 cubic centimeters of nitric acid, and 20 cubic centimeters of water; uranium nitride etchant: 60 cubic centimeters of lactic acid, 24 cubic centimeters of nitric acid, and 2 cubic centimeters of hydrofluoric acid.



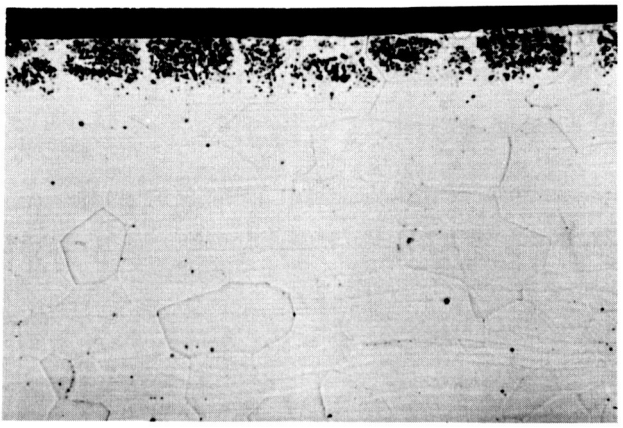
(a) Empty control capsule.



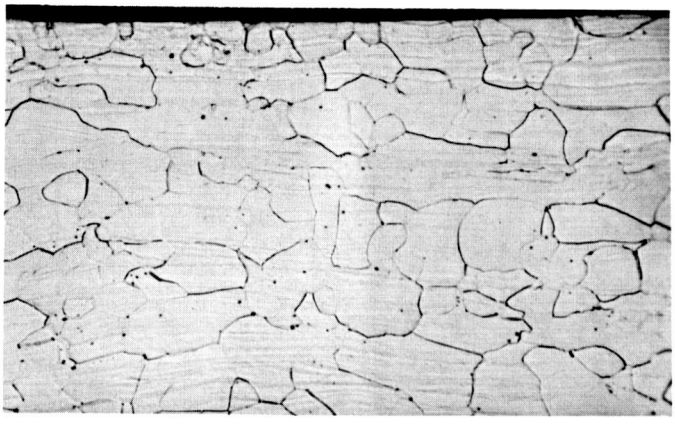
(b) Capsule that contained tungsten wire only.



(c) Capsule that contained uranium nitride pellet with oxygen content of 250 ppm in tungsten wire coil.

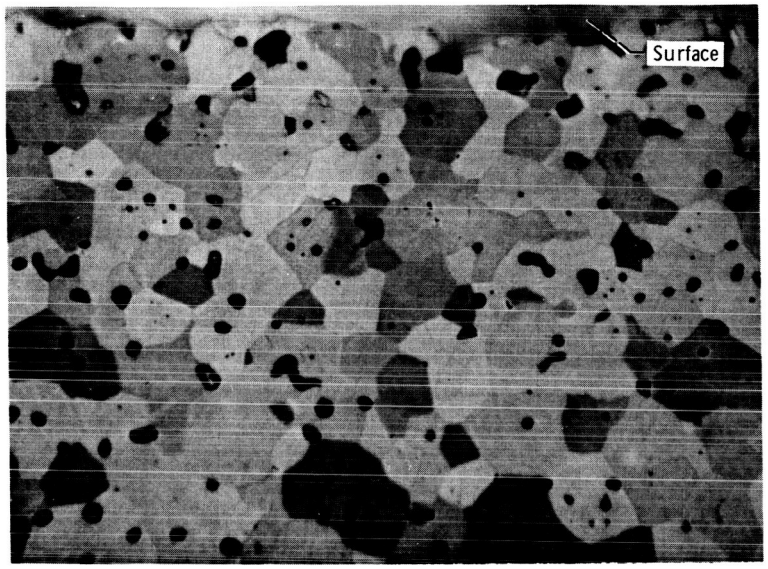


(d) Capsule that contained uranium nitride pellet with oxygen content of 800 ppm in tungsten wire coil.



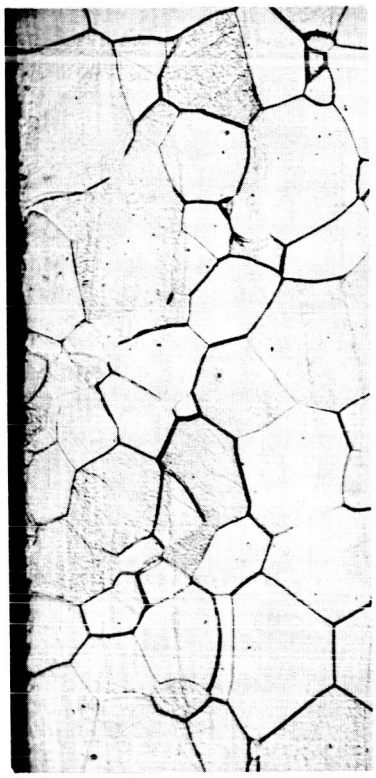
(e) Capsule that contained uranium nitride pellet with oxygen content of 1950 ppm in tungsten wire coil.

Figure 6. - Microstructures of T-111 capsule bottoms after testing at 1040° C (1900° F) for 2862 hours. Note that precipitation in T-111 is not related to capsule contents or oxygen level of uranium nitride; etchant: 30 grams of ammonium bifluoride, 50 cubic centimeters of nitric acid, and 20 cubic centimeters of water.



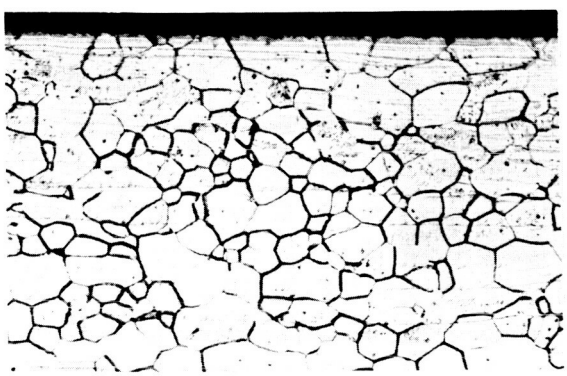
100 μm

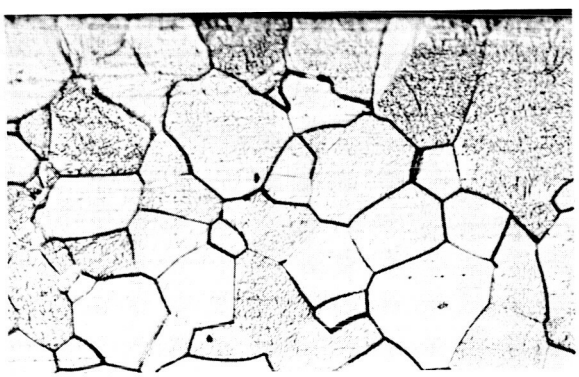
(a) Uranium nitride surface exposed to lithium.



100 μm

(b) T-111 capsule sidewall about 0.6 centimeter above weld.



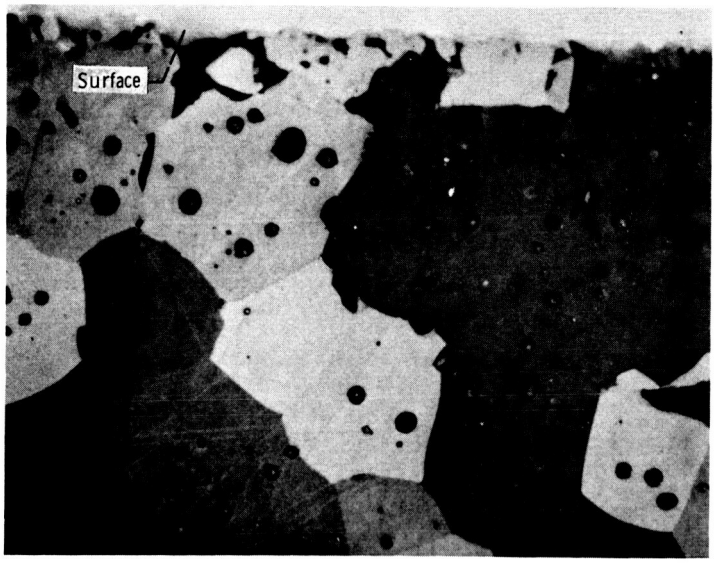


100 μm

(c) T-111 capsule bottom near center of capsule.

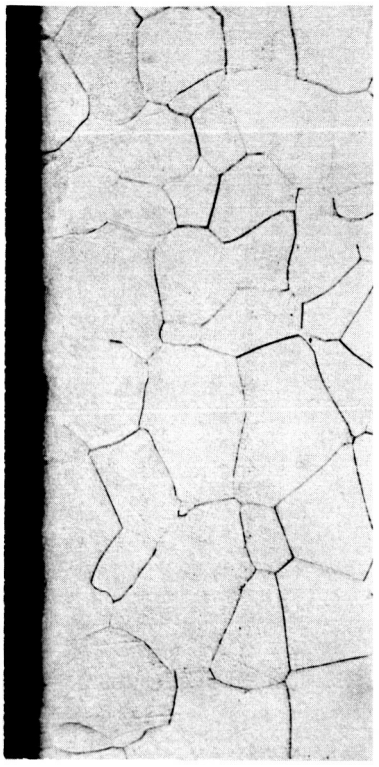
(d) T-111 capsule bottom near weld.

Figure 7. - Microstructures of uranium nitride with oxygen content of 800 ppm and T-111 tested in contact with lithium for 2862 hours at 1040° C (1900° F). Uranium nitride etchant: 60 cubic centimeters of lactic acid, 24 cubic centimeters of nitric acid, and 2 cubic centimeters of hydrofluoric acid; T-111 etchant: 30 grams of ammonium bifluoride, 50 cubic centimeters of nitric acid, and 20 cubic centimeters of water.



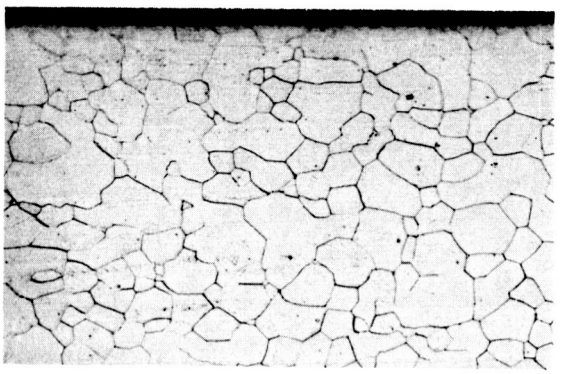
100 μm

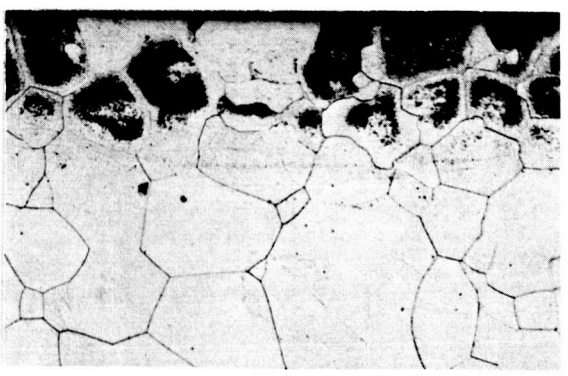
(a) Uranium nitride surface exposed to lithium.



100 μm

(b) T-111 capsule sidewall about 0.6 centimeter above weld.



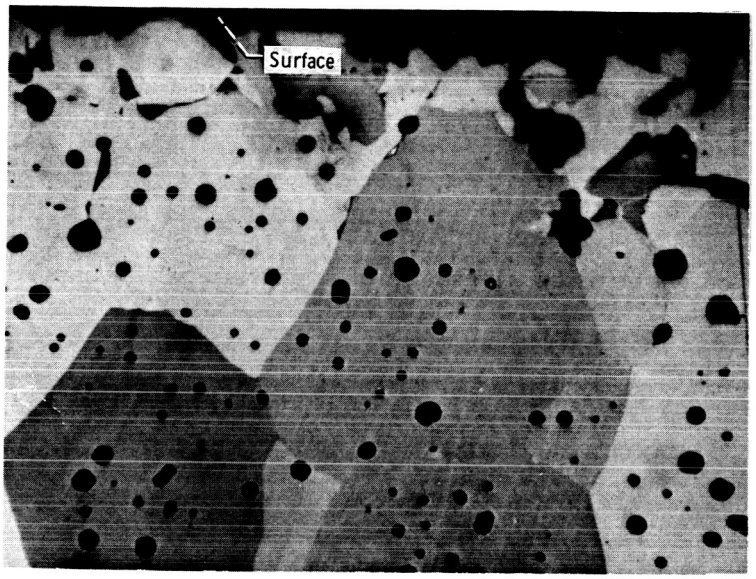


100 μm

(c) T-111 capsule bottom near center of capsule.

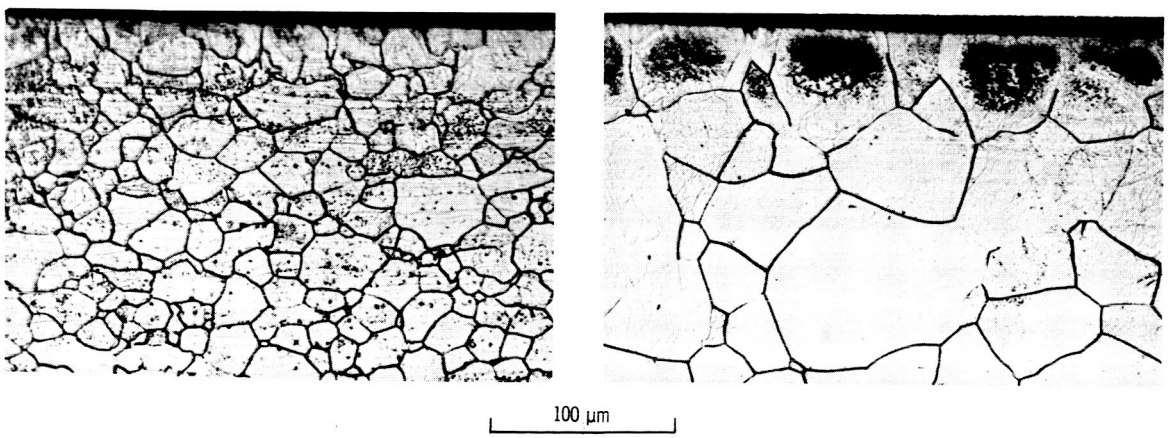
(d) T-111 capsule bottom near weld.

Figure 8. - Microstructures of uranium nitride with oxygen content of 1490 ppm and T-111 tested in contact with lithium for 2862 hours at 1040° C (1900° F). Uranium nitride etchant: 60 cubic centimeters of lactic acid, 24 cubic centimeters of nitric acid, and 2 cubic centimeters of hydrofluoric acid; T-111 etchant: 30 grams of ammonium bifluoride, 50 cubic centimeters of nitric acid, and 20 cubic centimeters of water.



(a) Uranium nitride surface exposed to lithium.

(b) T-111 capsule sidewall about 0.6 centimeter above weld.



(c) T-111 capsule bottom near center of weld.

(d) T-111 capsule bottom near weld.

Figure 9. - Microstructures of uranium nitride with oxygen content of 2300 ppm and T-111 tested in contact with lithium for 2862 hours at 1040° C (1900° F). Uranium nitride etchant: 60 cubic centimeters of lactic acid, 24 cubic centimeters of nitric acid, and 2 cubic centimeters of hydrofluoric acid; T-111 etchant: 30 grams of ammonium bifluoride, 50 cubic centimeters of nitric acid, and 20 cubic centimeters of water.

100 μm

(a) T-111 capsule wall near bottom weld; heated with TZM.

(b) Empty T-111 control capsule heated with capsule shown in (a).

Tested

100 μm

Untested

(c) Cross sections of TZM molybdenum tubing.

Figure 10. - Microstructures of T-111 and TZM heated together with lithium at 1040° C (1900° F) for 2862 hours, of heated control capsule, and of unheated TZM. T-111 etchant: 30 grams of ammonium bifluoride, 50 cubic centimeters of nitric acid, and 20 cubic centimeters of water; TZM etchant: Murakami's solution.