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URANIUM DIOXIDE COMPATIBILITY WITH REFRACTORY METALS, CARBIDES, BORIDES, NITRIDES, AND OXIDES BETWEEN 3500° AND 5000° F

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URANIUM DIOXIDE COMPATIBILITY WITH REFRACTORY METALS, CARBIDES, BORIDES, NITRIDES, AND OXIDES BETWEEN 3500° AND 5000° F

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SUMMARY

An investigation of the compatibility of uranium dioxide with 30 high-melting metals, oxides, carbides, borides, and nitrides was undertaken to indicate combinations that may be suitable for a dispersion-type fuel element for a nuclear reactor. Tests were conducted in vacuum or in a dried argon atmosphere for 10 minutes in the 3500° to 5000° F temperature range. Reactions were studied by means of an X-ray diffractometer and a metallurgical microscope, and temperatures were determined to the nearest 100° F.

Hafnium carbide, tantalum nitride, and the metals tungsten and tantalum were found to be compatible with uranium dioxide to its melting point of 5000° F. In addition, ditungsten boride, molybdenum carbide, and the metals columbium and molybdenum were found to be compatible with uranium dioxide to their melting points. Others were compatible but at slightly lower temperatures.

INTRODUCTION

Although extremely high temperatures can be theoretically attained in nuclear reactors, present-day nuclear powerplants are restricted to relatively low temperatures to stay within the limitations of currently available materials. Much higher temperatures are desirable to increase the power output of nuclear reactors proposed for rockets, ramjets, turbojets, and electrical powerplants. The refractory metals and ceramics appear to be promising as materials of construction for these high-temperature reactors.

The major effort in the investigation of materials for nuclear reactors has been on fuel elements, since they operate at higher temperatures than any other part of the reactor. Fuel elements for the previously mentioned applications will consist of a fissionable material

(usually a refractory uranium compound) most likely dispersed as discrete particles in a continuous dense matrix which provides strength and the required heat-transfer area. A major deterrent to the use of refractory metals and ceramics for the fuel-element matrix is the lack of information about their compatibility with the fissionable material at high temperatures. Compatibility is herein defined as that state which enables the fuel and matrix materials to exist in contact with one another without chemical or metallurgical interaction. Reactions leading to low melting or gaseous phases or to large volume changes would be detrimental to reactor operations. However, if a solid solution or an equally refractory compound is the result of a reaction, this lack of compatibility may not necessarily negate the use of a particular material.

There are not sufficient thermodynamic and phase diagram data to predict the compatibility of potential matrix and fuel materials at high temperatures. It is therefore desirable to study the compatibility of these materials experimentally.

The primary purpose of this investigation then is to survey refractory metals and ceramics to determine the maximum temperature at which they are compatible with a refractory uranium fuel. Such a survey would establish fuel-matrix combinations for further investigation for very high temperature fuel elements.

For the present study, uranium dioxide (UO_2) was chosen as the fuel material. Its compatibility was evaluated with 30 metals, oxides, carbides, borides, and nitrides, all having melting points above 4000° F.

High-density disks of UO_2 and disks of the potential matrix materials in intimate surface-to-surface contact were used to determine compatibility with adherence of the disks taken as the primary criterion. The reactions causing adherence were studied by X-ray diffraction and metallurgical microscopy.

The evaluations were conducted in vacuum or in a dried argon atmosphere for test periods of 10 minutes and for test temperatures ranging from 3500° F to the melting point of either the material or UO_2 (5000° F).

MATERIALS AND BASES FOR SELECTION

Melting points from the published literature and chemical analyses are given in table I. While the materials in the table were of the highest purity commercially available, it is recognized that higher purities might change results.

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Uranium Dioxide (UO_2)

Comparison of the refractory uranium compounds with respect to melting point and the available information on high-temperature stability indicate that UO_2 (melting point approx. 5000° F, ref. 1) is the most promising compound for very high temperature reactors. It was therefore chosen as the fuel material for this investigation. The UO_2 disks were produced by the Norton Company using as starting material UO_3 supplied by the Mallinckrodt Chemical Works. The disks were 1/2 inch in diameter by 1/4 inch thick and of a density of approximately 10.3 grams per cubic centimeter (94 percent of theoretical density).

Metals

The four metals evaluated as matrix materials were tungsten, tantalum, molybdenum, and columbium. The remaining metals with melting points above 4000° F, rhenium, osmium, iridium, and ruthenium, were considered too scarce for practical application and therefore were not included in this study.

Oxides

Although it was known from the literature (refs. 2 and 3) that thoria (ThO_2) and zirconia (ZrO_2) form solid solutions with UO_2, these materials were evaluated in order to give some indication of the extent of reaction for the test time. Chromia (Cr_2O_3) and UO_2 were evaluated because there was no information on this system. Beryllia and magnesia were excluded from the study in spite of their high melting points. The beryllia-urania system is being studied extensively elsewhere. Magnesia has such poor physical and mechanical properties that it is doubtful if it can be seriously considered for the high temperatures considered here.

Graphite and Carbides

Graphite and carbides are known to be among the most refractory of all materials. Thus, for such applications as high-temperature reactor fuel elements, they should receive primary consideration. Graphite and the 11 most refractory, commercially available carbides were therefore chosen for the study. These carbides are hafnium carbide (HfC), tantalum carbide (TaC), zirconium carbide (ZrC), the mixed carbide 4TaC:1ZrC, columbium carbide (CbC), titantium carbide (TiC), vanadium carbide

(VC), ditungsten carbide (W_2C), tungsten monocarbide (WC), molybdenum carbide (Mo_2C), and silicon carbide (SiC).

Borides

Although the borides are generally not as refractory as the carbides, they are known to be comparable to them in regard to such properties as volatility, electrical resistivity, and hardness, with the high-temperature stability of the borides being slightly superior to that of the carbides. Although natural boron is a neutron absorber having the high thermal neutron absorption cross section of 750 barns, and therefore probably not usable in a reactor fuel element, 81 percent of natural boron consists of a boron isotope (at. wt. 11), which has a very low cross section of less than 0.05 barn. Boride fuel elements consisting of this low-cross-section isotope might be considered practical if they have superior physical properties. Therefore, the seven most common refractory borides were included in this compatibility investigation: hafnium diboride (HfB_2), zirconium diboride (ZrB_2), tantalum diboride (TaB_2), titanium diboride (TiB_2), columbium diboride (CbB_2), tungsten boride (WB), and thorium tetraboride (ThB_4).

Nitrides

The nitrides as a class are unsatisfactory for general use because of extreme brittleness, low oxidation resistance, poor sinterability, and tendency to decompose at temperatures much below their melting points. Some were included in this investigation, however, because of their possible use as additives to carbides and borides to give refractories of superior properties. The four nitrides included in this investigation are hafnium nitride (HfN), tantalum nitride (TaN), zirconium nitride (ZrN), and titanium nitride (TiN).

APPARATUS

Figures 1 and 2 show the furnace used to heat the specimens for this compatibility study. The furnace is heated inductively by a 50-kilowatt, 9600-cycle-per-second motor generator. The induction coil is radially and axially centered between an outer $\left(4\frac{1}{2}\text{-in. diam.}\right)$ Pyrex tube and an inner $\left(3\frac{1}{4}\text{-in. diam.}\right)$ fused quartz tube, which forms the furnace chamber. Cooling water was circulated both within the induction coil and through the annular passage between the two tubes.

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The furnace is mounted directly on and supported by a 4-inch oil diffusion pump, which is backed by a mechanical pump. The chamber pressure is indicated by one of two gages, one for the zero to 800 millimeters of mercury pressure range, and a Phillips gage for the 0- to 25-micron range.

Because of possible interference by vapors and films deposited on the prism face in spite of the prism cover, the specimen temperature during the tests was established by careful calibrations of the coil voltage against temperature for the various furnace chamber pressures. The following steps were used to make this calibration:

(1) The optical pyrometer and prism assembly was calibrated against a National Bureau of Standards certified standard lamp.

(2) A temperature-against-power curve was made by sighting on a tungsten specimen placed in a test position which approached blackbody conditions. Tungsten was used because it has low volatility. The accuracy of the temperature measurements was considered to be $\pm 50^{\circ}$ F. (The optical pyrometer was also used during the tests to provide gross monitoring for temperatures and reactions detrimental to the furnace.)

(3) This calibration was checked in the furnace and frequently rechecked during the course of the investigation against the melting points of molybdenum (4710° F, ref. 4) and uranium dioxide (5000° F, ref. 1).

PROCEDURE

A weighed specimen of a refractory material, 3/16 of an inch thick and either 1/2 inch square or 1/2 inch in diameter, was placed on a similar-size, weighed disk of uranium dioxide, which in turn was placed on the tungsten platform. The contact surfaces of the specimens were diamond-ground to be flat and smooth. The surface roughness was about 10 microinches in the case of uranium dioxide and ranged from 5 to 20 microinches for the various refractory materials. The materials were placed in the furnace, which was then evacuated to a high vacuum (2×10^{-5} mm Hg). Tests at temperatures of 4000° F and below were run in vacuum, and, for test runs over 4000° F, static pressures of from 5 to 40 millimeters of argon were employed. This was necessary to reduce the excessive evaporation rate of UO_2. The argon was dried by means of activated alumina and molecular sieves.

The furnace was slowly heated to test temperature in a period of about 40 minutes to avoid thermal shocking the specimens and furnace components. During this heating period, the pressure was closely watched for abrupt changes which might indicate reaction. The specimens were

also watched during this heat-up period through the optical pyrometer. When the voltage setting corresponding to the desired test temperature was reached, it was held for a period of 13 minutes. The furnace temperature stabilized within 3 minutes, and the actual time at temperature was 10 minutes. Pressure and visual observations were made during this period, and, at its conclusion, the furnace was slowly cooled approximately at the same rate at which it was heated.

All initial compatibility tests were run at a temperature of 3500° F. After this run, the specimens were examined for adherence or such other signs of reaction as color changes or physical disturbances on the contact surfaces. Weight changes were also noted. If there was no clear evidence of reaction, the same specimens were further tested at 4000° F. If again there were no indications of reaction, the materials were further tested at 4500° F and, finally, at the melting point of uranium dioxide (5000° F) or the melting point of the refractory material. When reaction did occur, new specimens were used to determine the reaction temperature to the nearest 100° F.

In the case of strong adherence, where the pellets could not be separated manually, the pellets were sectioned, and the interface was studied by X-ray diffractometer and metaloscope. Where there was little or no adherence, but there were other indications of disturbance at the interface such as surface roughening and/or color changes, the contact surfaces were analyzed by X-ray diffraction. In certain instances X-ray analyses were made on noncontact surfaces of the test materials which had changed color or had given other indications of possible vapor reaction. It should be remembered that X-ray diffraction will not ordinarily detect substances present in quantities less than a few percent.

RESULTS AND DISCUSSION

Reaction temperatures are tabulated in table II with two temperatures being given in some cases to indicate both the point at which some reaction product was found and the point at which adherence occurred. Both are of importance since they give some indication as to the extent of reaction, which would be of value in determining the use time of a particular combination.

Metals

As shown in table II(a), uranium dioxide was completely inert toward the four refractory metals, tungsten, tantalum, molybdenum, and columbium, up to the melting point of the metal or uranium dioxide, whichever was less. For the test conditions given and from the standpoint of

compatibility as herein defined, these four metals can therefore be considered as promising matrix materials for fuel elements.

Oxides

The reactions of each oxide with uranium dioxide are discussed as follows and are listed in table II(a).

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Thorium dioxide (ThO_2). - The greatest stability and the highest melting point of all the oxides are characteristics of ThO_2. As anticipated from the phase diagram, ThO_2 formed a solid solution with UO_2. This was first detected on the contact faces after heating to 4000° F where slight adherence occurred. The lattice parameter computed from the X-ray diffraction analysis indicated the solid solution consisted of about 25 percent ThO_2 and 75 percent UO_2.

Zirconium dioxide (ZrO_2). - At 3500° F and above there was strong adherence between the ZrO_2 and UO_2 pellets because of the formation of a solid solution.

Chromium oxide (Cr_2O_3). - Although there was no sign of reaction at 3500° F between the Cr_2O_3 and UO_2 pellets, sudden unexplained outgassing occurred as the test temperature was reached. This happened for each test run when 3500° F was attained. At both 3500° and 3600° F weight losses for the materials were unusually high, and at the latter temperature contact surfaces were roughened slightly; no analyses were made of these surfaces. At 3700° F and above, a reaction took place in which the Cr_2O_3 was completely melted and the UO_2 partially melted. On the basis of the high weight losses of Cr_2O_3 and UO_2, it may be postulated that the Cr_2O_3 decomposed and that the decomposition products attacked the UO_2. X-ray diffraction analysis of the UO_2 contact face detected only the parent materials.

Although ThO_2 and ZrO_2 are not compatible with UO_2 for use as defined herein because of the formation of solid solutions, these solid solutions may have uses as prealloyed fuels since the phase diagrams indicate that they melt at temperatures above 4900° F.

Graphite and Carbides

Listed in table II(b) in decreasing order of reaction or melting temperature are the results of the compatibility tests between uranium dioxide and the carbides and graphite.

Hafnium carbide (HfC). - Of the carbides studied, only HfC was completely inert to UO_2 up to 5000° F. The very high thermal neutron absorption cross section for natural hafnium (120 barns) prohibits its use in thermal reactors, but a possible application would be the carbide of the hafnium isotope with mass number of 180. This isotope has a considerably lower thermal neutron absorption cross section of only 13 barns.

Tantalum carbide (TaC). - This material, which has a melting point very nearly that of hafnium carbide, reacted with UO_2 as low as 4500° F to produce a thin film of uranium monocarbide (UC) on the UO_2 contact face. There was no adherence. Test specimens were also heated to 4900° and 5000° F with slight adherence but with no appreciable increase in the amount of reaction (thickness of film). This reaction must therefore proceed at a slow rate with the UC apparently acting as a diffusion barrier. It is known that at high temperatures TaC loses carbon and eventually becomes the lower carbide, Ta_2C. This carbide was found on disk contact surfaces from the 5000° F run, and it may be hypothesized that the free carbon made available by this decomposition of TaC is the co-reactant with UO_2 in the formation of UC. At any rate, because of its melting point and its slow rate of reaction at very high temperatures, TaC may still be of interest as a fuel-element matrix material.

Mixed carbide (4TaC:1ZrC). - This, the highest-melting-point material reported in the literature, reacted with UO_2 at 4500° F without adherence and formed a small amount of UC with smaller-than-normal unit cell dimension of about 4.93 angstroms. Slight adherence occurred at 4800° F where the carbide reacted with UO_2 in the same way as did TaC to produce a thin film of UC at the interface.

Columbium carbide (CbC). - At 4000° and 4500° F there was no adherence between CbC and UO_2. However, at the lower temperature the CbC blistered, and at 4500° F there were signs of melting on the CbC pellet edges, with UC and UC_2 detected at the interface. A test run at 4600° F resulted in definite liquid formation with strong adherence between the pellets as shown in figure 3. Figure 3(b) shows the cross section of the adhering specimens and the liquid causing the adherence. Figure 3(a) is a photomicrograph showing the UO_2 and CbC phases; the melted area appears to be identical to the CbC. An X-ray diffraction pattern of the entire cross section of the adhering pellets indicated the presence of several weak unidentified lines in addition to the parent materials; UC and UC_2 were not detected. Because of the great difference between the reported melting point for CbC (6330° F) and what might be taken as simple melting at 4600° F, it is assumed that CbC reacted with UO_2. However, it should be pointed out that the columbium carbide used was carbon deficient

and that CbC probably forms solid solutions with CbN and CbO (ref. 4, p. 110). Either of these may account for the evidence of melting.

Zirconium carbide (ZrC). - In addition to the very high melting point of ZrC, another property of this material which makes it of particular interest is its very low thermal neutron absorption cross section (about 0.18 barn). However, its limit of compatibility with UO_2 was only 4400° F. At 4500° F the pellets adhered strongly as a result of the formation of a solid film consisting of the parent materials and UC. The presence of UC would indicate that ZrO_2 was also a reaction product. On the basis of the results with ZrO_2, a solid solution of UO_2-ZrO_2 was expected. However, this was not detected by X-ray diffraction.

Tungsten monocarbide (WC). - The carbide appeared to melt at 4500° F with subsequent wetting of and adherence to the UO_2 pellet, with no apparent attack on the latter. This temperature is 270° below its reported melting point. Metallographic and X-ray examination of the sectioned specimens did not reveal the presence of a new phase, but the X-ray analysis indicated a greater amount of ditungsten carbide (W_2C) present than existed in the specimen before test. Norton (ref. 4, pp. 155-157) reports a eutectic between WC and W_2C at 4575° F, and this may explain the lower observed melting temperature of 4500° F. Although there was no adherence at 3500° and 4000° F, UC was detected at the interface and on all noncontact surfaces. A possibility for the generation of the W_2C would be the reaction $WC \xrightarrow{heat} W_2C + C$. The latter reaction would result in a carbonaceous atmosphere, which would then account for the uranium monocarbide found on all noncontact faces above 3500° F.

Ditungsten carbide (W_2C). - Ditungsten carbide behaved in somewhat similar manner as did WC, appearing to melt slightly at 4400° F with no adherence but with UC formed on all surfaces. The WC-W_2C eutectic was possible here again, since the W_2C before test contained some WC.

Titanium carbide (TiC). - Although there was no interfacial reaction between UO_2 and TiC until 4000° F was reached (a film of UC was produced causing slight adherence), a black, glassy coating formed on all the TiC exposed surfaces at 3600° F and above. It is believed that this reaction is one of TiC and UO_2 vapor phases with TiO_2 and UC being the reaction products. X-ray diffraction analysis identified UC in the coating, but TiO_2 was not found, probably because it decomposes. This explanation for the formation of the coating is substantiated by accompanying high weight losses of UO_2 (vapor consumed as it forms) and by a comparison 4000° F

run under 40-millimeter static argon atmosphere where the interfacial reaction was verified (UC formed). In this case, however, there was no black, glassy coating formed because the rate of vaporization of the materials was suppressed by the partial atmosphere.

Molybdenum carbide (Mo_2C). - The case for this carbide was very similar to that of the tungsten carbides. Incipient melting at 3700° F was observed for Mo_2C with resultant wetting of and adherence to the UO_2. This followed blistering of all Mo_2C exposed surfaces at 3500° and 3600° F. At 4000° F the carbide melted, became hemispherical in shape, and reacted with the UO_2 to form UC at the interface. A cut revealing the cross section of the Mo_2C disk showed several gas holes. Evolution of gas was evidenced by a greatly increased furnace pressure, which indicated instability of Mo_2C in vacuum. It is reported (ref. 4, pp. 132-133) that a eutectic between Mo and Mo_2C is formed at 3990° F. It is presumed that the lower observed melting temperatures of Mo_2C resulted from a decomposition and subsequent eutectic formation. A disk of the carbide heated alone acted similarly.

Vanadium carbide (VC). - Vanadium carbide reacted with UO_2 as low as 3700° F to produce a liquid phase at the interface in which were detected uranium and uranium monocarbide in addition to the parent materials. Figure 4(a) shows the reactants at the lowest temperature of reaction, 3700° F, where a thin film of liquid phase causes adherence, while figure 4(b) shows a cross section of the pellets which had adhered because of the more extensive reaction at 4000° F. Figure 4(c) is a photomicrograph of the center of the reaction zone seen in figure 4(b). This "necked down" portion of the reaction zone was selected so that the VC above and the UO_2 below could also be included in the photomicrograph. It should be pointed out that the reactions described involve a vanadium carbide with great amount of free carbon, a considerable departure from stoichiometry, and the likelihood of appreciable oxygen and/or nitrogen content (about 6.3 percent unaccounted for in chemical analysis). The latter would result in the presence of VN and VO, which are isomorphous with VC.

Silicon carbide (SiC). - The best oxidation resistance and the lowest thermal neutron absorption cross section of any of the carbides studied are characteristics of SiC and make it of considerable interest for reactor use. Unfortunately, SiC reacted with UO_2 at 3500° F, the temperature at which all compatibility studies were initiated. A liquid phase was formed in which UC and possibly uranium disilicide were detected.

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Graphite. - As expected, graphite reacted with UO_2 at 3500° F forming UC and UC_2, which resulted in strong adherence.

Although HfC was the only carbide compatible with UO_2 to 5000° F, TaC, the mixed carbide 4TaC:1ZrC, ZrC, and CbC should still be considered for fuel elements. Their high melting points and good nuclear properties recommend their use at approximately 4500° F, the limit of their compatibility with UO_2.

Borides

The results of the compatibility tests between the seven borides and UO_2 are listed in table II(c) in order of decreasing temperatures. A face-centered cubic phase with a lattice constant of 4.91±0.02 angstroms was found in the reactions of UO_2 with the diborides of columbium, zirconium, hafnium, titanium, and tantalum. This lattice constant corresponds to that hypothesized for uranium monoxide (ref. 5). This phase is therefore considered to be UO.

Columbium diboride (CbB_2). - Although there was no adherence, first indication of reaction was noted at 4500° F where the presence of UO was detected. Extensive reaction occurred when UO_2 and CbB_2 were heated to a test temperature of 4900° F. A molten mass containing all the UO_2 was produced. X-ray examination of the sectioned mass and remaining CbB_2 showed the presence of CbB and/or WB, the parent materials, and possibly W and UB_2. The tungsten and its boride probably resulted from an attack on the tungsten platform by the molten mass. Metallographic examination revealed only CbB_2 and an apparently homogeneous liquid phase.

Ditungsten boride (W_2B). - From the X-ray analysis after test it is evident that WB, the starting tungsten boride, decomposed to W_2B and was the material evaluated. This observation verifies the findings reported in reference 6. Table II(c) therefore gives the results of the W_2B-UO_2 compatibility test. At 4700° F there was no evidence of reaction, but the W_2B melted with no adherence to the UO_2 disk. The melted mass was a smooth globule. It lost 69 percent of its weight. Since the reported melting point of W_2B is 5020° F, it may be that the W_2B lost boron resulting in a W-W_2B eutectic.

Zirconium diboride (ZrB_2). - The first indication of reaction of UO_2 with ZrB_2 occurred at 4400° F where UO was detected at the interface.

Strong adherence at 4700° F was due to a reaction film which consisted of an unidentified substance, the parent materials, and possibly ZrB in addition to UO. At 4800° F the reaction was extensive with both materials being consumed.

Hafnium diboride (HfB_2) and titanium diboride (TiB_2). - Both of these diborides reacted with UO_2 without adherence as low as 4500° F to form UO. At 4700° F, in each case, a liquid phase was produced in which only the original materials could be detected. The UO_2 pellets were more affected than the diborides, with complete melting of the former when in contact with HfB_2 and partial melting when in contact with TiB_2.

Tantalum diboride (TaB_2). - First reaction between UO_2 and TaB_2 occurred at 4000° F without adherence; UB_2 and UO were detected by X-ray diffraction analysis on the UO_2 contact face. At 4500° F the first slight adherence occurred; UO was again detected at the interface with some X-ray indication of UB_2, UB_4, and UB_{12}. From 4500° to 5000° F the adherence continued to be slight. At 5000° F, UO and TaB were detected on both the TaB_2 and UO_2 contact surfaces.

Thorium tetraboride (ThB_4). - At 4200° F the pellets of UO_2 and ThB_4 adhered strongly because of a slight melting of the boride. Because this liquid phase appeared 300° F below the reported melting point of ThB_4, it was felt that the material might be lower melting because of the presence of the oxyboride of reference 6. However, X-ray diffraction analysis indicated that the melted phase consisted of a UO_2 of slightly increased cell size, UB_2, UB_4, ThB_4, and some unidentified material. Therefore, this melted phase is considered to be the product of a reaction.

As a class, the borides appear to be more stable with UO_2 than are the carbides. Six of the seven borides were compatible between 4500° and 4900° F.

Nitrides

The results of the compatibility tests between the four nitrides and UO_2 are listed in table II(d) in order of decreasing temperature.

Tantalum nitride (TaN). - As shown in table II(d), TaN is compatible with UO_2 at 5000° F. The nitride disks exhibited high weight losses and displacement by blistering at temperatures above 4000° F. Therefore, for

higher temperature test runs, a static argon pressure of 240 millimeters of mercury was employed to suppress these actions. It is likely that these actions are the result of dissociation, but no definite evidence of the lower nitride, Ta_2N, or Ta was found by X-ray diffraction analysis of the TaN specimens. The UO_2 disks from the 4800° and 4900° F runs came out of test with contact surfaces as shown in figure 5. The craters in the UO_2 which formed around the TaN disks were about 1/16 inch deep and indicate an excessive amount of UO_2 lost at the contact area. No reaction or dissociation products could be detected at the contact faces, and there was no adherence. The extra loss of the UO_2 over that normally encountered may be the result of a vapor erosion by the TaN. The UO_2 disk melted in the 5000° F test without any sign of another phase.

Zirconium nitride (ZrN). - Although there was no adherence, reaction was first indicated at 4000° F where nitrides of uranium were found at the interface. At 4400° F adherence was caused by formation of a liquid phase in which UN and UN_2 were detected.

Hafnium nitride (HfN). - Initial reaction at 4000° F with no adherence was the case for this nitride as indicated by the presence of HfO_2, with U_2N_3 and UN_2 probable. Adherence of the disks first occurred at 4000° F with the formation of UN, in addition to HfO_2, and UN_2, which were found before. Complete melting of both materials occurred at 4700° F.

Titanium nitride (TiN). - The lowest adherence temperature for UO_2 and the nitrides was that for TiN; it adhered to UO_2 at 4200° F with the formation of a liquid phase in which UN or UO was detected in addition to the parent materials.

In general, the nitrides were observed to be less stable than the carbides and borides as evidenced by high weight losses for TaN, HfN, and TiN. In addition, the final pressures for the TaN and HfN compatibility runs were high, indicating possible dissociation. Thus, it appears unlikely that the nitrides would be suitable for use as a matrix material except in pressurized systems.

SUMMARY OF RESULTS

An experimental investigation was conducted to determine the high-temperature compatibility of uranium dioxide in contact with 30 refractory metals, oxides, carbides, borides, and nitrides. The results were as follows:

1. Uranium dioxide was compatible with four materials up to its melting point of 5000° F. These were tantalum, tungsten, hafnium carbide, and tantalum nitride.

2. Uranium dioxide was compatible up to the melting point of molybdenum (4700° F) and columbium (4500° F).

3. Uranium dioxide was compatible with ditungsten boride to 4700° F and with molybdenum carbide to 3700° F at which points both materials melted presumably because of decomposition and resulting eutectic formation.

4. Uranium dioxide reacted with the 22 remaining materials at the following temperatures:

Material	Adherence temperature, °F	Initial reaction temperature, °F
ThO_2	4000	4000
Cr_2O_3	3700	3700
ZrO_2	3500	3500
TaC	4900	4500
4TaC:1ZrC	4800	4500
CbC	4600	4500
ZrC	4500	4500
WC	4500 (melted)	3500
W_2C	4400 (melted)	3500
TiC	4000	4000
VC	3700	3700
Graphite	3500	3500
SiC	3500	3500
CbB_2	4900	4500
ZrB_2	4700	4400
HfB_2	4700	4500
TiB_2	4700	4500
TaB_2	4500	4000
ThB_4	4200	4200
HfN	4600	4000
ZrN	4400	4000
TiN	4200	4200

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CONCLUDING REMARKS

The temperatures and amount of reaction depend upon the chemical and physical state of the materials. Therefore, it should be remembered that the data reported herein are for materials of a given analysis in intimate surface-to-surface contact.

Although there are four materials that were determined to be compatible with UO_2 up to 5000° F, there are many materials that can be considered for fuel elements, providing their fabrication and operation are at temperatures where reaction does not occur or the rate of reaction is negligible.

The nitrides appear to be unsuitable for high-temperature applications because of the high dissociation pressures.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, November 2, 1959

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TABLE I. - MELTING POINTS AND ANALYSES OF REFRACTORY MATERIALS

(a) Metals and oxides

Material	Melting point		Approximate spectrographic impurities (a)				Impurity phases found by X-ray diffraction (b)
	°F	Reference	0.5-5%	0.1-1%	0.05-0.5%	0.005-0.05%	
UO_2	5000	1	----------	------	----------	Si	--
W	6120	4	----------	------	----------	Si	--
Ta	5430	4	----------	------	Si, Ca	Mg, Mo	--
Mo	4710	4	----------	------	----------	Ca	--
Cb	4530	4	Zr	------	Fe, Ti	Al (0.03%), Cr	Zr
ThO_2	5520	4	----------	Al, Ca	----------	Si, Fe, Ti, B	--
ZrO_2	4870	4	Ca (3%), Si	Al	Fe, Mg, Na	Ti, K	--
Cr_2O_3	4109	7	Ti	------	V, Ca, Na	Mg, K	--

[a]Determined by semiquantitative spectrographic analysis supplied by National Spectrographic Laboratories, Cleveland, Ohio.

[b]Analyses were made by Los Alamos Scientific Laboratory and by Lewis Research Center. Literature values of interplanar spacings and lattice constants used in the identification of materials by X-ray diffraction were taken from refs. 5 and 8.

TABLE I. - Continued. MELTING POINTS AND ANALYSES OF REFRACTORY MATERIALS

(b) Carbides

Nominal material	Melting point		Chemical analysis, weight percent (a)			Approximate spectrographic impurities (b)				Corrected chemical analysis, weight percent			Calculated formula	Impurity phases found by X-ray diffraction (d)
	°F	Reference	Total metal	Combined carbon	Free carbon	0.5-5%	0.05-0.5%	0.01-0.1%	0.005-0.05%	Major metal	Combined carbon[c]	Total		
4TaC:1ZrC	7110	7 (p. 114)	----	6.6	-----	Al, Ti	Si, Fe, Co, Cb	V, Ca, B	Cr	[e]90.9	6.0	96.9	$(80\ Ta\text{-}20\ Zr)C_{0.90}$	ZrO_2 (weak)
HfC	7030	4	92.3[f] (incl. Zr)	6.2	0.1	Zr (1.8%)	Ti (0.3%), Ca	Na	Al, Cu, Ni, V	[e]90.5	5.8	96.3	$HfC_{0.96}$	ZrO_2 (weak)
TaC	7020	4	94.1	5.4	<.05	---------	Si, Al	---------	Ca, Mg, Zr, Cb	[e]93.9	5.3	99.2	$TaC_{0.86}$	----------
C	6600 (sublimes)	9	----	---	-----	Spectrographically pure rods				----	---	----	C	----------
CbC	6330	4	85.2	10.2	2.8	---------	Fe	---------	Si, Ti, Ca, Mo, B	[e]85.0	10.2	95.2	$CbC_{0.92}$	C (weak)
TiC	5880	4	78.5	18.5	.1	Mo	Co	---------	Si, Fe, Cr, Ca	[e]77.4	18.4	95.8	$TiC_{0.94}$	----------
ZrC	5750	4	----	10.3	2.0	---------	Ti	Fe	Si, Al, Ni, Cr, Ca, B	[g]84.7	10.3	95.0	$ZrC_{0.93}$	----------
VC	5130	4	----	12.6	11.1	---------	----------	---------	Ca, Na	[g]70.0	12.6	82.6	$VC_{0.76}$	C (medium)
W_2C	4890	4	----	3.1	<.05	---------	----------	---------	Si, Fe, Cr, Ca	[g]96.8	3.1	99.9	$W_2C_{0.97}$	WC (weak)
Mo_2C	4870	4	94.5	5.5	<.05	---------	----------	---------	Si, Al, Ca, Na, K	[e]94.4	5.5	99.9	$Mo_2C_{0.93}$	----------
WC	4770 (decomposes)	4	----	Total carbon 6.1	-----	---------	----------	---------	Si, Fe, Ti, Ca, Na	[e]93.8	6.1	99.9	$WC_{1.0}$	W_2C (weak)
SiC	4350 (decomposes)	7 (p. 119)	----	27.9	.7	---------	Al, Fe (0.3%), Ca	---------	Cb, Na	[g]68.8	27.7	96.5	$SiC_{0.94}$	Si (medium) SiO_2 (weak)

[a]All analyses were made by Los Alamos Scientific Laboratory with the exception of WC, which was made by Lewis Research Center.

[b]Determined by semiquantitative spectrographic analysis supplied by National Spectrographic Laboratories, Cleveland, Ohio.

[c]Combined C equals total combined carbon minus carbon combined with carbide forming metal impurities.

[d]Analyses made by Los Alamos Scientific Laboratory and by Lewis Research Center. Literature values of interplanar spacings and lattice constants used in the identification of materials by X-ray diffraction were taken from ref. 8.

[e]Major metal equals total metal by combustion minus total metal impurity.

[f]Value is for hafnium and zirconium only.

[g]Major metal by wet chemistry analytical methods.

TABLE I. - Concluded. MELTING POINTS AND ANALYSES OF REFRACTORY MATERIALS

(c) Borides and nitrides

Nominal material	Melting point		Chemical analysis, weight percent (a)		Approximate spectrographic impurities (b)				Corrected chemical analysis, weight percent			Calculated formula	Impurity phases found by X-ray diffraction (c)
	°F	Reference	Major metal[d]	Boron or nitrogen	0.5-5%	0.05-0.5%	0.01-0.1%	0.005-0.05%	Major metal	Combined boron or nitrogen[e]	Total		
HfB_2	5880	4	86.9 (incl. Zr)	9.1	[f]C (1.2%), Zr (1.7%), Ti	Ca	---------	Al, Fe, V	85.2	8.1	93.3	$HfB_{1.6}$	HfO_2, ZrO_2, TiO_2 (weak)
ZrB_2	5500	4	79.2	18.9	----------	---------	---------	----------	79.2	18.9	98.1	$ZrB_{2.0}$	----------
TaB_2	5430 (decomposes)	4	85.4	10.7	----------	Ti, Mg	Ca, Na	Si, Fe, K	85.4	10.6	96.0	$TaB_{2.1}$	Ta_3B_4, TaB (medium) Ta_2B, Ta (weak)
TiB_2	5400	4	65.0	29.5	Fe	---------	Al, Co	Cr, Zr	65.0	29.3	94.3	$TiB_{2.0}$	----------
CbB_2	>5250 (decomposes)	4	77.3	16.8	----------	---------	---------	Fe, Ti, Cr, Ca, Mg	77.3	16.8	94.1	$CbB_{1.9}$	Cb_3B_4 (medium)
WB	5180	4	92.7	5.2	Mo (0.3%)	Ti	Si, Ca	Al, Fe, Na	92.7	5.1	97.8	$WB_{0.93}$	----------
W_2B	5020	4	----	----	----------	---------	---------	----------	----	----	----	------	----------
ThB_4	>4530	7 (p. 141)	82.7	14.6	[f]C (2.7%)	Si, Fe	---------	Cu, Ca	82.7	14.6	97.3	$ThB_{3.8}$	B_4C, C (weak)
HfN	5990	4	92.3 (incl. Zr)	7.5	Zr (3%)	[f]C	Ca, Na	Si, Fe	89.3	7.0	96.6	$HfN_{0.99}$	ZrO_2, ZrN (weak)
TaN	5590	4	[g]92.5	6.6	----------	[f]C, Si	---------	Al, Cr, Ca, Mo	92.4	6.5	98.9	$TaN_{0.91}$	Ta_2O_5 (weak)
ZrN	5400	4	86.1	12.1	Si (0.3%)	Al, Ti, Ca	Na	Fe, Ni, Cr	86.1	11.8	97.9	$ZrN_{0.89}$	----------
TiN	5310	4	78.2	19.9	----------	[f]C, Fe	---------	Si, Ca, Zn, Cb	78.2	19.9	98.1	$TiN_{0.87}$	----------

[a]All analyses made by Los Alamos Scientific Laboratory.

[b]Determined by semiquantitative spectrographic analysis supplied by National Spectrographic Laboratories, Cleveland, Ohio.

[c]Some analyses made by Los Alamos Scientific Laboratory, the remainder by Lewis Research Center. Literature values of interplanar spacings and lattice constants used in the identification of materials by X-ray diffraction were taken from refs. 6 and 8.

[d]Major metal by wet chemistry analytical methods.

[e]Combined boron or nitrogen total combined boron or nitrogen minus boron or nitrogen combined with boride or nitride forming metal impurities.

[f]Determined by combustion.

[g]Total metal.

TABLE II. - COMPATIBILITY OF UO_2 WITH REFRACTORY MATERIALS

(a) Metals and oxides

Material	Melting and/or reaction temperature, °F	Pressure, mm		Remarks (a)
		Initial	Final	
W	5000	20 Argon	37	UO_2 melted; no reaction at interface
Ta	5000	20 Argon	31	UO_2 melted; no reaction at interface
Mo	4700	40 Argon	--	Mo melted; no reaction at interface
Cb	4500	5 Argon	--	Cb melted; no reaction at interface
ThO_2	4000	3×10^{-5}	7×10^{-5}	Slight adherence; UO_2-ThO_2 solid solution formed at interface
Cr_2O_3	3700	3×10^{-5}	5×10^{-5}	Extensive interaction; UO_2 and Cr_2O_3 detected in liquid phase
ZrO_2	3500	2×10^{-5}	8×10^{-5}	Strong adherence; UO_2-ZrO_2 solid solution formed at interface

[a]Literature values of interplanar spacings and lattice constants used in the identification of substances by X-ray diffraction were taken from refs. 5 and 8.

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TABLE II. - Continued. COMPATIBILITY OF UO_2 WITH REFRACTORY MATERIALS

(b) Carbides

Material	Melting and/or reaction temperature, °F	Pressure, mm		Remarks (a)
		Initial	Final	
		Argon		
HfC	5000	40	89	No adherence; UO_2 melted
TaC	4900	40	86	Slight adherence; UC detected at interface
	4500	10	35	No adherence; UC detected at interface
4TaC:1ZrC	4800	40	80	Slight adherence; UC detected at interface
	4500	10	26	No adherence; UC (a ~4.93 A) found at interface
CbC	4600	40	85	Strong adherence; unidentified material in liquid phase at interface
	4500	10	35	No adherence; UC and UC_2 detected at interface
ZrC	4500	10	35	Strong adherence; UC detected at interface
WC	4500	10	53	Strong adherence; WC melted
	3500	17×10^{-5}	35×10^{-5}	No adherence; UC detected at interface
W_2C	4400	10	44	Slight adherence; W_2C melted
		Vacuum		
W_2C	3500	2×10^{-5}	6×10^{-5}	No adherence; UC detected at interface
TiC	4000	2×10^{-5}	80×10^{-5}	Slight adherence; UC detected at interface
Mo_2C	3700	2×10^{-5}	50×10^{-5}	Strong adherence; Mo_2C melted
VC	3700	3×10^{-5}	47×10^{-5}	Strong adherence; UC detected in liquid phase at interface
Graphite	3500	2×10^{-5}	18×10^{-5}	Strong adherence; UC and UC_2 detected at interface
SiC	3500	3×10^{-5}	150×10^{-5}	Slight adherence; UC detected in liquid phase at interface

[a]Literature values of interplanar spacings and lattice constants used in the identification of substances by X-ray diffraction were taken from refs. 5 and 8.

TABLE II. - Continued. COMPATIBILITY OF UO_2 WITH REFRACTORY MATERIALS

(c) Borides

Material	Melting and/or reaction temperature, °F	Pressure, mm		Remarks (a)
		Initial	Final	
		Argon or vacuum		
CbB_2	4900	40	68	Extensive interaction; CbB_2 and UO_2 detected in liquid phase
	4500	10	29	No adherence; UO detected at interface
W_2B	4700	40	61	No adherence; W_2B melted
ZrB_2	4700	40	72	Strong adherence; UO, UO_2, ZrB_2, and unidentified material detected at interface
	4400	10	24	No adherence; UO detected at interface
HfB_2	4700	40	62	Extensive interactions; HfB_2 and UO_2 detected in liquid phase
	4500	10	32	No adherence; UO detected at interface
TiB_2	4700	40	73	Slight adherence; UO detected in liquid phase
	4500	10	25	No adherence; UO detected at interface
TaB_2	4500	10	29	Slight adherence; UO detected at interface
	4000	4×10^{-5}	26×10^{-5}	No adherence; UO and UB_2 detected at interface
ThB_4	4200	40	83	Strong adherence; UB_2 and UB_4 detected in liquid phase

[a]Literature values of interplanar spacings and lattice constants used in the identification of materials by X-ray diffraction were taken from refs. 5, 6, and 8.

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TABLE II. - Concluded. COMPATIBILITY OF UO_2 WITH REFRACTORY MATERIALS

(d) Nitrides

Material	Melting and/or reaction temperature, °F	Pressure, mm		Remarks (a)
		Initial	Final	
		Argon or vacuum		
TaN	5000	400	626	UO_2 melted; no reaction at interface
HfN	4600	40	76	Slight adherence
	4300	10	39	No adherence; HfO_2 and UN_2 detected at interface
	4000	2×10^{-5}	17×10^{-5}	No adherence; some U_2N_3 or UN_2 probable at interface
ZrN	4400	10	25	Strong adherence; UN and UN_2 detected in liquid phase
	4000	4×10^{-5}	42×10^{-5}	No adherence; U_2N_3 and/or UN_2 probable at interface
TiN	4200	10	27	Strong adherence; UN (or UO), UO_2, and TiN detected in liquid phase

[a]Literature values of interplanar spacings and lattice constants used in the identification of materials by X-ray diffraction were taken from refs. 5 and 8.

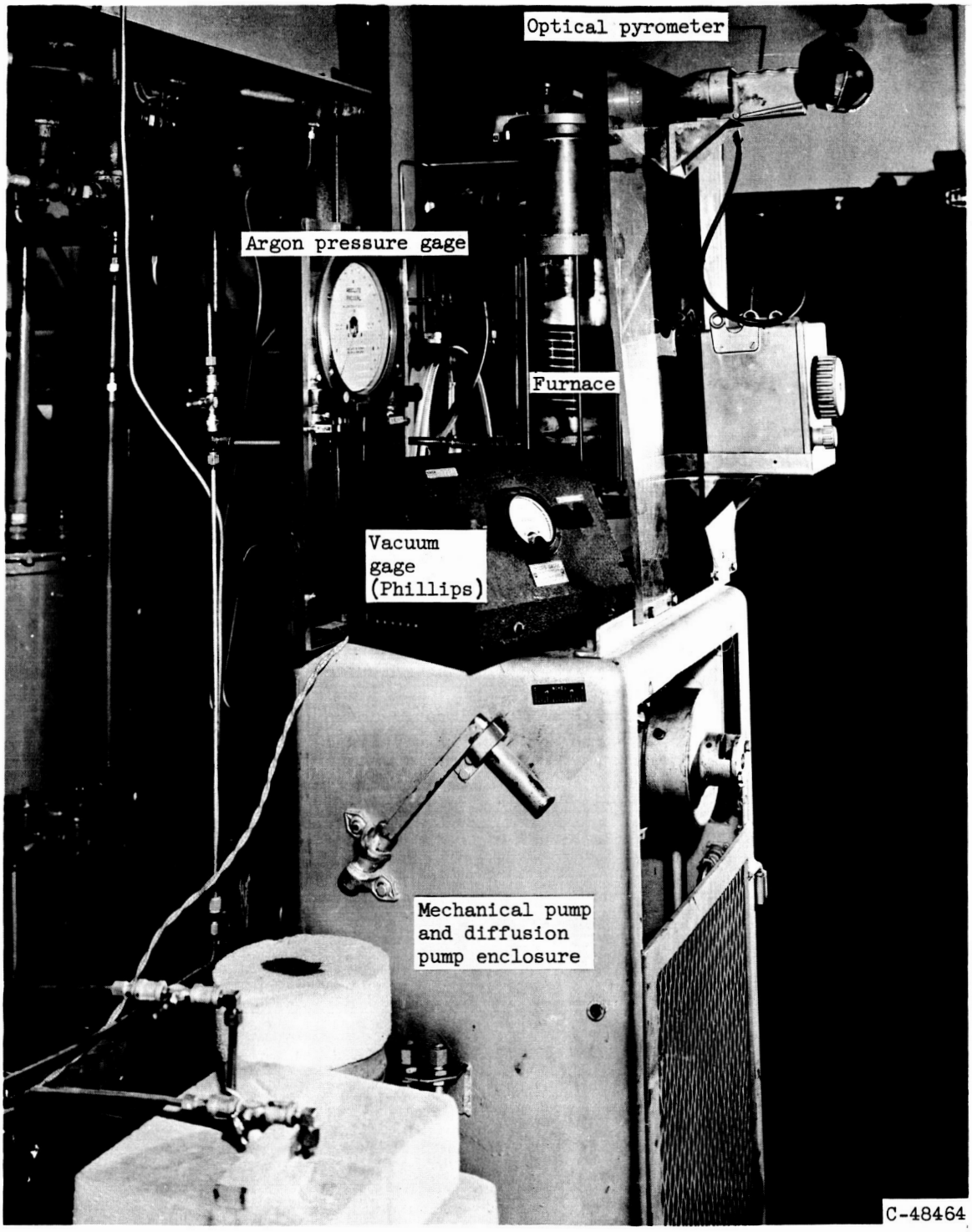

Figure 1. - Compatibility apparatus.

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CL-4

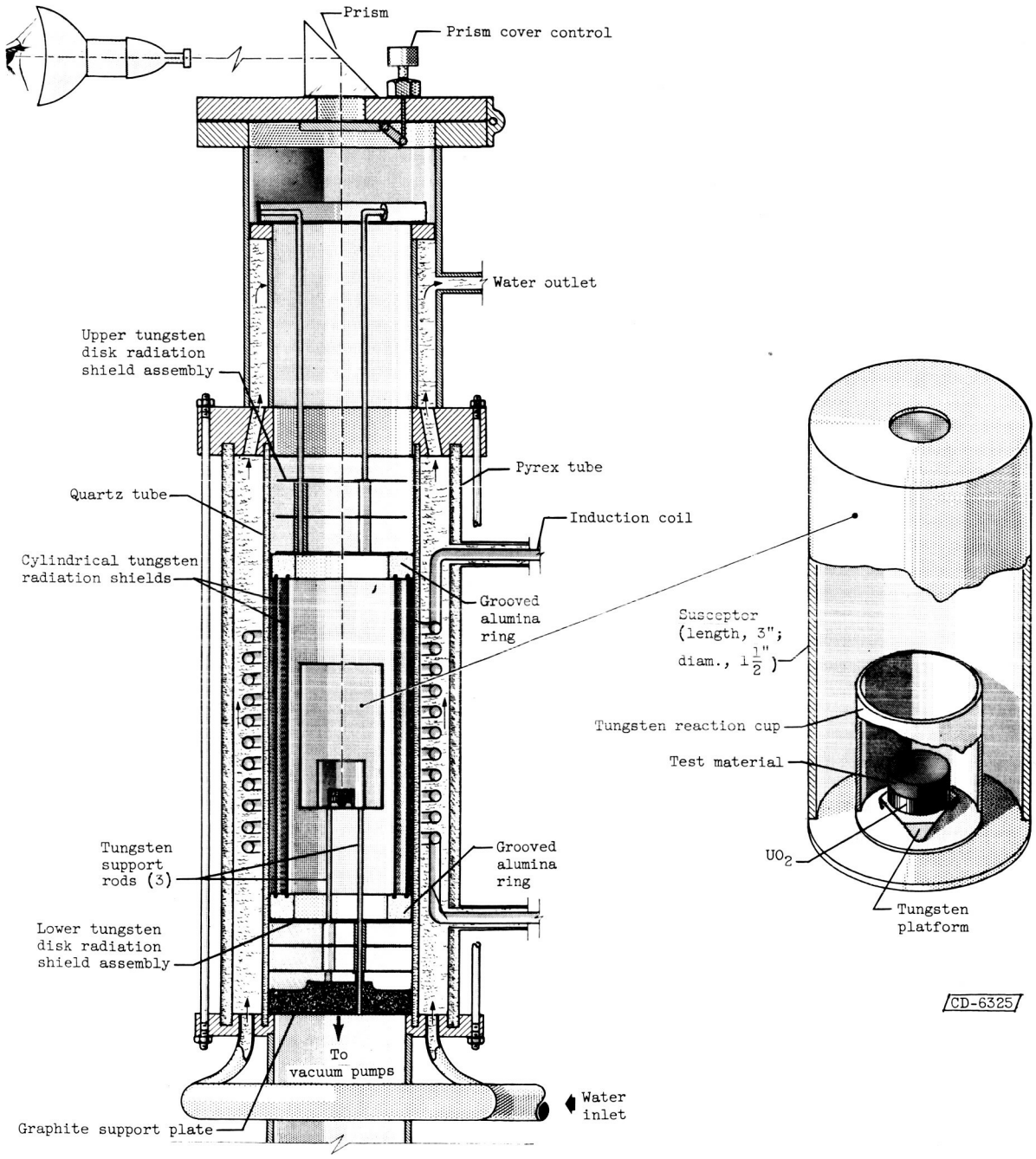
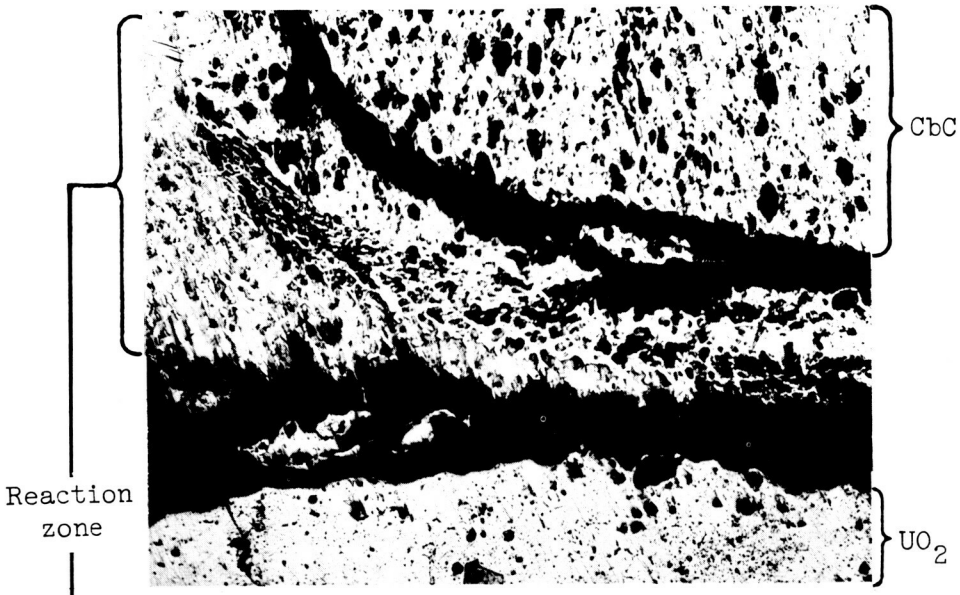
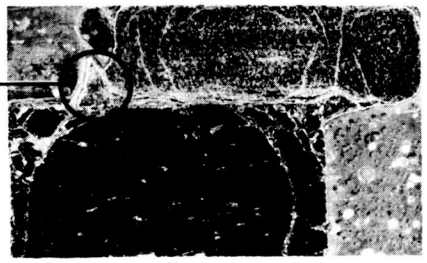


Figure 2. - Schematic view of compatibility furnace.



(a) Photomicrograph of triangular reaction zone (left). X50.



(b) Photomacrograph of adhering CbC and UO_2 disks. X3.25.

Figure 3. - Cross sections of adhering CbC and UO_2 disks at 4600° F.

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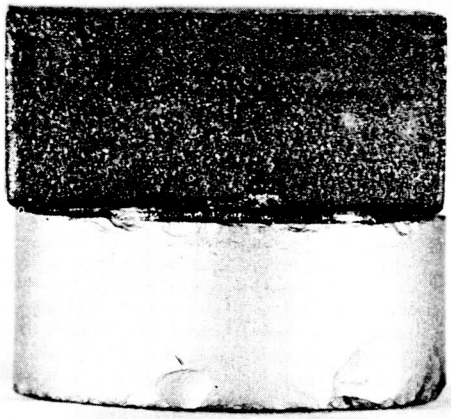
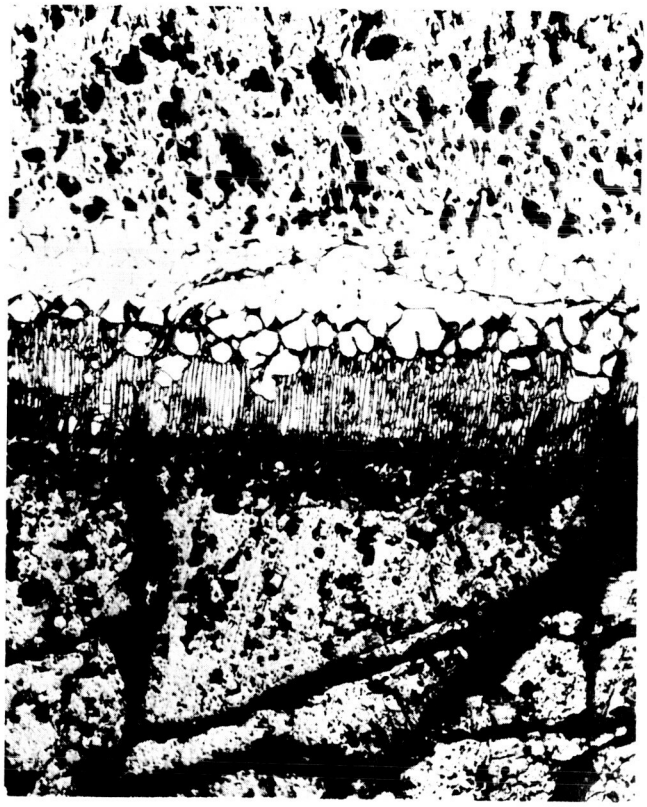


(a) 3700° F; pellets adhering after test. X4.5.

(b) 4000° F cross section. X4.5.



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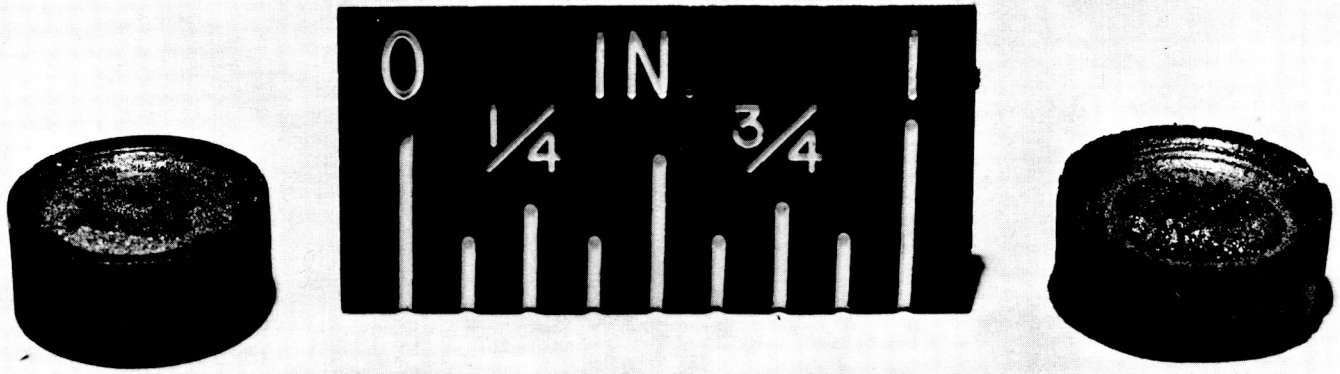
(c) Photomicrograph of narrow reaction zone of figure 4(b) with VC above and UO_2 below. X100.

Figure 4. - Photomacrographs and photomicrograph of vanadium carbide - uranium dioxide adhering disks and cross sections.



4800° F

4900° F

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Figure 5. - UO_2 disks after 4800° and 4900° F compatibility tests with TaN.

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