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COMPATIBILITY OF REFRACTORY MATERIALS FOR NUCLEAR REACTOR POISON CONTROL SYSTEMS

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16. Abstract

Metal-clad poison rods have been considered for the control system of an advanced space power reactor concept studied at the NASA Lewis Research Center. Such control rods may be required to operate at temperatures of about 1400° C. Selected poison materials (including boron carbide and the diborides of zirconium, hafnium, and tantalum) were subjected to 1000-hour screening tests in contact with candidate refractory metal cladding materials (including tungsten and alloys of tantalum, niobium, and molybdenum) to assess the compatibility of these materials combinations at the temperatures of interest. Zirconium and hafnium diborides were compatible with refractory metals at 1400° C, but boron carbide and tantalum diboride reacted with the refractory metals at this temperature. Zirconium diboride also showed promise as a reaction barrier between boron carbide and tungsten.

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SUMMARY

Poison control rods have been considered for the control system for an advanced liquid-metal-cooled, nuclear space power reactor concept which was studied at the NASA Lewis Research Center. The rods are expected to operate at temperatures to approximately 1400° C for times of about 50 000 hours. The rods would be cylindrical and consist of a refractory poison control material clad with a refractory metal. The potential poison control materials considered included boron carbide (B_4C), tantalum diboride (TaB_2), hafnium diboride (HfB_2), and zirconium diboride (ZrB_2); all would be enriched in the B^{10} isotope. The potential cladding materials considered were as follows: unalloyed tungsten (W); a tantalum alloy, T-111 (Ta-8W-2Hf); a niobium alloy (Nb-1Zr); and a molybdenum alloy, TZM (Mo-0.5Ti-0.08Zr-0.03C). The poison control rod materials must be chemically compatible with the cladding material so that the rods remain intact and stable in dimensions over the lifetime of the reactor.

Combinations of these materials were subjected to chemical-compatibility screening tests at temperatures of 1200°, 1400°, and 1650° C for times to 1000 hours. In 1000 hours, B_4C reacted with all of the cladding candidates at 1400° C and to a lesser extent at 1200° C. The TaB_2 reacted with all of the cladding candidates at 1400° C. The HfB_2 and ZrB_2 showed no reaction with tungsten but they showed some reaction with the other three metals at 1400° C. Tungsten also remained unattacked after being tested in contact with HfB_2 and ZrB_2 for 1000 hours at 1650° C. Thus, tungsten or possibly a tungsten-lined refractory alloy may be suitable for cladding control rods of these diborides.

A thin barrier layer of ZrB_2 between W and B_4C was tested for 1000 hours at 1650° C with no reaction between the B_4C and tungsten. Therefore, it may be possible to use B_4C (with its greater boron content) with ZrB_2 as a diffusion barrier. Tests with tantalum monoboride (TaB) also suggest that it could be used in a similar manner as a diffusion barrier between B_4C and tungsten, T-111, or TZM.

INTRODUCTION

A fast-neutron, liquid-metal-cooled, nuclear space power reactor concept was studied at the NASA Lewis Research Center (ref. 1). This reactor concept would provide about 2.2 megawatts of thermal energy with a reactor coolant outlet temperature of about 950° C. For this temperature, lithium was selected as the coolant. The high reactor operating temperature and the 50 000-hour lifetime goal limited the choice of structural materials to refractory metals or their alloys (i.e., Ta, Nb, W, Mo, and alloys) and led to the selection of uranium mononitride (UN) as the fuel (ref. 2). An important problem area for this reactor is the selection and development of an effective and reliable control system.

The prime control system concept which was considered for this reactor uses lithium-cooled internal drums which can rotate fuel rods in and out of the fueled core. But, because of potential loss of coolant through failure of reactor vessel penetration devices required for rotating the drums, several other control concepts were studied (refs. 1, 3, and 4). One of the leading ones is internal poison control rods which can be moved in and out of dry wells penetrating the fueled core (fig. 1).

This report is concerned with chemical compatibility problems that might arise between refractory metal cladding and poison control material combinations which could be used in the control rods or drums. The cladding is necessary to restrain swelling of the control material and to prevent disintegration of the poison material during irradiation The cladding and poison materials must be compatible for the life of the reactor at temperatures up to about 1400° C if they are passively cooled by radiation to the lithium-cooled walls of the reactor vessel. Active cooling (e.g., with flowing inert gas) would make it possible to operate at much lower temperatures but at the cost of greater complexity and the risk of coolant loss.

The poison control materials of greatest interest are boron carbide (B_4C) and refractory metal borides such as zirconium, hafnium, and tantalum diborides (ZrB_2, HfB_2, and TaB_2) because of their high boron contents. The boron-10 isotope has the largest neutron absorption cross section of any practical material available (ref. 5) so these materials would be highly enriched in the boron-10 isotope in actual control systems. Of the candidate boron compounds, B_4C has the highest density of boron per unit volume, is easily fabricated, and has a low density (enabling a lightweight mechanism to move control rods containing this material) (ref. 5). In addition, B_4C has been used successfully in reactors at temperatures from 285° to 750° C (ref. 5), whereas little experience is available for the refractory metal borides. Thus, prime emphasis was placed on testing B_4C in this study. But the refractory metal borides were included because they may be more compatible with refractory metal cladding candidates at the required high temperatures ($\sim 1400^{\circ}$ C).

The major objective of this work was to test the chemical compatibility of B_4C and selected refractory metal borides in contact with selected refractory metal cladding candidates to screen promising materials combinations for poison control rods. The approach used was to heat capsules containing contacting couples of these materials for up to 1000 hours at temperatures from 1200° to 1650° C (with most testing done at 1400° C). The specimens then were examined by determining weight changes, metallography, X-ray diffraction, electron-beam microprobe, and scanning electron microscopy. In addition, a few cursory tests were run to test the effectiveness of reaction barriers between B_4C and tungsten.

MATERIALS AND PROCEDURE

Materials

Boron carbide (B_4C) was obtained from commercial sources in the form of sintered cylindrical compacts. Properties of four lots of B_4C tested are shown in table I; the lots are designated I, II, III, and IV in order of increasing boron content. The boron to carbon atom ratios for lots I to IV are 3.83, 3.89, 4.13, and 5.39, respectively. (For convenience, the boron carbide is referred to as B_4C throughout the report although none of the lots were of the stoichiometric composition.) The densities of the pellets varied between 1.99 and 2.46 grams per cubic centimeter. Representative photomicrographs of three lots of untested B_4C specimens are presented in figure 2. (Photomicrographs of untested B_4C from lot IV are not presented because only enough material was received for testing.) Posttest examinations indicated that testing did not alter the appearance of any of the B_4C lots shown in figure 2. Posttest observations also showed that B_4C from lot IV looked very similar to that from lot III (fig. 2) except that the B_4C from lot IV has a little more porosity than that from lot III.

Pellets of the refractory metal borides HfB_2, TaB_2, and TaB were obtained commercially. The ZrB_2 pellets were prepared in-house from 80 mesh powder described as hafnium-free 99+ percent ZrB_2. They were cold isostatically pressed at 5×10^8 newtons per square meter (70 000 psi), placed in tungsten cups, and vacuum sintered for 2 hours in an induction furnace. Two lots of ZrB_2 pellets were prepared. Since the procedure was experimental and very little ZrB_2 was available, we could not risk the entire supply of powder at one time. The first lot of pellets was sintered at 2200° C. The pellets appeared to be suitable for testing. Results of chemical analyses made on sintered pellet material are presented in table II.

Second and third attempts to sinter ZrB_2 pellets at 2200° C resulted in failures. Apparently enough boron vaporized from the ZrB_2 to allow formation of some free zirconium. Zirconium forms a eutectic with tungsten at about 1660° C, and this apparently occurred during the second and third sintering runs. A lot of pellets was finally sintered at 1900° C.

These were more porous than those from the first lot. The effect of this difference in ZrB_2 pellet lots on the results is covered in the RESULTS AND DISCUSSION section. (All of the ceramic specimens used in this study were naturally enriched in boron-10.)

Compositions of the refractory metal alloys used are given in table III. Tungsten, T-111 (Ta - 8 percent tungsten - 2 percent hafnium), and Nb - 1 percent Zr were obtained in the form of rods. Both T-111 and Nb - 1 percent Zr were in a recrystallized condition. The TZM (Mo - 0.5 percent Ti-0.08 percent Zr - 0.03 percent C) was obtained in the form of wrought sheet. Wrought tungsten rods (99.9 percent pure) produced from powder metallurgy products also were used as contact specimens.

Procedure

T-111 test capsules. - The T-111 capsules used to contain these tests were made from 1.27-centimeter-diameter tubing with a 0.081-centimeter wall thickness machined into 5.1-centimeter lengths. Capsule bottoms were stamped from 0.051-centimeter-thick T-111 sheet. Capsule tops were machined from 1.43-centimeter-diameter cold-worked T-111 rod. Capsule bottoms and tops were sealed by electron beam welding. The full procedure used to manufacture these capsules is described in reference 6.

Compatibility test specimen preparation. - The B_4C test specimens were made from the as-received cylindrical compacts by diamond sawing and grinding the contact surfaces with 220-grit diamond wheels. After they were machined, the test specimens were ultrasonically cleaned in acetone followed by ethanol. They were then oven dried at 150° C, dimensionally measured, and weighed prior to assembly into test capsules with the appropriate metals.

Refractory metal boride specimens (TaB, TaB_2, and HfB_2) were obtained as cylindrical pellets (about 0.9 cm in diameter and 0.9 cm in length). Sectioning and machining of test surfaces were done with the same equipment as that used for boron carbide. The specimens were cleaned, measured, and weighed as was described for B_4C specimens, and then they were assembled into test couples with the desired refractory metals within T-111 test capsules.

All refractory metal specimens were cut to size from 0.95-centimeter-diameter rod or 0.15-centimeter-thick sheet and were mounted in epoxy resin. The contact surfaces were then metallographically polished. Following removal from the mounting material, the specimens were ultrasonically cleaned - first in acetone and then in ethanol. The final step was a heat treatment for 1 hour in a vacuum of approximately 1.3×10^{-4} newton per square meter (10^{-6} torr). Tungsten and TZM specimens were heated at 1540° C to develop a stable grain size that would be unaffected by subsequent testing at temperatures as high as 1400° C. Both T-111 and Nb-1Zr were received in a recrystallized condition; thus, heat treatment to stabilize the grain size was not necessary. They were, however, heat treated in vacuum at 1090° C for 1 hour for surface cleaning. The Nb-1Zr and T-111 specimens were wrapped in Nb-1Zr and Ta foil, respectively, prior to vacuum heat treatment to protect them from contamination by interstitials.

Test capsule assembly. - Foil liners were used between the T-111 capsule walls and the stacks of contact specimens to reduce the possibilities of unwanted reactions between the T-111 capsule walls and the test pellets. These foil liners consisted of approximately 5×10^{-3} to 8×10^{-3}-centimeter-thick layers of W, Mo, or Nb-1Zr, as appropriate to the type of specimens being tested.

A radiograph of a typical capsule with test specimens is shown in figure 3(a). The test specimens were stacked in this capsule with the appropriate polished test surfaces in contact with each other. At the top, there is a tungsten weight and some dished springs made of T-111 to assure contact between the metals and poison control material surfaces. In this case the T-111 capsule was lined with two layers (0.0025 cm each) of tungsten foil.

Test specimens and foil were placed in the capsule using "white glove" techniques. Capsule tops were sealed by electron beam welding in a vacuum chamber. All completed capsules were examined by X-ray radiography to assure that proper orientation of test specimens was maintained. Following this X-ray examination the capsules were then leak checked, degreased with acetone followed by ethanol, and oven dried at 150° C. They were then weighed, enclosed in two layers of 0.005-centimeter-thick Nb-1Zr foil followed by two layer of 0.0075-centimeter-thick molybdenum foil to inhibit pickup of interstitials from the test chamber during testing, and placed in the test furnace.

Capsule testing procedure. - Testing was done in a liquid-nitrogen-trapped, oil-diffusion-pumped vacuum furnace facility in which the temperature was maintained at 1200°±20° C, 1400°±20° C, or 1650°±25° C, as required, and the pressure was maintained at approximately 1×10^{-5} newton per square meter (10^{-7} torr) during the tests. Tests lasted either 500 or 1000 hours.

Most of the initial tests were run at 1400° C for 1000 hours. But some of the capsules were removed after 500 hours to determine the effect of time at temperature. In addition, selected specimens were subsequently tested at either 1200° or 1650° C, depending on the results of the 1400° C tests. That is, some material combinations that exhibited reactions at 1400° C were tested at the lower temperature, while some of the materials that showed good compatibility at 1400° C were tested at 1650° C.

Evaluation procedures. - On completion of the tests, the capsules were removed from the test furnace, the protective refractory metal foils were removed, and the capsules were weighed and re-examined by X-ray radiography. The capsules were cut open with a fine-toothed hacksaw, and the specimens were removed, examined visually, weighed, and photographed (e.g., fig. 3(b)). Test specimens were then prepared for metallographic examination in the unetched and etched condition. In addition to metallography and weighting, emission spectroscopy, X-ray diffraction, electron microprobe, and scanning electron microscopy were used for evaluating as deemed appropriate.

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

Tungsten and TZM	Murakami's etchant: 10 g potassium ferricyanide ($K_3Fe(CN)_6$) 10 g potassium hydroxide (KOH) 100 cm^3 distilled water
T-111	30 g ammonium bifluoride ($NH_4F.Hf$) 50 cm^3 nitric acid (HNO_3) 20 cm^3 distilled water
Nb-1Zr	30 cm^3 lactic acid ($CH_3CHOHCOOH$) 10 cm^3 nitric acid (HNO_3) 10 cm^3 hydrofluoric acid (HF)
Boron carbide, B_4C	10 percent chromic acid (CrO_3)
Zirconium diboride (ZrB_2) and hafnium diboride (HfB_2)	33 cm^3 distilled water 33 cm^3 acetic acid (CH_3COOH) 33 cm^3 nitric acid (HNO_3) 1 cm^3 hydrofluoric acid (HF)
Tantalum borides (TaB and TaB_2)	15 cm^3 nitric acid (HNO_3) 15 cm^3 hydrofluoric acid (HF) 10 cm^3 distilled water

RESULTS AND DISCUSSION

Boron Carbide

Boron carbide (B_4C) was tested in direct contact with the four different candidate refractory metals. Tests were made first at 1400° C, and then later some were made at 1200° C after a study of the results obtained at 1400° C. Only one 1650° C test was run to check a calculation predicting results at 1650° C based on data obtained at 1200° and 1400° C. Test conditions and the resultant severity of attack observed in the metals are summarized in table IV. Severe reaction was observed with all four refractory metals under all conditions tested. The relative degree of this attack on each refractory metal is summarized in figure 4 for some of the 1000-hour tests at 1400° C. Metallographic evidence of these reactions is shown in figures 5 to 10, and the reactions are discussed in the subsequent paragraphs.

B_4C/W reactions. - Figure 5 shows the appearance of tungsten tested in contact with B_4C from lot I after 500 and 1000 hours at 1400° C. The tungsten was attacked to a depth of 0.018 centimeter in 500 hours and to a depth of 0.025 centimeter in 1000 hours (table IV).

Note in figure 5(b) that there are two distinct attack layers or zones in the tungsten. The outermost layer consists of a broken film about 0.0013 centimeter thick; below this is a fingerlike attack zone which reaches a depth of approximately 0.025 centimeter. Although it does not show up in figure 5, microscopic examination showed that the attack is intragranular - grain boundaries appear to be no more prone to attack that the grains themselves. The appearance of the attack may be explained by the fact that when several components are involved in a diffusion reaction, the equilibrium interface can be nonplanar (ref. 7).

The phases WC, W_2B, WB, and W were found by X-ray diffraction techniques in the outer attack zone (fig. 5(b)). The inner, columnar layer shown in the same figure was then exposed by milling off the surface layer. Only W_2B and W were found by X-ray diffraction in this inner layer.

Figure 6 illustrates the fact that diffusion of constituents of B_4C into the metals occurred not only into areas in contact with B_4C but also by vapor-phase transport into other nearby areas. This illustration is for tungsten, but similar vapor-phase attack occurred with T-111, TZM, and Nb-1Zr. Vapor-phase attack by B_4C could destroy the integrity of a control rod cladding of any of these metals if a protective diffusion barrier placed between the B_4C and cladding should crack.

Figure 7 shows the effect of temperature on the attack of tungsten by B_4C. The tests were made for 1000 hours at 1200°, 1400°, and 1650° C. On the basis of attacks to a depth of 0.008 centimeter into the tungsten at 1200° C and to a depth of 0.03 centimeter at 1400° C (figs. 7(a) and (b), respectively), it was calculated that a test at 1650°C should result in an attack to a depth of 0.11 centimeter. The attack actually obtained was to a depth of 0.08 centimeter, as shown in figure 7(c). The calculation was made assuming a diffusion-controlled reaction and is presented in the appendix. The agreement between the calculated depth of attack and that actually found by the test at 1650° C is considered reasonable. This type of calculation could be useful in predicting the attack severity for other temperatures in this range.

Microstructural changes in B_4C as a result of testing were not observed in any of the specimens examined during the test program. Hence, tested B_4C is not shown.

B_4C/T-111 reactions. - Reactions between B_4C and T-111 for 1000 hours at 1400° and 1200° C are shown in figure 8. Surprisingly, much less attack occurred with the T-111 than with the tungsten specimens. The T-111 is affected to a depth of about 0.018 centimeter at the higher temperature and to a depth of about 0.005 centimeter at the lower one. The T-111 tested at 1400° C formed a low-density phase near the area contacting B_4C. This large increase in volume resulted in severe swelling and cracking of the T-111. This phase was much less apparent in the specimen tested in 1200° C. Figure 9 illustrates this: it shows T-111 and tungsten tested in contact with B_4C for 1000 hours at 1400° and 1200° C. Swelling of the T-111 surfaces near the B_4C is observed in figure 9(a) (1400° C test) but not in figure 9(b) (1200° C test). The same observation was made, but to a lesser extent, for tungsten. Note also the rounded edges of the B_4C pellets in the 1400° C test. Much material was lost by vaporization from the B_4C pellets tested at 1400° C (fig. 9(a)), but those tested at 1200° C (fig. 9(b)) show no apparent changes.

B_4C/TZM reactions. - As shown in table IV and plotted in figure 4, the reaction zones found in the TZM specimens were the deepest of those tested. Also, the relative amounts of reaction found in the different TZM specimens after being tested in contact with lots II and III B_4C were very different. The TZM in contact with lot III B_4C was attacked to a depth of 0.076 centimeter (fig. 10(a)), while that in contact with lot II had a reaction to depth of 0.19 centimeter after 1000 hours at 1400° C. Lot II B_4C actually bonded to the TZM. The reasons for these differences in attack depths were not investigated, nor were the compostions of the three phases shown in the attack zone of figure 10(a) determined. (Note that fig. 10(a) is at one-fifth the magnification that was used for the rest of the report.)

B_4C/Nb-1Zr reactions. - The depth of attack on the Nb-1Zr specimens was similar to that on T-111 (fig. 4). However, the Nb-1Zr surfaces in contact with B_4C were swollen, and they cracked worse than the T-111 surfaces discussed earlier. A typical reaction zone found in Nb-1Zr after being in contact with B_4C for 1000 hours at 1400° C is shown in figure 10(b). Again, identification of the three phases shown in the attack zone was not attempted.

Effect of B_4C quality. - As indicated in the previous paragraphs, some variations in the degree of reaction were observed for the various lots of B_4C. Attempts to correlate these variations with the two major pellet variables (B/C ratio and bulk density) are shown in figure 11 for the 1000-hour tests at 1400° C. No clear-cut trends are apparent from these plots. But generally, the lower-density, substoichiometric pellets seem to be somewhat less reactive than the others. The differences also may be due to other factors not examined here (e.g., impurity content, grain size, pore size and distribution, contact pressure, etc.).

Predictions of longer-term effects. - During the course of the program, the data obtained from the 500-hour tests were used to predict the depth of penetration for the 1000-hour tests. The calculations assumed a diffusion-controlled reaction; that is,

$$\text{Penetration for 1000 hr} = (\text{Penetration for 500 hr}) \times \sqrt{2}$$

The predicted values for the 1000-hour tests are compared to the subsequently measured values in table V. These values agree quite well, which gives some confidence in the assumption of a diffusion-controlled reaction.

The same prediction method was used with the data from the 1000-hour tests to predict the degree of attack expected in much longer-term reactor operation (50 000 hr). The resultant values are also included in table V. In all cases, the indicated penetration zones are expected to have very detrimental effects on the cladding properties. Thus, B_4C in direct contact with refractory metals is concluded to be unacceptable for 50 000 hours of operation in this temperature range.

Refractory Metal Diborides

In seeking an alternate to the use of B_4C, three refractory metal diborides - TaB_2, HfB_2, and ZrB_2 - were tested in direct contact with tungsten, T-111, TZM, and Nb-1Zr at 1400° C for 1000 hours. Later, the combinations showing the best results were tested at 1650° C for 1000 hours. The results of these tests are presented in table VI and in figures 12 to 16.

Tantalum diboride (TaB_2) was incompatible with all four metals at 1400° C (fig. 12). The phases formed in the metals were of lower density than the metals, and this condition resulted in swelling and cracking of the metal surfaces that contacted the TaB_2. Because TaB_2 showed greater attack than B_4C, it was dropped from further consideration.

Hafnium diboride (HfB_2) (fig. 13) and ZrB_2 (fig. 14) appeared promising from a compatibility standpoint after tests at 1400° C for 1000 hours, particularly with tungsten which showed no attack (figs. 13(a) and 14(a)). The other three metals showed only slight attack. The depths of attack found in the metals are recorded in table VI. A comparison of figures 13 and 14 with figures 7(b), 8(b), 10(a), and 10(b) illustrates the contrast between the attack of these refractory metals by B_4C and by these metal diborides. Therefore, as a part of the screening studies to determine the maximum temperature capabilities of these material combinations, HfB_2 and ZrB_2 were then tested in contact with the four refractory metals (W, T-111, TZM, and Nb-1Zr) for 1000 hours at 1650° C. These reactions are shown in figures 15 and 16. Again tungsten appears unattacked by either diboride (figs. 15(a) and 16(a)). Both T-111 and Nb-1Zr were attacked to a maximum depth of about 0.03 centimeter (figs. 15(b) and (d) and 16(b) and (d)), and TZM exhibited only a slight reaction with either diboride (0.005 cm) (figs. 15(c) and 16(c)). These limited reactions are encouraging since the 1650° C test temperature caused gross changes in the structure of the ZrB_2 (fig. 16), presumably due to vapor transport.

Based on these results, it appears that either HfB_2 or ZrB_2 could be considered for control system use to temperatures of at least 1400° C. Tungsten or molybdenum alloys offer the best potential for reaction-free containment of these diborides.

Barrier Materials Between B_4C and Refractory Metal Cladding

Since HfB_2 and ZrB_2 did not attack tungsten in 1000 hours at temperatures as high as 1650° C, these borides offer possibilities for use not only as poison control materials but as diffusion barriers which could be placed between the better reactor control material, B_4C, and a control rod cladding material. If such a barrier worked and could be adapted to control rod fabrication, the rods could still be made largely of $^{10}B_4C$ with its high cross section for absorption of neutrons.

To test this concept, samples of B_4C and tungsten were tested with a thin disk of ZrB_2 interposed between them. The ZrB_2 disks were prepared in-house to a minimum thickness of 0.063 centimeter. Metallographic results of 1000-hour tests at both 1650° and 1400° C are presented in figure 17. There is almost no attack of the tungsten for the 1650° C test (fig. 17(b)). However, the 1400° C test resulted in some reaction with the tungsten. The reason for this difference in behavior is believed to be due to differences in the quality of ZrB_2 used in these two tests. The test at 1400° C was made with the second lot of sintered ZrB_2 previously discussed in the Procedures section of this report. The specimens were more porous than those used for the 1650° C test. Thus, vapor transport of boron probably occurred through the porous ZrB_2, and for this reason, ZrB_2 did not protect the tungsten from attack by B_4C as well at 1400° C as it did at 1650° C.

Based on the good results obtained in the test at 1650° C, it is concluded that high density ZrB_2 probably could be considered as a barrier layer between W and B_4C in reactor control rods. Also, it is assumed that HfB_2 could be considered as a barrier material, although it was not tested as such in this program. Further work would be required to establish this positively and to establish required barrier thickness and application methods.

An alumina (Al_2O_3) coating on tungsten was also tested as a potential diffusion barrier between B_4C and the tungsten. Approximately 0.025 centimeter thick Al_2O_3 was plasma sprayed onto the polished surface of tungsten specimens. The sprayed Al_2O_3 was polished through 600-grit metallographic paper. This specimen was then tested at 1400° C for 1000 hours. Subsequent examination indicated that the Al_2O_3 did not prevent diffusion of boron into the tungsten. Therefore, further testing of alumina as a protective coating was not done.

Although tantalum boride (TaB) does not have a high boron content and would be of little interest as a poison control material, it might be useful as a diffusion barrier between B_4C and a tungsten or other refractory metal control rod cladding. Therefore, pellets of TaB were tested in contact with W, T-111, TZM, and Nb-1Zr for 1000 hours at 1400° C. The results are presented in table VI and figure 18. Tantalum boride looks promising from a compatibility viewpoint. There was little reaction with tungsten, T-111, or TZM (figs. 18(a), (b), (c), respectively). In contrast, TaB and Nb-1Zr bonded together (fig. 18(d)). Although TaB may offer possibilities as a diffusion barrier between B_4C and its metal cladding, thin disks were not available at this time for testing. Therefore, further testing of this material in a thin barrier form is needed.

Applicability of Results

The B_4C cannot be used as a control rod material in direct contact with refractory metal claddings because of the severity of reactions at the temperature of interest, 1400° C. Even if the control system temperature could be lowered enough so that the temperature of B_4C would reach only 1200° C, it would be risky to use B_4C in contact with any of the four metals tested for long-term operation. However, a thin barrier of the more compatible ZrB_2, HfB_2, or TaB placed between B_4C and the refractory metal might be adequate to prevent harmful reactions between B_4C and the cladding metal. This would make it possible to take advantage of the higher boron content found in B_4C compared to that in the metal diborides. Further long-time testing would be required to determine if such a barrier would be successful. The effect of a cracked barrier should also be tested because the cladding might then be susceptible to attack by vapor-phase transport of B_4C through the diffusion barrier cracks.

Because cladding for control rods should have high strength and good ductility in an actual application, the more ductile T-111 is more attractive than tungsten. However, tungsten is less prone to attack by HfB_2 and ZrB_2 than T-111. Thus, tungsten-lined T-111 might be a usable compromise. Whether B_4C with a diffusion barrier of a material such as ZrB_2 could be used for control rods would depend also on such factors as irradiation effects on control rod properties, stresses on cladding from swelling of poison control materials, etc. This information should be obtained by further testing.

SUMMARY OF RESULTS

Boron carbide and several refractory metal borides were tested in direct contact with candidate control rod cladding materials of refractory metals for up to 1000 hours at temperatures from 1200° to 1650° C. Thin ceramic diffusion barriers were also tested between B_4C and tungsten. The following principal results were obtained:

1. The B_4C was not compatible with tungsten, T-111 (Ta-8W-2Hf), Nb-1Zr, or TZM for 1000 hours at 1200° C or higher. The reaction appeared to be diffusion controlled.

2. Both HfB_2 and ZrB_2 exhibited generally good compatibility with all four refractory metals at 1400° C and with tungsten and TZM at 1650° C in the 1000-hour tests.

3. The TaB_2 was incompatible with all four refractory metals at 1400° C, while TaB exhibited good compatibility at this temperature.

4. The use of a thin layer of ZrB_2 between B_4C and tungsten prevented reactions for 1000 hours at 1650° C.

Lewis Research Center,

National Aeronautics and Space Administration,

Cleveland, Ohio, August 30, 1973,

503-25.

APPENDIX - CALCULATION OF TEMPERATURE EFFECT ON PENETRATION OF TUNGSTEN BY B_4C

From the data obtained for all lots of B_4C tested in contact with tungsten for 1000 hours the average depth of attack in the tungsten was 0.030 centimeter at 1400° C and 0.008 centimeter at 1200° C. A calculation for depth of penetration for 1000 hours at 1650° C was made (diffusion-controlled reaction assumed):

$$\text{Penetration} = K_o e^{-Q/RT}$$

where

K_o penetration constant, cm

Q activation energy for penetration, J/mole

R gas constant, 8.314 J/(mole) (K)

T temperature, K

For 1200° C:

$$0.008 = K_o \exp - \frac{Q}{(8.314)(1473)} \qquad (1)$$

For 1400° C:

$$0.030 = K_o \exp - \frac{Q}{(8.314)(1673)} \qquad (2)$$

Dividing equation (1) by equation (2) yields

$$\frac{0.008}{0.030} = \exp\left[- \frac{Q}{(8.314)(1473)} + \frac{Q}{(8.314)(1673)}\right]$$

$$= \exp\left\{- Q \left[\frac{(1673)(8.314) - (8.314)(1473)}{(8.314)^2 (1473)(1673)}\right]\right\}$$

$$\ln \frac{1}{3.75} = - Q(9.765\times10^{-6})$$

$$-1.3218 = - Q(9.765\times10^{-6})$$

$$Q = \left(\frac{1.321}{9.765}\right) \times10^{-6}$$

$$= 1.354\times10^{5} \text{ J/mole}$$

Substituting this value for Q in equation (1) gives

$$K_o = 505 \text{ cm}$$

For T = 1650° C (or 1923 K),

$$P = 505 \exp \left[- \frac{1.354\times10^{5}}{(8.314)(1923)}\right] = 0.11 \text{ cm}$$

which is the depth of penetration expected in 1000 hours at 1650° C in tungsten contacting B_4C.

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2. Gluyas, R. E.; and Lietzke, A. F.: Materials Technology Program for a Compact Fast Reactor for Space Power. NASA TM X-67869, 1971.
3. Mayo, Wendell; and Westfall, Robert M.: Reflector-Based Poison-Drum Control on Equal-Size Reactor Cores Fueled with Uranium-233 and with Uranium-235. NASA TM X-1883, 1969.
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5. Holden, A. N.; Weidenbaum, B.; and Leitten, C. F., Jr.: Control Rod Materials. Reactor Materials Vol. 9 of Proceedings of the Third International Conference on the Peaceful Uses of Atomic Energy. United Nations, 1965, pp. 419-429.
6. Sinclair, John H.: Compatibility Tests of Materials for a Lithium-Cooled Space Power Reactor Concept. NASA TN D-7259, 1973.
7. Taylor, C. W., Jr.; Dayananda, M. A.; and Grace, R. E.: Multiphase Diffusion in Ternary Cr-Zn-Ni Alloys. Met. Trans., vol. 1, no. 1, Jan. 1970, pp. 127-131.

TABLE I. - BORON AND CARBON CONTENT AND DENSITY

OF FOUR LOTS OF B_4C TESTED

Lot	Chemical analysis, wt %		Boron to carbon atom ratio	Apparent density of pellets, g/cm^3
	Boron	Carbon		
I	76.49	22.20	3.83	1.989
II	76.60	21.86	3.89	2.456
III	77.95	20.95	4.13	[a]2.287
				[a]2.349
IV	76.7	15.9	5.39	2.231

[a]Two specimens.

TABLE II. - ANALYSIS AND DENSITIES OF METAL BORIDE SPECIMENS

Element	Specimens			
	Tantalum diboride (TaB_2)	Tantalum boride (TaB)	Hafnium diboride (HfB_2)	Zirconium diboride (ZrB_2)
	Analysis[a]			
Oxygen	87	1490	1530	ND[b]
Iron	3000	1000	<300	ND
Silicon	<50	100	<300	80
Aluminum	800	400	<300	ND
Calcium	<100	<100	500	↓
Titanium	300	1000	<200	↓
Niobium	1000	500	ND	↓
Tin	<10	<10	<50	↓
Lead	<10	<10	<50	↓
Chromium	200	100	<100	↓
Magnesium	<10	<10	<5	↓
Copper	<10	<10	<50	↓
Silver	150	50	20	↓
Beryllium	<10	<10	<5	↓
Nickel	500	500	100	↓
Zirconium	ND	ND	2.6 percent	80.8 percent
Halides	<10	<10	<11	ND
Boron	9.37 percent	5.52 percent	[c]10.66 percent	19.32 percent
Molybdenum	ND	ND	ND	50
Tantalum	89.45 percent	94.47 percent	ND	ND
Hafnium	ND	ND	89.34 percent	ND

Variable	TaB_2	TaB	HfB_2	ZrB_2
Density, percent of theoretical	87.4	90.0	78.3	ND
Boron to metal ratio	1.75	0.98	1.97	2.02

[a]Analyses in ppm by weight unless otherwise designated.
[b]ND, not determined.
[c]By difference.

TABLE III. - ANALYSES OF REFRACTORY METAL SPECIMENS

Element	Specimens			
	T-111 capsule tubing	T-111 contact specimens	TZM contact specimens	Nb-1Zr contact specimens
	Analysis[a]			
Tantalum	Balance	Balance	ND	ND
Tungsten	7.30 percent	7.94 percent	ND	↓
Hafnium	1.93 percent	1.89 percent	ND	↓
Molybdenum	15	40	Balance	↓
Niobium	500	<25	ND	Balance
Zirconium	500	510	0.10 percent	0.98 percent
Titanium	ND[b]	ND	0.52 percent	ND
Oxygen	13	9	17	430
Hydrogen	2.3	2.5	4	13
Nitrogen	32	34	54	135 ± 30
Carbon	18	26	377	<33
Chromium	<1	<1	ND	ND
Cobalt	<20	<5	↓	↓
Copper	ND	<1	↓	↓
Iron	10	5	↓	↓
Vanadium	<5	2	↓	↓
Silicon	ND	27	↓	↓
Manganese	ND	<1	↓	↓

[a]Analyses in ppm by weight unless otherwise designated.
[b]Items not determined.

TABLE IV. - AVERAGE DEPTHS OF ATTACK IN REFRACTORY METALS

IN CONTACT WITH B_4C

B_4C lot	Boron to carbon atom ratio	Test temperature, °C	Test time, hr	Refractory metals			
				Tungsten	T-111	TZM	Nb-1Zr
				Penetration into metal, cm			
I	3.83	1400	500	0.018	0.010	NT[a]	NT
			1000	.025	.013	NT	NT
II	3.89	1400	500	0.025	0.013	0.147	0.015
			1000	.032	.018	.19	.018
		1200	1000	.008	.002	NT	NT
III	4.13	1400	500	0.023	0.015	0.030	0.013
			1000	.030	.018	.076	.020
		1200	1000	.005	.005	.056	.025
IV	5.39	1400	1000	0.030	0.008	NT	NT

[a]Not tested.

TABLE V. - COMPARISON OF EXPERIMENTAL AND PREDICTED RESULTS FOR PENETRATION OF VARIOUS REFRACTORY METALS BY B_4C AT 1400° C

B_4C lot	Metal	Penetration, cm			
		Found after 500-hr test	Predicted for 1000-hr test on basis of 500-hr test results ($P_{1000} = P_{500}\sqrt{2}$)	Found after 1000-hr test	Predicted for 50 000-hr reactor life
I	W	0.018	0.025	0.025	0.17
	T-111	.010	.014	.013	.092
II	W	0.025	0.035	0.032	0.226
	T-111	.013	.018	.018	.127
	TZM	.147	.206	.190	1.34
	Nb-1Zr	.015	.021	.018	.127
III	W	0.023	0.032	0.030	0.212
	T-111	.015	.021	.018	.127
	TZM	.030	.042	.076	.537
	Nb-1Zr	.013	.018	.020	.141

TABLE VI. - DEPTHS OF ATTACK OF REFRACTORY METALS IN CONTACT WITH METAL BORIDES FOR 1000-HOUR TESTS

Metal boride	Test temperature, °C	Refractory metals							
		Tungsten		T-111		TZM		Nb-1Zr	
		Penetration into metal, cm							
		Average	Maximum observed	Average	Maximum observed	Average	Maximum observed	Average	Maximum observed
TaB_2	1400	0.076	------	0.015	-----	0.046	-----	0.028	-----
HfB_2	1400	NP[a]	------	.0005	0.006	-----	0.003	-----	0.002
	1650	NP	------	.016	.024	.002	.003	.003	-----
ZrB_2	1400	NP	------	.004	-----	.001	-----	.003	-----
	1650	NP	------	.010	.030	NP	-----	.010	.024
TaB	1400	<.0002	------	<.0002	-----	.0004	-----	.0001	-----

[a]No penetration.

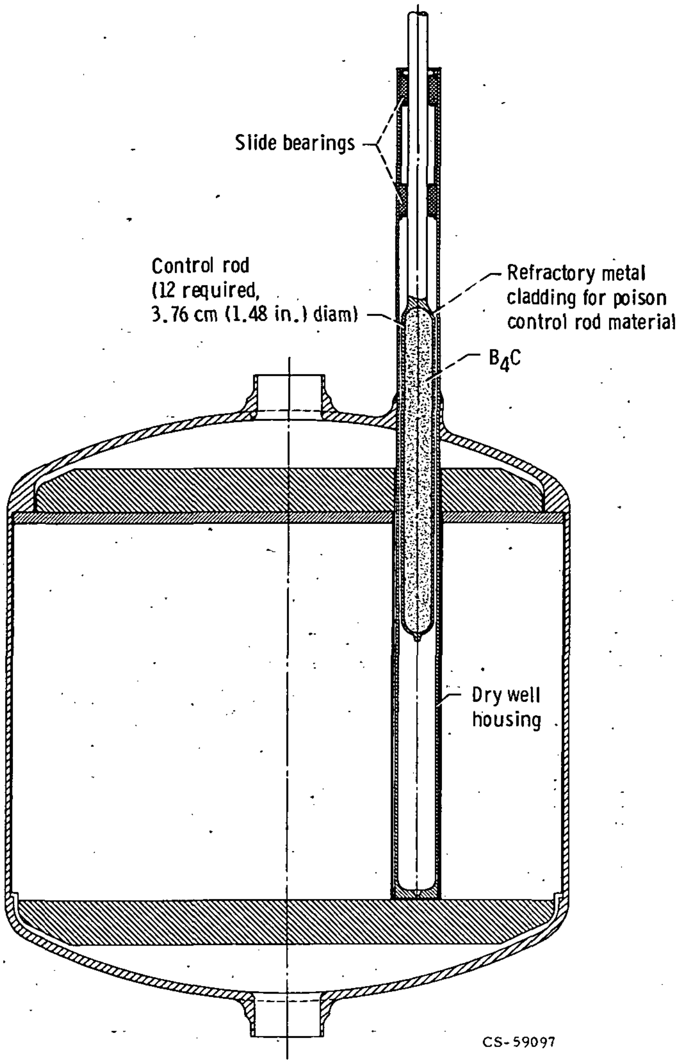
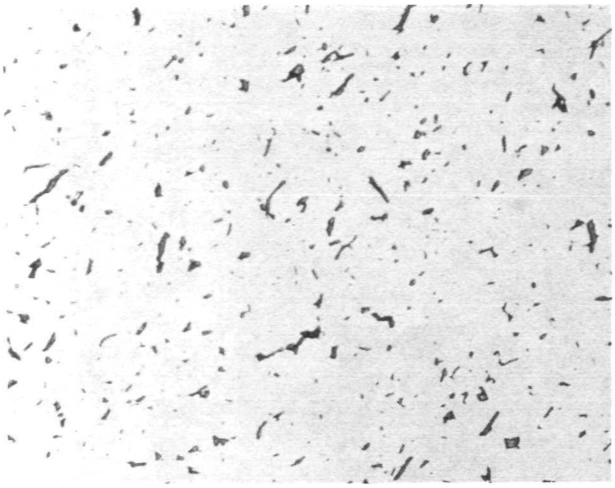
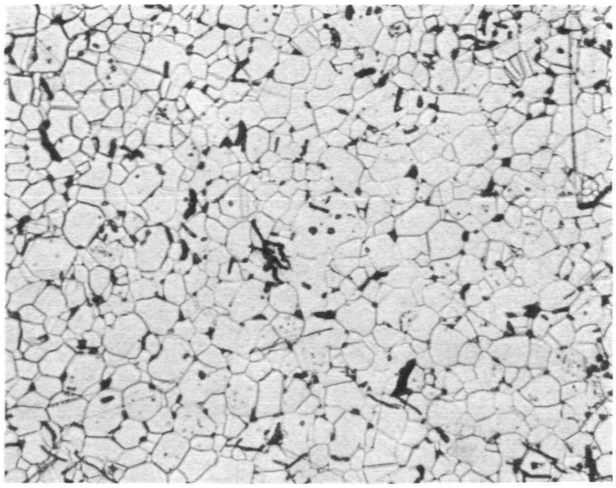


Figure 1. - Control concept using rods of poison control material moving within a dry well housing.

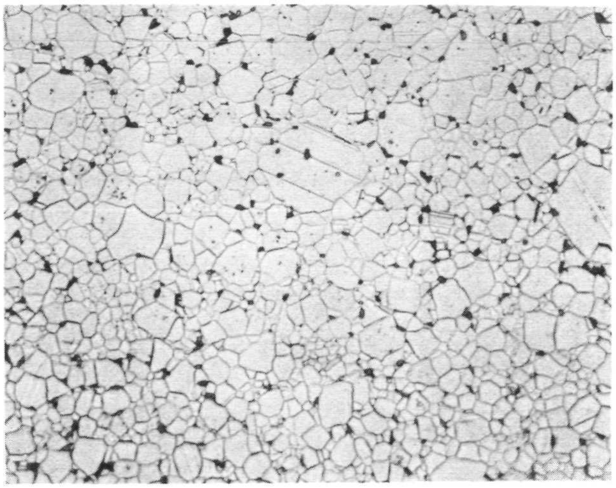


(a) Lot I. Unetched.

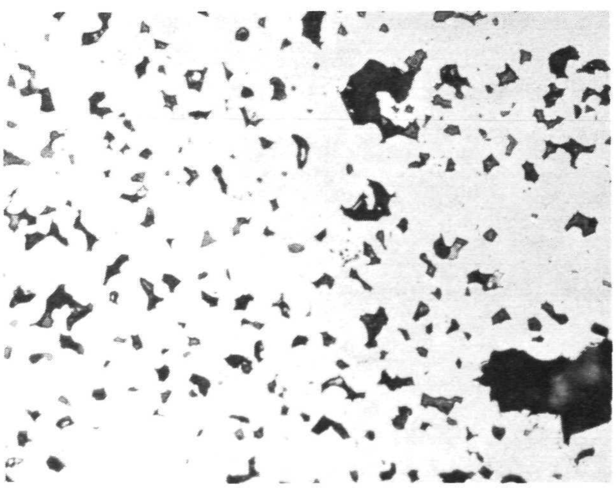


(b) Lot I. Etched, 10 percent CrO_3.

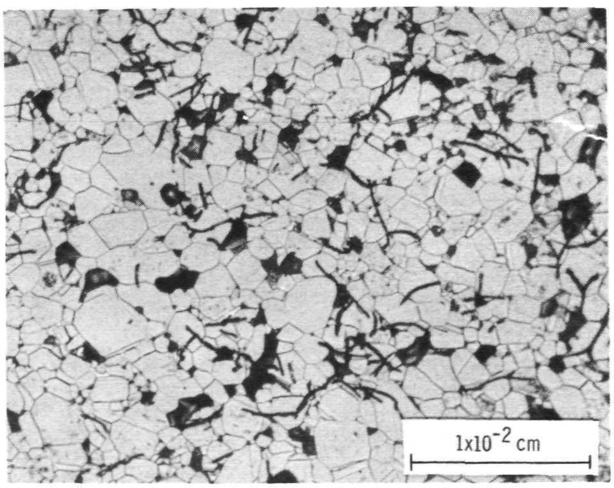
(c) Lot II. Unetched.



(d) Lot II. Etched, 10 percent CrO_3.

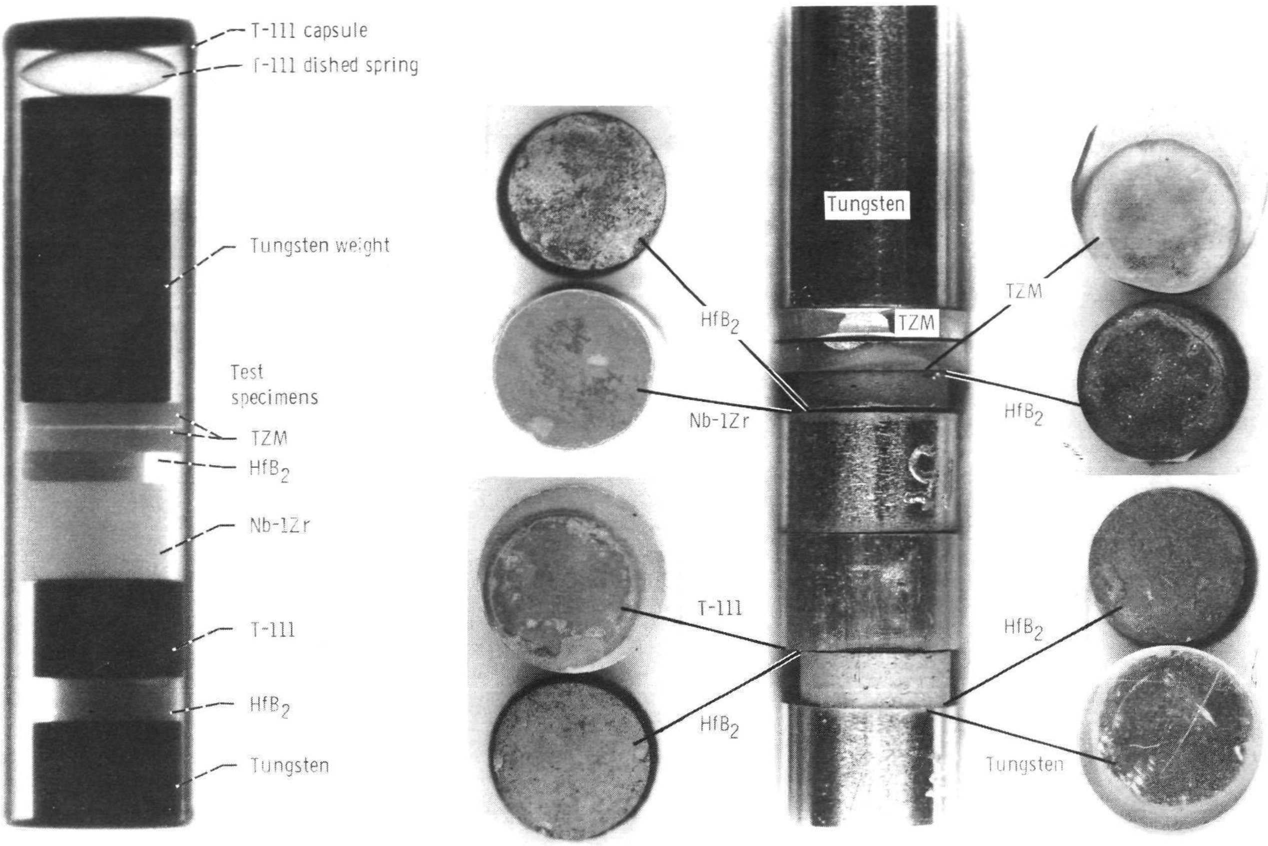


(e) Lot III. Unetched.



(f) Lot III. Etched, 10 percent CrO_3.

Figure 2. - Boron carbide control material in untested condition.



(a) Pretest X-ray radiograph.

(b) Posttest view of test specimens from part (a) and view of tested specimens. X2.3.

Figure 3. - Example of a test capsule before and after test.

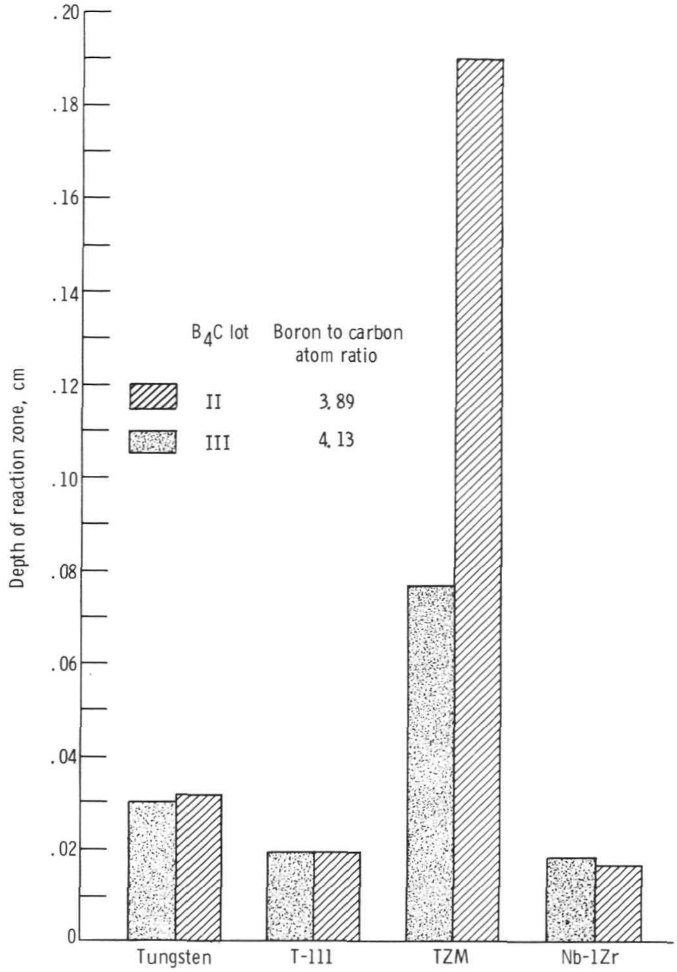
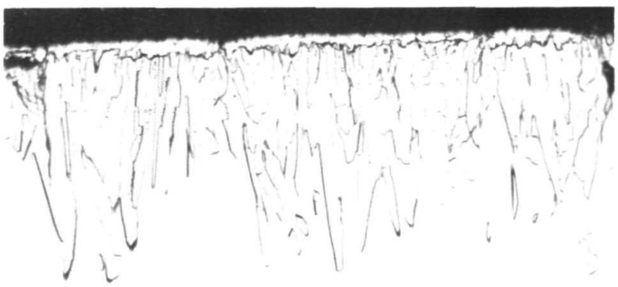


Figure 4. - Depth of reaction zone in refractory metals resulting from contact with B_4C after 1000 hours at 1400° C.



(a) Tungsten tested in direct contact with B_4C for 500 hours. Depth of attack, 1.8×10^{-2} centimeter; etched.

(b) Tungsten tested in direct contact with B_4C for 1000 hours. Depth of attack, 2.5×10^{-2} centimeter; etched.

Figure 5. - Effect of time on attack of tungsten by B_4C at 1400° C.

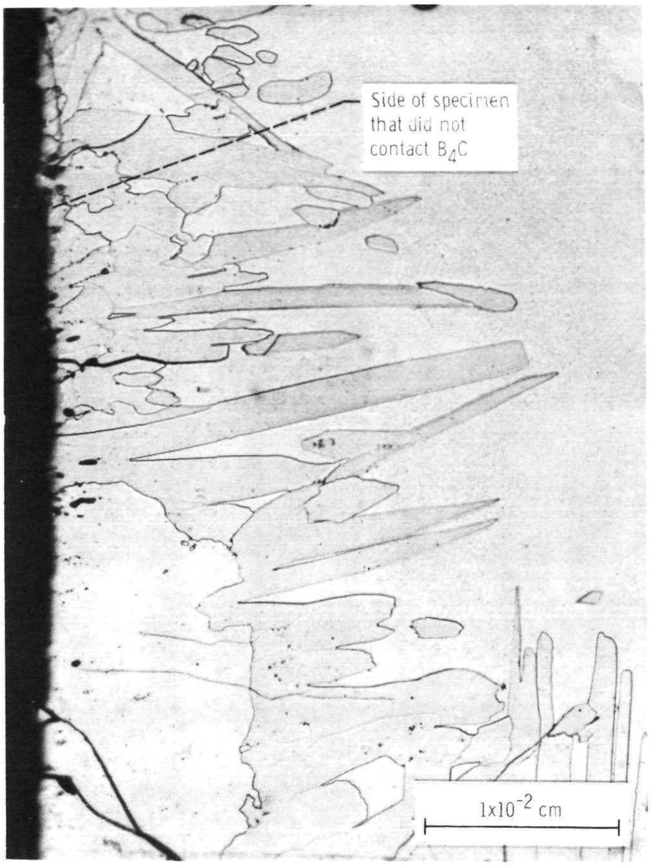
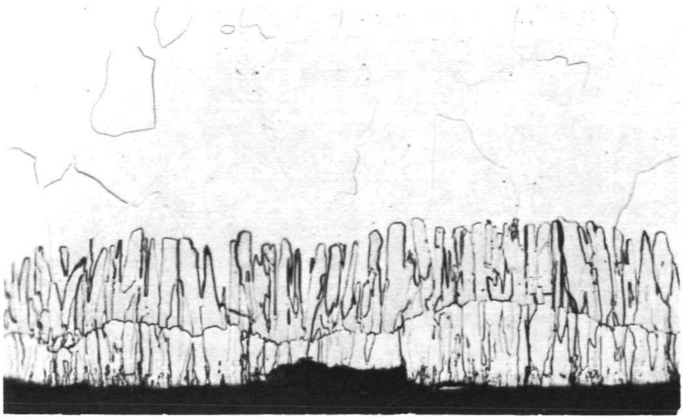
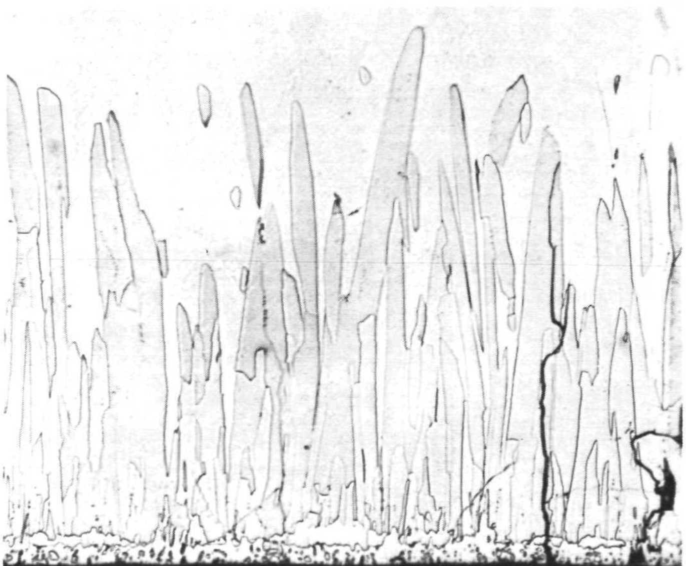


Figure 6. - Attack of tungsten by vapor-phase transport from B_4C during 1000 hours at 1400° C.

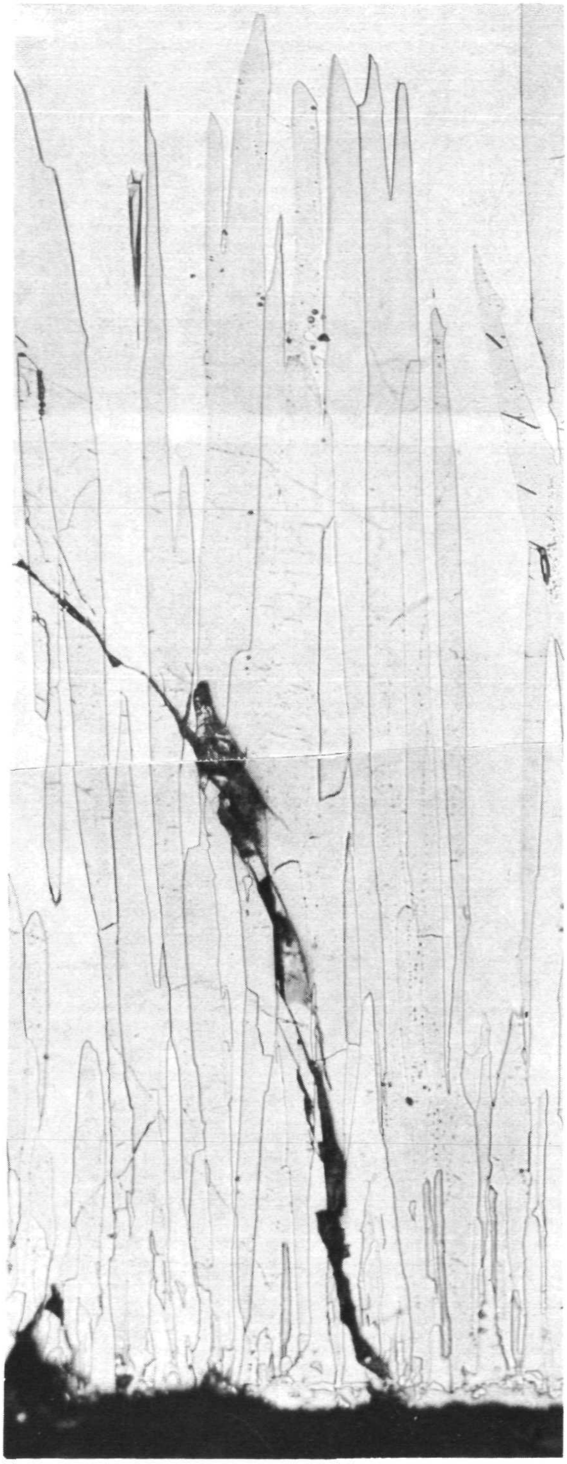


(a) Temperature, 1200° C.

1×10^{-2} cm

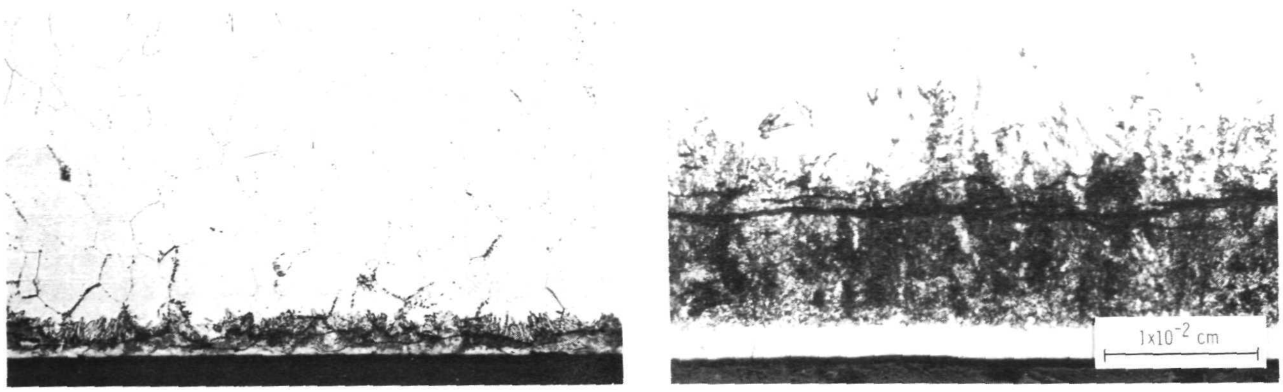


(b) Temperature, 1400° C.



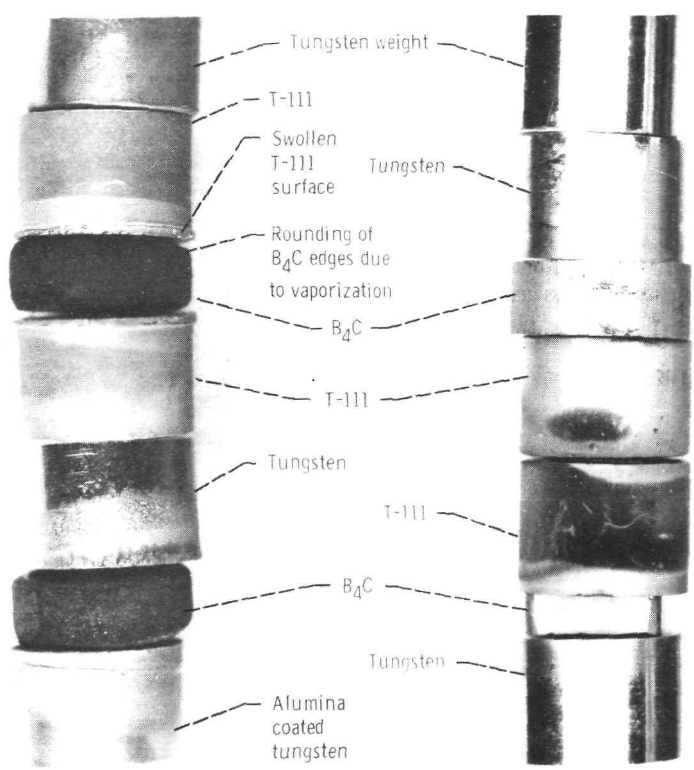
(c) Temperature, 1650° C.

Figure 7. - Effect of temperature on attack of tungsten by B_4C in contact for 1000 hours. Murakami etchant.



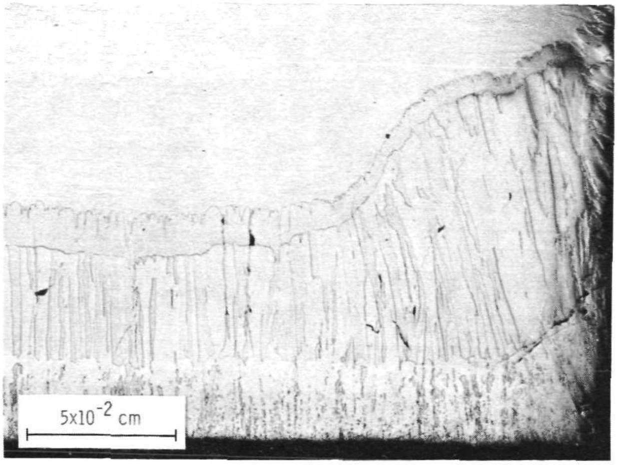
(a) Temperature, 1200° C. (b) Temperature, 1400° C.

Figure 8. - Effect of temperature on attack of T-111 by B_4C in contact for 1000 hours.

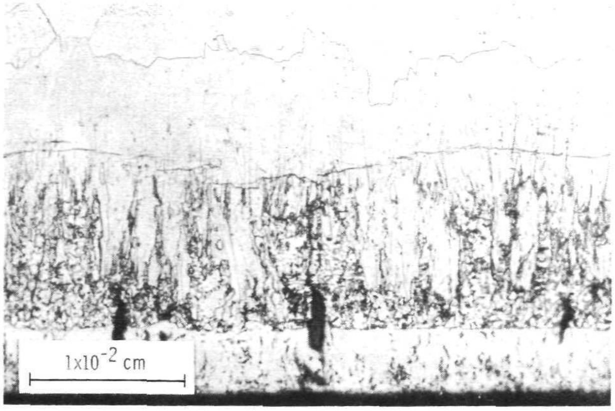


(a) Temperature, 1400° C. (b) Temperature, 1200° C.

Figure 9. - Comparison of appearance of B_4C, tungsten, and T-111 specimens after 1000 hours at 1400° C and 1200° C.



(a) TZM.



(b) Nb-1Zr.

Figure 10. - Surface attack zones of TZM and Nb-1Zr that contacted B_4C (lot III) for 1000 hours at 1400° C. Etched.

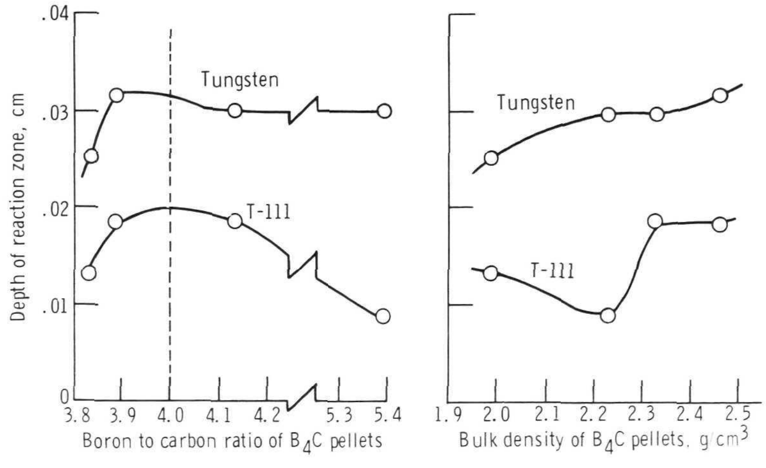
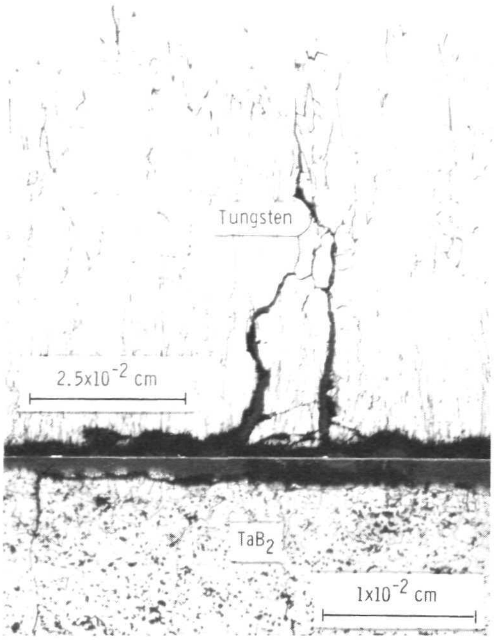
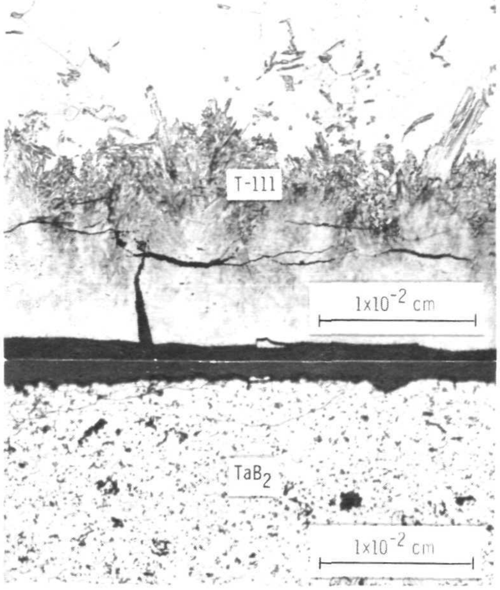


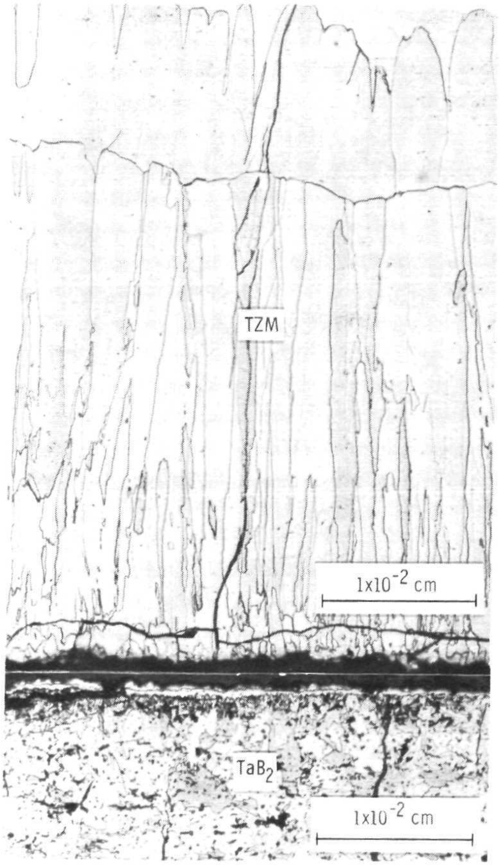
Figure 11. - Effect of B_4C quality on reaction with contacting refractory metals at 1400° C for 1000 hours.



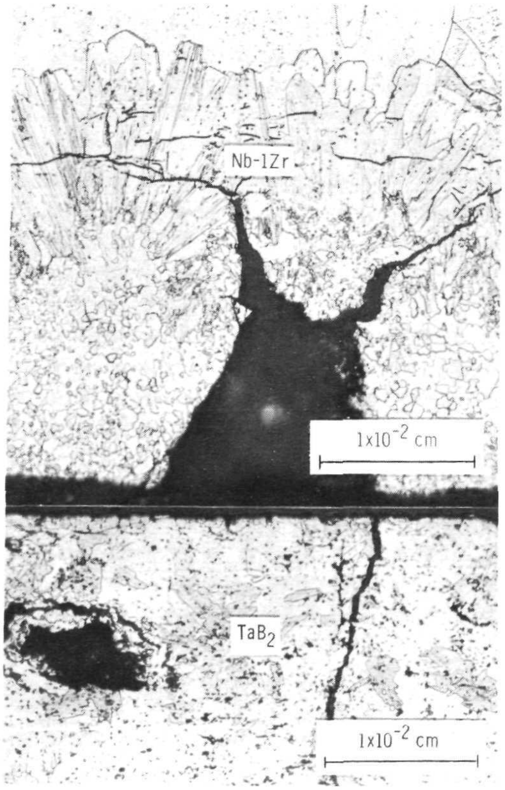
(a) Tungsten and TaB_2.



(b) T-111 and TaB_2.

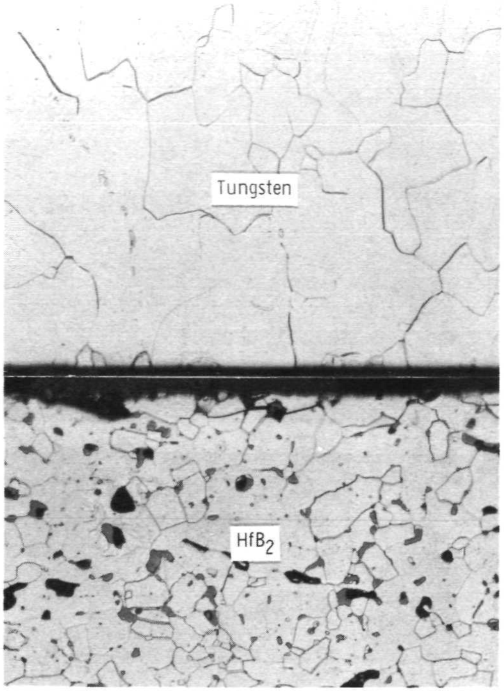


(c) TZM and TaB_2.

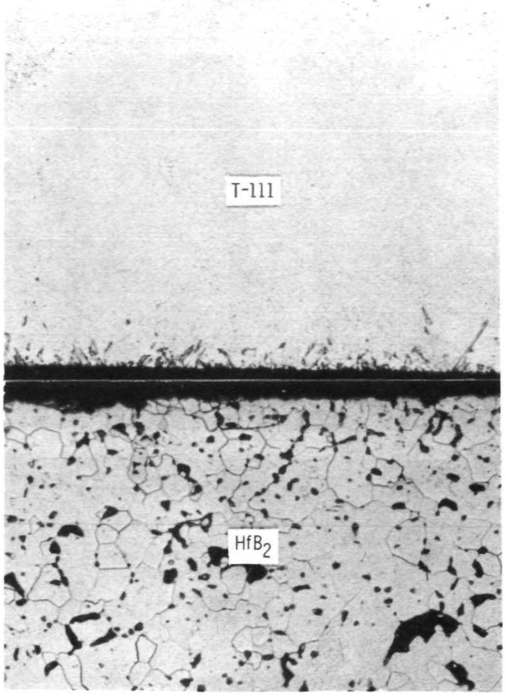


(d) Nb-1Zr and TaB_2.

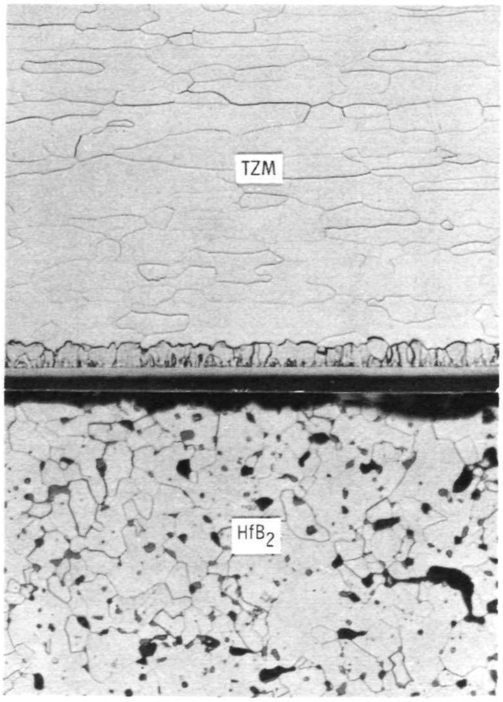
Figure 12. - Effects of 1000-hour tests at 1400° C on contacting tantalum diboride (TaB_2)/refractory metal specimens. Etched.



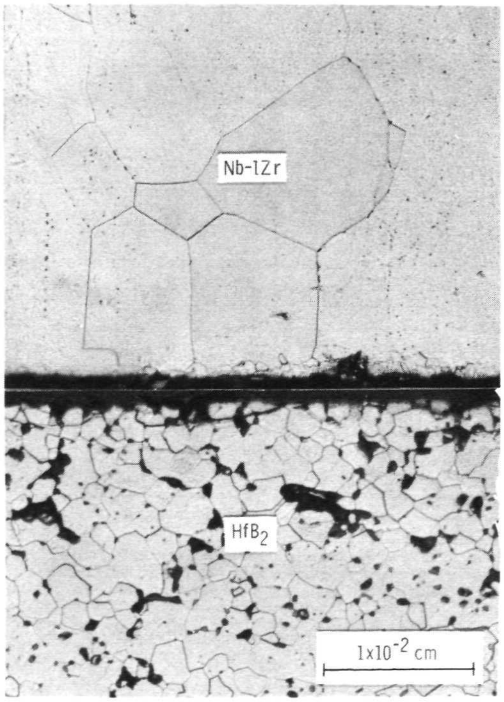
(a) Tungsten and HfB_2.



(b) T-111 and HfB_2.

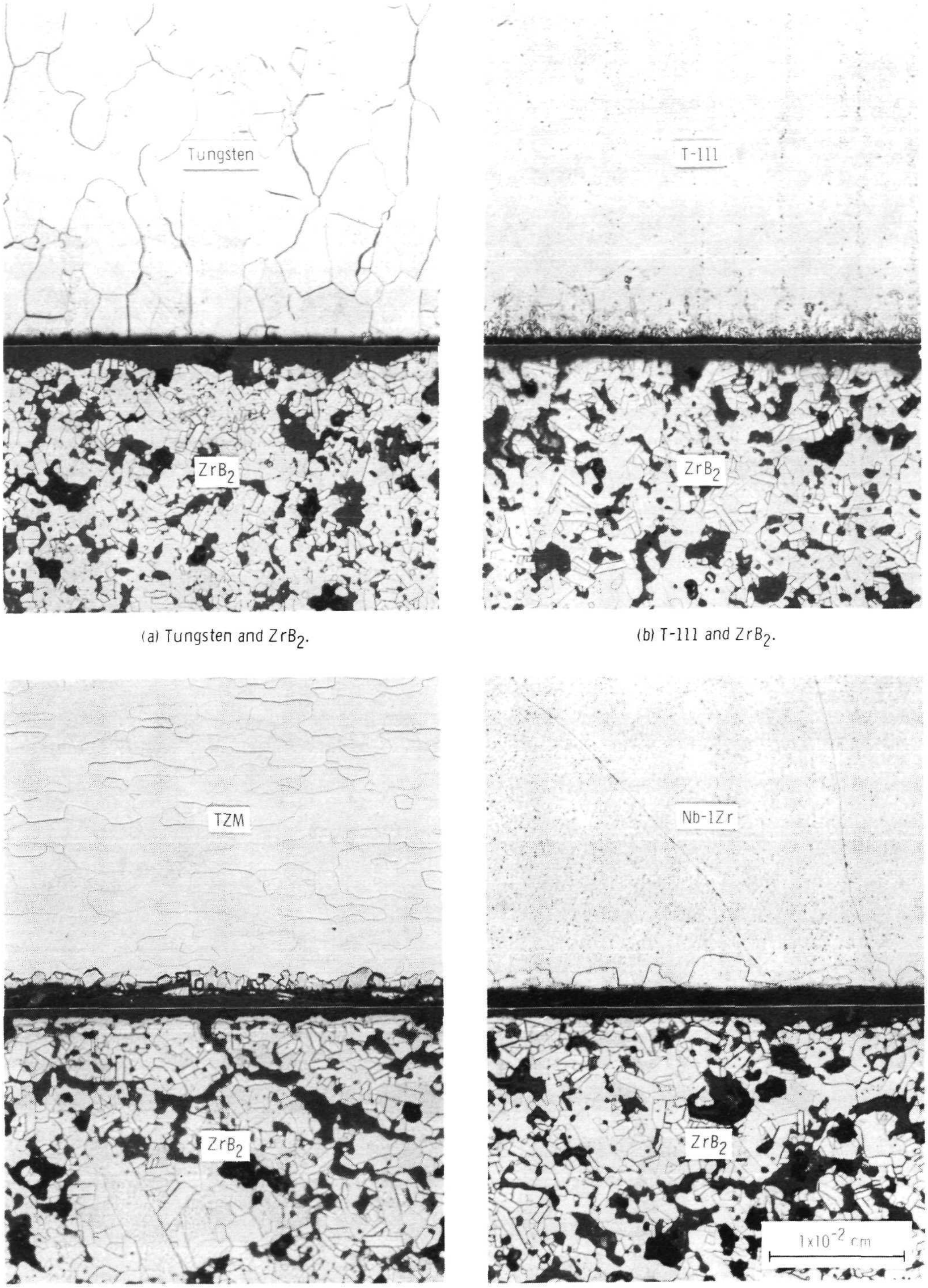


(c) TZM and HfB_2.



(d) Nb-1Zr and HfB_2.

Figure 13. - Effects of 1000-hour tests at 1400° C on contacting hafnium diboride (HfB_2)/refractory metal specimens. Etched.



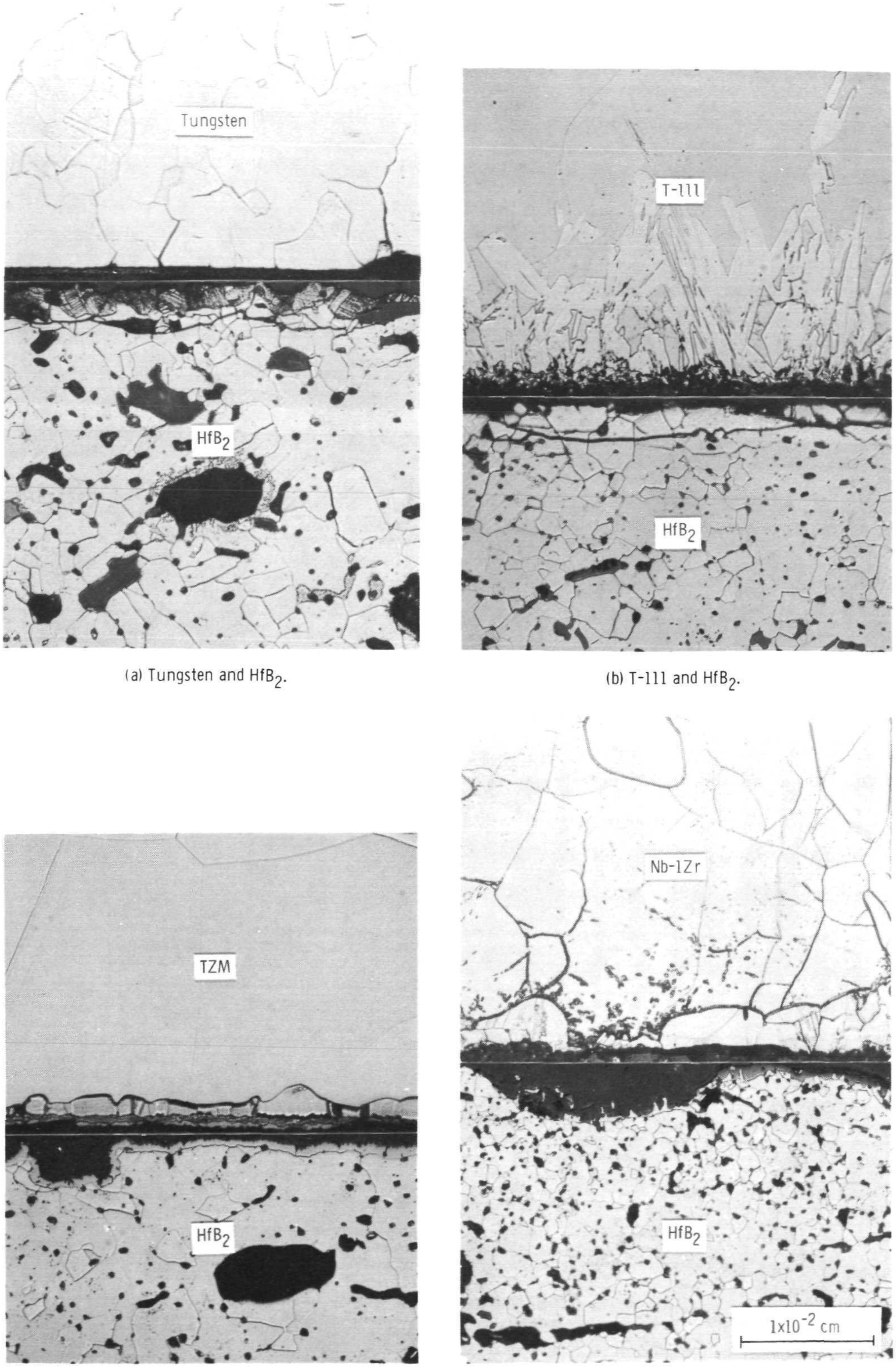
(a) Tungsten and ZrB_2.

(b) T-111 and ZrB_2.

(c) TZM and ZrB_2.

(d) Nb-1Zr and ZrB_2.

Figure 14. - Effects of 1000-hour tests at 1400° C on contacting zirconium diboride (ZrB_2)/refractory metal specimens. Etched.



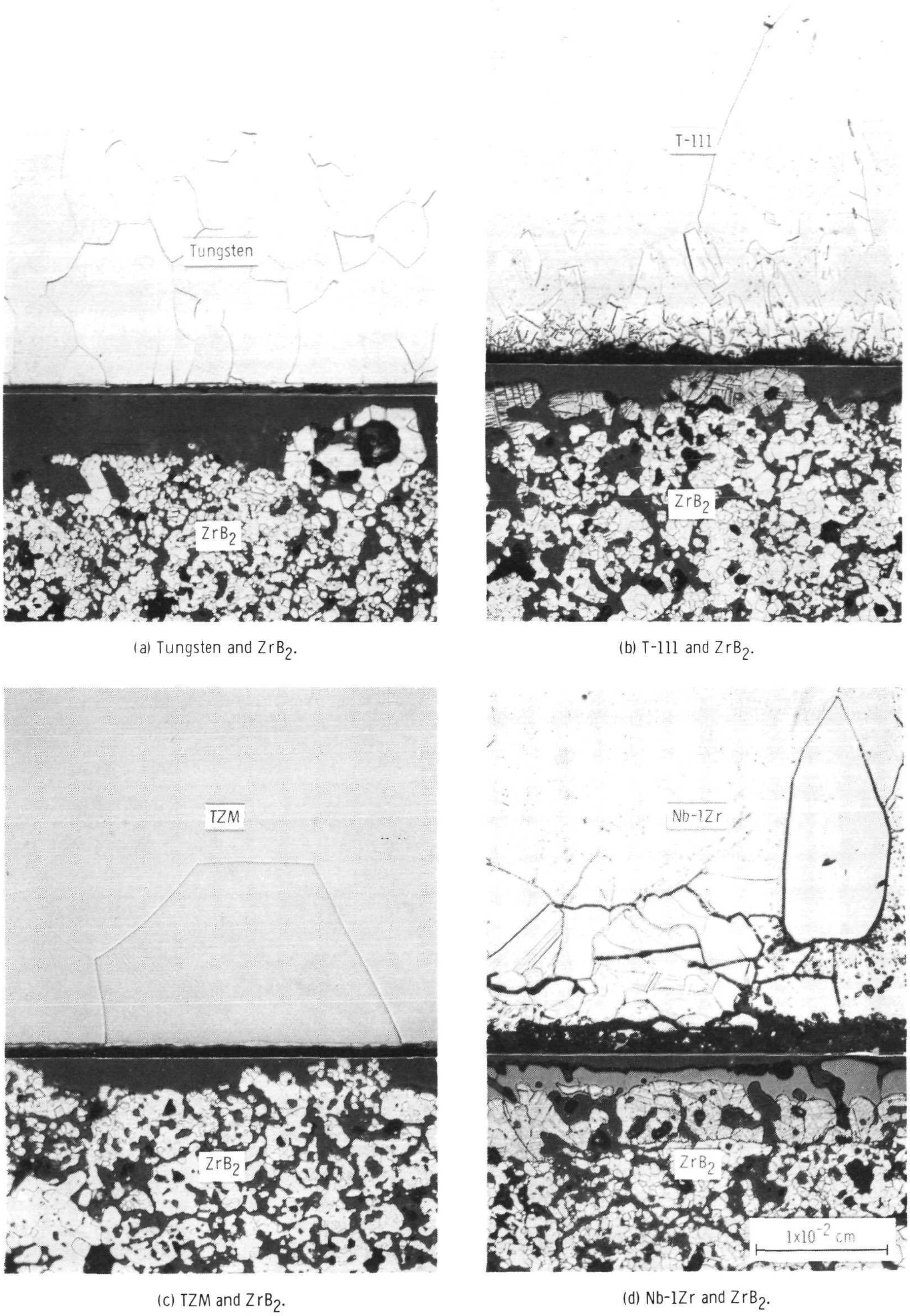
(a) Tungsten and HfB_2.

(b) T-111 and HfB_2.

(c) TZM and HfB_2.

(d) Nb-1Zr and HfB_2.

Figure 15. - Effect of 1000-hour tests at 1650° C on contacting hafnium diboride (HfB_2)/refractory metal specimens. Etched.



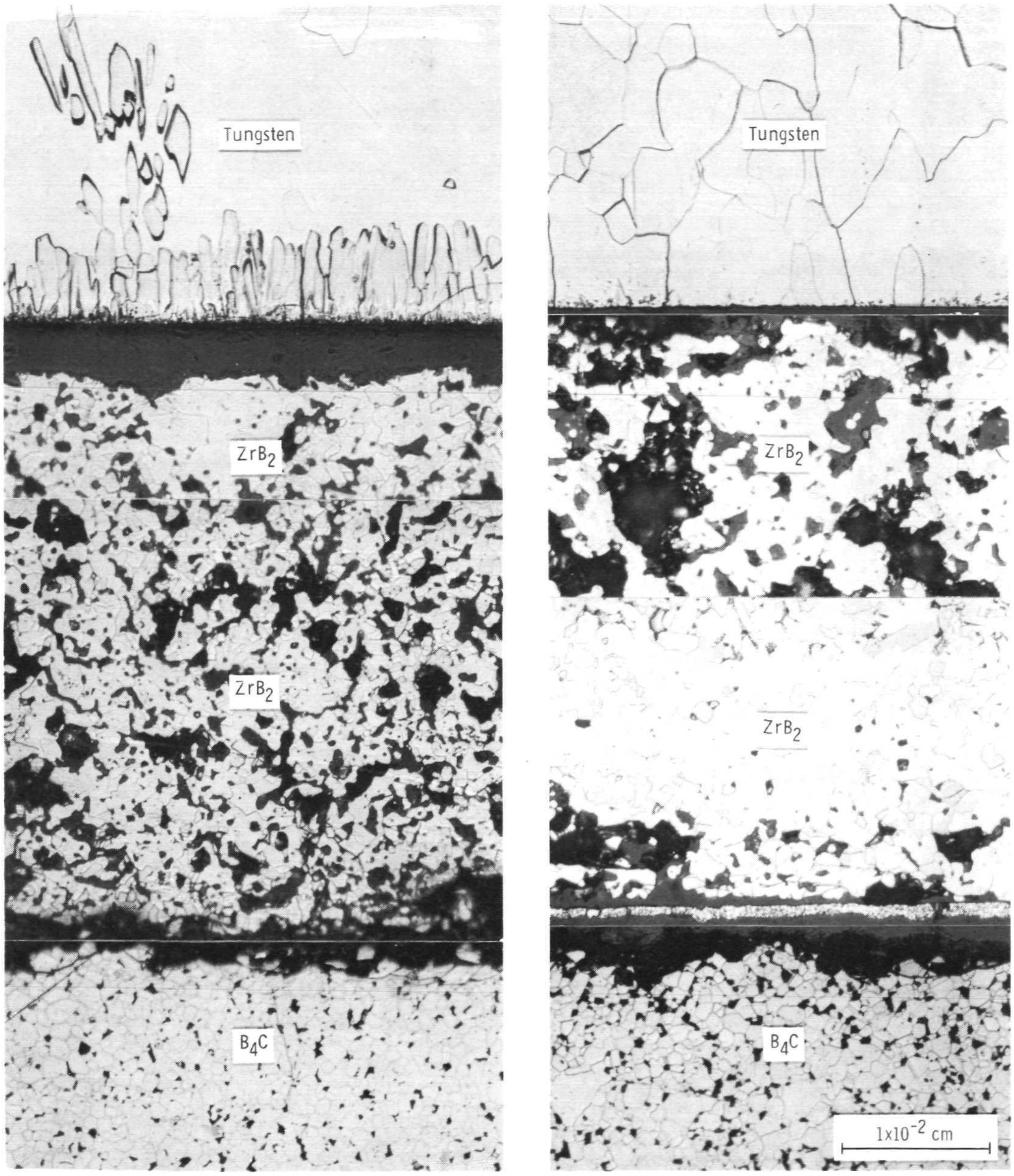
(a) Tungsten and ZrB_2.

(b) T-111 and ZrB_2.

(c) TZM and ZrB_2.

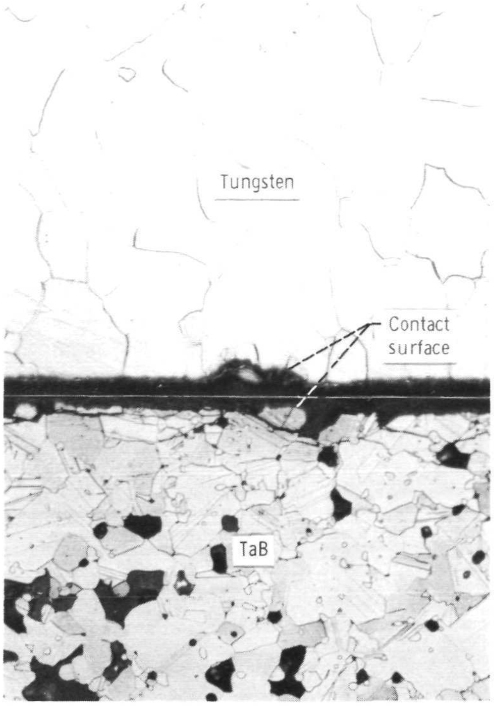
(d) Nb-1Zr and ZrB_2.

Figure 16. - Effect of 1000-hour tests at 1650° C on contacting zirconium diboride (ZrB_2)/refractory metal specimens. Etched.

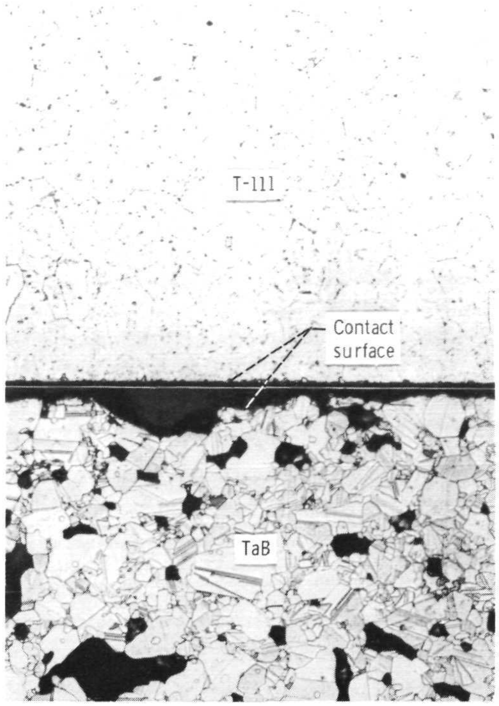


(a) Test temperature, 1400° C. (b) Test temperature, 1650° C.

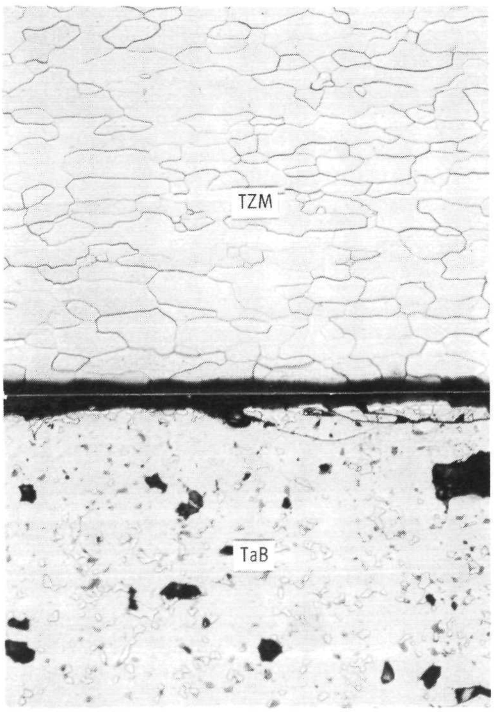
Figure 17. - Effects of thin (0.063 cm) interposed layer of ZrB_2 on the compatibility of B_4C and tungsten after 1000-hour tests at 1400° and 1650° C. Etched.



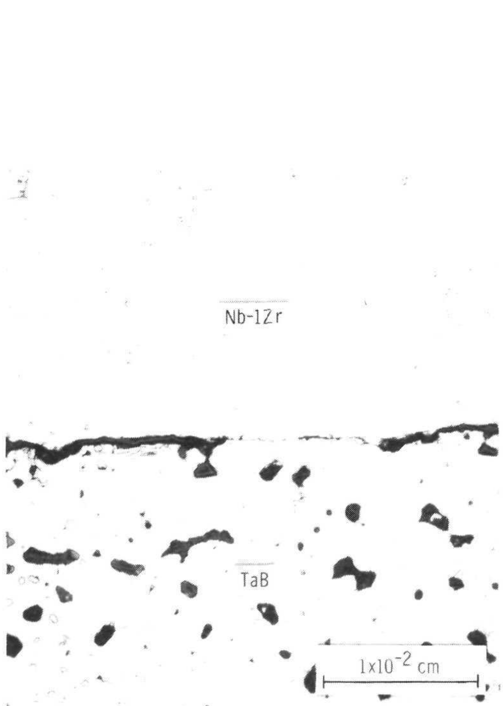
(a) Tungsten and TaB.



(b) T-111 and TaB.



(c) TZM and TaB.



(d) Nb-1Zr and TaB.

Figure 18. - Effect of 1000-hour tests at 1400^{0} C on contacting tantalum boride (TaB)/refractory metal specimens. Etched.

NASA-Langley, 1974 E-7581

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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