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A STUDY OF THE REFRACTORY BORIDES

by

Leo Brewer, Dwight L. Sawyer, D. H. Templeton, and Carol H. Dauben

February 24, 1950

Berkeley, California

[redacted]

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February 24, 1950

Abstract

The phases of the boron systems of Ce, Ti, Zr, Nb, Ta, Mo, and W were determined by X-ray examination of various mixtures of boron and the respective metal after heating to elevated temperatures. Data on the sintering behavior and stability at high temperatures of many of the phases were obtained. Several phases have been found to have promising refractory properties.

A STUDY OF THE REFRACTORY BORIDES

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Introduction

Although some of the borides should be very useful refractories, a survey of the literature at the time of the commencement of this research indicated that virtually no such work had been done with the borides. Since it was desired to find phases which would be useful as refractory containers, the study which was undertaken was restricted to those boride systems which could possibly provide compounds stable at very high temperatures. Brewer, Bromley, Gilles, and Lofgren[1,2] have discussed the factors which fix the melting

(1) L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, National Nuclear Energy Series, Plutonium Project Record, Division IV, Vol. 19B, Paper 4 (1950).

(2) L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, National Nuclear Energy Series, Plutonium Project Record, Division IV, Vol. 19B, Paper 7 (1950).

points and stabilities of the halides, oxides, sulfides, nitrides, carbides, silicides, and other similar compounds. By similar considerations, one can limit the region of stable borides. From the data given by Hansen[3], one finds that Cu, Ag, Au, Zn, Tl, Sn, Pb,

(3) M. Hansen, Der Aufbau der Zweistofflegierungen, (Julien Springer, Berlin), 1936.

and Bi are all immiscible with boron and form no intermediate phases. Likewise Na forms no intermediate phases. If one considers an extended periodic table in which the sub groups are not placed

together with the main groups but are extended out to the right, one sees that boron does not form any intermediate phases with elements to the far left or right of the periodic table. This behavior is similar to that of carbon and silicon. The trend toward such a behavior is seen when one starts with the halides and oxides and compares the shifting of the region of maximum stability as the non-metal shifts to the left in the periodic table toward carbon and boron. An analysis of these trends leads one to predict that the most refractory and most stable borides will be borides of metals in the region of the periodic table bounded by Ti, Nb, Mo, W, the actinide metals, and the rare earth metals. This is the region which was studied in the present research.

Experimental

The phases of the boride systems of Ce, Ti, Zr, Th*, Nb, Ta, Mo, W, and U* have been investigated. The preparations of various compositions were made by mixing boron powder with the metal powder. The mixed powder was tamped into a crucible which was made of molybdenum unless otherwise noted. The heating was carried out in the high frequency apparatus used by Eastman, Brewer, Bromley, Gilles, and Lofgren[4,5] for the preparation of the refractory

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[4] E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, Journal of American Chemical Society, March 1950.

[5] L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, Declassified Atomic Energy Commission Paper MDDC-367, Aug. 1945.

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* The results of the study of the U and Th borides has been reported separately in UCRL-603.

sulfides. Temperatures were observed with an optical pyrometer.

Sudden temperature rises had to be avoided since absorbed gases tended to spray the powder out of the crucible when suddenly released. The reaction between the boron and the metal usually started at about 950-1250°C. The heat of reaction was rather high and the temperature would often suddenly rise as reaction commenced. To avoid spraying, the temperature was rather slowly raised until after reaction had started. Also a half atmosphere of argon was maintained to minimize spraying and to reduce the vaporization of the free boron. In addition one or more holes were pressed through the powder, so that the gases could escape without lifting the powder. These precautions were usually sufficient to prevent loss of powder. The molybdenum crucibles suffered little attack with most samples although they sometimes became coated with a thin layer of Mo_2B. When samples containing a large excess of boron were heated in Mo crucibles, a large amount of boron was taken up by the crucibles and they sometimes cracked due to the expansion. However, there was no contamination of the sample by Mo.

After the reaction had started, the temperature was raised to a maximum between 1300 to 2050°C. depending upon the sample. After the heating of a very refractory sample, the compact was quite powdery and had not sintered or shrunk together. For other samples, for which sintering did take place, the compact shrunk away from the wall leaving a cylinder of sintered boride. For a few samples, the sintered cylinder had slumped which was taken as a sign of the formation of a small amount of eutectic liquid. The least refractory samples actually did partially melt. These observations were used to estimate the eutectic temperatures and the melting points of the

pure phases.

The samples were converted to a finely divided powder in a dry box containing argon. X-ray diffraction patterns were taken on a 9 cm. diameter cylindrical camera with copper Kα radiation ($\lambda = 1.5418$Å), and with CrKα radiation ($\lambda = 2.2909$Å).

The boron powder used was obtained from the City Chemical Co., New York. The main impurity was several percent of magnesium. Since the magnesium all vaporized out of the samples, it did not cause any difficulty. Due to the volatility of boron, some boron was also lost. To compensate for the weight loss of magnesium and boron, an excess of ten percent of boron over that calculated on the basis of pure boron with no losses was used in making up the preparations. The Mo, W, Nb, and Ta powders were furnished by the Fansteel Metallurgical Co., N. Chicago, Ill. They were 400 mesh and better than 99.9% pure. The Ti and Zr powders were obtained from Chas. Hardy Inc., New York and were at least 99.5% pure with respect to other metals, but considerable amounts of hydrogen, nitrogen, and oxygen impurities were present. The thorium metal powder was furnished by A. D. Mackay, New York as being 99% pure. Actually it was found to contain 14 mol% oxide. However, it was possible to use it to determine the boride phases of the thorium system. The uranium and cerium were obtained in compact form from the Manhattan District Project and were powdered by hydriding. They were both quite pure.

Tungsten-Boron System

Kiessling[6] has worked out the phases of the W-B system. Our

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[6] R. Kiessling, Acta Chem. Scand., 1, 893 (1947).

observations verify his conclusions and check his lattice constants very closely.

The following stability tests were made under a half atmosphere of argon. The hexagonal W_2B_5 phase was found to be only slightly decomposed after 24 minutes at 1700°C. but completely decomposed after 9 minutes at 1810°C. The tetragonal WB phase decomposed to a large extent after 15 minutes at 2040°C, but only to a small extent after 11 minutes at 1730°C . The tetragonal W_2B did not lose boron rapidly even at 2040°C. The tungsten borides were all quite refractory and virtually no sintering or shrinking took place even though the W_2B_5 had been heated to 1700°C., and the WB to 1810°C. The W_2B had not shrunk appreciably after heating for 15 minutes at 2040°C., but it had sintered enough to produce a compact that did not crumble readily. From the behavior of the preparations containing two phases, it is clear that the eutectic temperatures are very high for the W-B system. They are probably all well above 2000°C. with the melting points of the pure phases very much higher yet. Agte[7] has

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[7] C. Agte, Dissert. Techn. Hochschule, Berlin, 1931.

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reported a melting point of 2920 ± 50°C. for WB.

To test the stability of tungsten borides compared to borides of other metals, W_2B was heated with other metals. From the phases observed, one finds that W_2B is reduced by Ti, Ta and Zr. W_2B which was heated with carbon for 19 minutes at 1990°C. gave WB, WC and a slight amount of carbon. For WC, we obtained a = 2.905 ±0.003 and c = 2.798 ± 0.003Å. These values correspond to those for pure WC. Likewise the WB lattice constants were the same as those obtained for pure WB. This is taken to indicate no large solid

solubilities between WB and WC.

Using the powder metallurgy techniques described by Eastman, Brewer, Bromley, Gilles, and Lofgren[8], several 5/8" dia. W_2B

(8) ~~E. D. Eastman~~, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, Declassified AEC Paper AECD-~~2254~~ 2253, Oct. 27, 1945.

crucibles were pressed and sintered for 30 minutes at 2150°C. The crucibles shrank 10% and were still rather porous and not too well sintered, as they could be scratched with an iron point. Much higher sintering temperatures will be required for dense crucibles.

Molybdenum-Boride System

Kiessling[6] has worked out the phases of the Mo-B system. Our preparations verify his conclusions and check his lattice constants.

To test the relative stabilities of the molybdenum and tungsten borides, molybdenum metal was heated with W_2B. Both the metals and the M_2B phases of these elements are isomorphous and only two phases were obtained. A cubic metal phase which had a lattice constant intermediate between those of molybdenum and tungsten and a tetragonal phase with lattice constants intermediate between those of Mo_2B and W_2B were found. As would be expected from the relative stabilities of other similar compounds of Mo and W, the stabilities are very close. In view of the observations that the tungsten borides are not as stable as other borides of interest, no extensive work was done with the molybdenum borides. No rapid loss of boron was observed upon heating either Mo_2B or MoB at 1810°C. for 9 minutes under one half atmosphere of argon. A mixture of Mo_2B and MoB shrank

slightly after 9 minutes at 1810°C., but the sample was well enough sintered so that the compact did not crumble. A mixture of Mo_2B and Mo under the same conditions shrank enough so that the compact fell out of the crucible easily. It also was well enough sintered so that some force was required to crush the compact. These experiments indicated the molybdenum borides to be very similar to the tungsten borides in regard to melting points and stabilities.

Tantalum-Boron System

After the work on this system was complete, two papers on this system appeared. The paper by Kiessling[9] covered the same range

(9) R. Kiessling, Acta Chem. Scand., 3, 603 (1949).

as our work and our work is in substantial agreement with his except for one additional phase which we find. Thus we obtain $a = 3.060 \pm 0.002$ and $c = 3.290 \pm 0.002$Å for the high boron end of the hexagonal $TaB_{1.78 - 2.57}$ solid solution range while Kiessling obtains $a = 3.057$ and $c = 3.291$Å. We obtain $a = 3.097 \pm 0.003$ and $c = 3.227 \pm 0.002$Å for the low boron end of the range while Kiessling obtains $a = 3.099$ and $c = 3.224$Å. Norton, Blumenthal, and Sindeband[10], who discuss only the MB_2 phases, were in agreement

(10) J. T. Norton, H. Blumenthal, and S. J. Sindeband, Metals Transactions AIME 749 (1949).

in regard to the crystal structure of TaB_2, but they were not certain about the possibility of a wide homogeneity range of TaB_2.

In agreement with Kiessling, the orthorhombic Ta_3B_4 and TaB phases were found with the same lattice constants given by Kiessling.

No variation of constants were found with composition indicating narrow homogeneity ranges. However, TaB was observed together with TaB_2 in a sample heated to 1780°C. which might indicate Ta_3B_4 disproportionates at high temperature. The tetragonal Ta_2B phase gave lattice constants a = 5.785 ± 0.003 and c = 4.867 ± 0.003Å compared to a = 5.778 and c = 4.864Å given by Kiessling. As Kiessling found, it was not possible to prepare pure Ta_2B. Ta_2B and Ta were found in samples with 20 and 25 atomic % boron. TaB, Ta_2B, and Ta were found in a sample with an overall composition of Ta_2B or 33 atomic % boron. A sample with 40 atomic % boron showed TaB and Ta_2B with a trace of Ta. A trace of Ta_2B together with TaB could be detected in samples up to almost 50 atomic % boron. In an effort to determine the stability range of Ta_2B, preparations were made in the temperature range 1650 to 2040°C., but the temperature of preparation did not seem to have any effect. A mixture of Ta and Ta_2B was heated to 1950°C. under 4×10^{-5}mm. pressure and then suddenly quenched by turning off the high frequency power and letting in one half atmosphere of argon. The sample contained Ta and Ta_2B plus a weak phase isomorphous with the phase tentatively designated as Nb_3B. A sample of overall composition Ta_2B was heated to 1950°C. under 4×10^{-5}mm. pressure and slowly cooled under vacuum conditions taking 70 minutes to cool to 1140°C. and several hours more to cool to room temperature. The three phases TaB, Ta_2B, and Ta were still found. The only change noted was that the powder pattern lines were more spotty indicating larger crystals. Thus it was not possible to determine whether Ta_2B is stable at high temperatures and disporportionates upon cooling like FeO or whether Ta_2B is unstable at high temperatures and forms by the reaction of

Ta with TaB upon cooling as does SnO. The difficulty in distinguishing appears to be due to a narrow temperature range in which the rates of reaction are rapid. Rapid and slow cooling through this range should allow one to distinguish between the two possibilities. The phase designated as Ta_3B appears to be stable only at very high temperatures and disproportionates upon cooling. Kiessling[9], who did not heat to as high temperatures nor quench as rapidly, did not report this phase. Thus of the five intermediate phases of the Ta - B system, Ta_3B (?), Ta_2B, and Ta_3B_4 have only limited temperature ranges of stability. Only TaB and TaB_2 are apparently stable from room temperature to the melting points. In agreement with Kiessling, the Ta metal lattice was found to be expanded indicating appreciable solid solubility of boron in the metal.

Although compositions up to 86 atomic % boron were prepared, at 1565°C. all excess boron vaporized leaving hexagonal $TaB_{2.57}$. The $TaB_{1.78-2.57}$ phase loses boron at 1780°C. under a half atmosphere of argon to form Ta_3B_4, but more than half of the $TaB_{1.78}$ is left after 8 minutes. However, 10 minutes at 1820°C. will completely decompose the hexagonal $TaB_{1.78}$ as well as the orthorhombic Ta_3B_4 leaving only the orthorhombic TaB. Both TaB and Ta_2B are found after 15 minutes at 2040°C. in argon. There is some loss of boron at this temperature but it is not rapid.

None of the tantalum boride samples which were heated at 1810°C. or below had shrunk or sintered. All of the eutectic temperatures must be quite high. Pure TaB was still an unsintered powder after 10 minutes at 1820°C. Samples with more tantalum which contained Ta, Ta_2B, and TaB phases were somewhat sintered after 10 minutes at 1820°C., but there was no appreciable shrinkage. However,

further heating of these samples for 15 minutes at 2040°C. did not produce shrinkage. Although they were better sintered and stronger compacts, they still could be broken up rather easily.

As mentioned in the tungsten boride system discussion, tantalum reduces W_2B to form TaB, W and the phase designated as Ta_3B. It is believed that the Ta_3B phase formed during this heating since the sample was heated for 47 minutes at 1980°C. As noted above, it is believed that Ta_3B forms only at very high temperatures. Thus TaB should be a more satisfactory container material for very electropositive metals than W_2B. TaB was heated with excess carbon at 1700°C. and TaC and TaB_2 were produced.

From the information we have obtained, it is clear that tantalum borides, particularly TaB, should prove very useful as very refractory materials. However, very high sintering temperatures will be necessary to produce compact non-porous material.

Niobium-Boron System

The highest boride found was hexagonal NbB_2, isomorphous with AlB_2 (C 32 type). It was found to have an appreciable solid solution range with lattice constants a = 3.110 ± 0.002 and c = 3.264 ±0.002Å when in equilibrium with Nb_3B_4 and a = 3.085 ± 0.002, c = 3.311 ± 0.002Å when prepared by heating a sample with 86 mol % boron for 22 minutes at 1565°C. The exact composition limits of the solid solution range are not known due to loss of boron during the heatings. After this work was complete, a paper by Norton, Blumenthal and Sindeband[10] appeared in which they find the same structure for NbB_2, but they did not have definite information on

the homogeneity range. Kiessling[11] has also since reported

(11) R. Kiessling, Acta Chem. Scand. 3, 90 (1949).

finding the same structure, although he has not yet published any lattice constants.

The next boride, Nb_3B_4, was found to have the orthorhombic Ta_3B_4 structure with lattice constants a = 3.30 ± 0.001, b = 14.1 ± 0.1, and c = 3.13 ± 0.01Å. NbB was found to have the orthorhombic FeB structure and thus is isomorphous with TaB and CrB. The lattice constants a = 3.292 ± 0.003, b = 8.713 ± 0.008, and c = 3.165 ± 0.003Å were found to be independent of the composition of the sample and thus a narrow homogeneity range is indicated. Most samples with more than 50 atomic percent niobium gave only the NbB and Nb phases. The Nb lattice constant was a = 3.300 ± 0.015Å. The metal was not well crystallized and thus one can not determine if boron has changed the lattice constant.

In addition to Nb and NbB, two additional phases were found in some of the samples containing 25 to 50 atomic % boron. These were tentatively designated as Nb_3B and Nb_2B although they could not be indexed. No phases isomorphous with Ta_2B were observed. The Nb_3B phase was isomorphous with the Ta_3B phase.

A sample with 25 atomic % boron gave Nb_3B in addition to Nb and NbB after 8 minutes at 1650°C. and a new sample of the same composition still gave the same results after 10 minutes at 1820°C. A sample with 20 atomic % boron gave no Nb_3B after 47 minutes at 1980°C. and only consisted of NbB and Nb. Nor did any samples with 33 atomic % boron or higher give any Nb_3B after 10 minutes at 1820°C.

A sample of 50 atomic % boron after 21 minutes at 1530°C. gave a strong pattern of NbB and a weak pattern of a phase tentatively designated as Nb_2B, which was not isomorphous with Ta_2B. Another sample of 50 atomic % boron gave only NbB and Nb_2B after 9 minutes at 1810°C.

Of the five intermediate phases of the niobium - boron system, apparently Nb_3B (?), Nb_2B (?), and possibly Nb_3B_4 have limited temperature ranges of stability and only NbB and NbB_2 are stable from room temperature up to the melting point.

Although preparations up to 86 atomic % boron were made, no phases above the hexagonal NbB_2 solid solution were found after heatings at 1565°C. The NbB_2 solid solution range was very refractory and there were little signs of sintering even after 24 minutes at 1700°C. Mixtures of NbB_2 and Nb_3B_4 showed no signs of sintering after 14 minutes at 1550°C. However, mixtures of Nb and NbB did show slight signs of sintering after 21 minutes at 1530°C. 47 minutes at 1980°C. produced a compact that did not crumble readily or which was not easily scratched by iron. The core of the compact was especially well sintered. The excess Nb metal was not hard as the sintered mixture of Nb and NbB was malleable and could be flattened out in a B_4C mortar. It is thus clear that the Nb borides are not as refractory as the Ta borides and can be sintered at lower temperatures. This might be an advantage under some circumstances when high enough temperatures are not available to produce dense well sintered Ta boride containers. Of the niobium borides, NbB or possibly Nb_3B_4 should be the most promising refractory material for very rigorous conditions.

Zirconium-Boron System

Since our work has been completed, Kiessling[11] has published work on the system. Both studies indicate only one intermediate phase, ZrB_2. It has the hexagonal AlB_2 (C 32 type) structure. Kiessling reports a = 3.169 and c = 3.530Å. Our work yields a = 3.168 ± 0.002 and c = 3.528 ± 0.002Å. Both studies tend to indicate a narrow homogeneity range for ZrB_2 and an appreciable solid solubility of boron in zirconium as indicated by expansion of the metal lattice. Norton, Blumenthal, and Sindeband[10] have also recently studied ZrB_2 and report a = 3.170 and c = 3.533Å.

After 15 minutes heating at 1600°C. in 1/2 atmosphere of argon, a preparation with 68 atomic % boron lost the excess boron to form pure ZrB_2, but no further decomposition occurred. Virtually no sintering took place and the final compact was still a loose powder. Mixtures of Zr and ZrB_2 shrank and sintered after 15 minutes at temperatures between 1515 and 1575°C. Mixtures containing from 60 to 75 atomic % zirconium were well sintered and compact even after 8 minutes at 1500°C. It might appear that the eutectic between Zr and ZrB_2 is below the melting point of Zr which is probably around 1800°C. when quite pure, and that the eutectic composition contains a fair concentration of boron. The melting point of pure ZrB_2 is undoubtedly well above 2000°C. Agte[7] reports a melting point of 3190 ± 50°C. for a zirconium boride which probably corresponds to ZrB_2.

The relative stabilities of ZrB_2 and W_2B were determined by melting Zr in a W_2B crucible. The Zr reduced W_2B to W forming ZrB_2.

Titanium-Boron System

Samples prepared with more than 66 atomic % boron lost any excess boron to give pure hexagonal TiB_2, isomorphous with AlB_2 (C 32 type). The lattice constants a = 3.030 ± 0.003 and c = 3.227 ± 0.003Å were found in agreement with the constants reported by Zachariasen[12]. TiB_2 found in samples of composition

(12) W. H. Zachariasen, Acta Cryst. 2, 94 (1949).

from 60 atomic % boron to the highest boron compositions studied always had the same lattice constants indicating a probable narrow homogeneity range. Ehrlich[13] has also reported the TiB_2 phase

(13) P. Ehrlich, Angew. Chem., 59, 163 (1947); Z. anorg. Chem., 259, 1 (1949).

with a = 3.03 and c = 3.22Å, but he also reports a TiB phase of cubic zincblende structure with a = 4.25Å. The cubic face centered phase which we find in our samples with a = 4.25 ± 0.01Å is interpreted to be merely TiN due to nitrogen contamination and we believe that Erlish's results might best be interpreted on the same basis. His lattice constant would correspond to a solid solution of TiO and TiN. The Ti phase was distorted due to solution of boron in the metal, but no other phases were found between TiB_2 and the Ti solid solution other than TiO and TiN phases which appear in some samples due to contamination from the atmosphere. The solid solution of boron in Ti appears to be a very wide one as also indicated by Ehrlich. The powder pattern of the Ti phase changed continually as the boron composition was varied from 25 to 50 atomic percent.

Pure TiB_2 was found to be unsintered after 15 minutes at 1600°C. A sample containing some TiN in addition to TiB_2 shrank

noticeably and was somewhat sintered after 15 minutes at 1515°C. Samples containing the solid solution of boron in Ti metal were well sintered even after 8 minutes at 1500°C. The higher the titanium composition of these samples, the greater was the degree of sintering observed. The well sintered samples were very hard and brittle. This might indicate that boron dissolves in Ti metal to raise the melting point and there may be a maximum melting point in the solid solution range.

When Ti was heated with W_2B powder or in a crucible made of a mixture of W_2B and WB, tungsten was found in the powder patterns indicating reduction of the tungsten borides by titanium, but the titanium phase formed was not TiB_2 or the Ti metal solid solution. It looked almost isomorphous with TaB and NbB, but the pattern could not be indexed. A ternary phase of Ti, W, and B was possibly formed although one can not overlook the possibility of the presence of oxygen or nitrogen in the phase.

Silicon-Boron System

Two silicon samples with 50 and 80 atomic % boron were heated in BeO crucibles for 20 minutes at 1725°C. The powder patterns showed strong lines of a pure silicon metal phase with some weak lines possibly due to boron. No evidence for any silicon boride was found.

Cerium-Boron System

Samples ranging in composition from 25 to 86 atomic % boron were studied. The cubic CeB_6 phase previously reported by both Allard and Stackelberg and co-workers[14] was obtained upon heating

(14) G. Allard, Bull. Soc. Chem. France 51, 1213 (1932); M. V. Stackelberg, F. Neumann, Z. physik Chem. (B) 19, 14 (1932).

a sample containing 86 atomic % boron for 13 minutes at 1730°C. The lattice constant was a = 4.1390 ± 0.0007Å. Even though there was a half atmosphere of argon to diminish the rate of decomposition with loss of boron, the existence of this compound at 1730°C. indicates a rather high stability. No other compounds above MB_4 were obtained for any of the other systems studied.

The only other boride found was tetragonal CeB_4, isomorphous with UB_4 and ThB_4[15]. Its lattice constants were a = 7.205 ± 0.008

(15) A. Zalkin and D. H. Templeton, J. Chem. Phys. (in press).

and c = 4.090 ± 0.005Å. Samples from 50 to 67 atomic % boron gave both CeB_4 and Ce which would eliminate the possibility of any lower borides. The Ce lattice constant was 5.119 ± 0.013Å. Some of the samples, particularly those with more than 50 atomic % cerium, had oxidized somewhat during the grinding process and CeO_2 was also observed.

Of all the systems investigated, this system was the only one which gave completely molten samples. Samples containing between 75 and 60 atomic % of cerium were completely melted at 1530°C. A sample containing 50 atomic % cerium was partially melted at 1300°C. Since cerium melts at 785°C., it is quite likely that the Ce - CeB_4 eutectic temperature is close to 785°C. with the eutectic composition very close to pure cerium.

A CeB_4 sample had shrunk considerably and was well sintered after 13 minutes at 1730°C. A mixture of CeB_4 and CeB_6 shrank less

and was less sintered after the same treatment and pure CeB_6 under the same conditions did not shrink or sinter at all and remained a fluffy light purple powder. Thus CeB_6 is not only very stable, but very high melting in addition. In view of the more refractory behavior of a mixture of CeB_4 + CeB_6 than pure CeB_4, it is possible that a peritectic rather than a eutectic will be found between CeB_4 and CeB_6. It undoubtedly will be found at temperatures well above 2000°C.

Experiments to determine the relative stabilities of W_2B and CeB_4 were not too conclusive. Ce which was melted in a W_2B crucible soaked into the porous crucible. X-ray powder patterns of the crucible appeared to indicate an increase in the amount of W metal, but no CeB_4 was observed. However, the W_2B lattice constants were about 0.1% larger with almost the same c/a ratio, thus indicating solution of the cerium in the W_2B.

Summary

The X-ray examination of the various preparations have indicated the following definite phases: W_2B, $WB_{0.92-1.02}$, $WB_{2.0-2.13}$, Mo_2B, $MoB_{0.96-1.06}$, $MoB_{2.33}$, Ta_3B(?), Ta_2B(?), TaB, Ta_3B_4, $TaB_{1.78-2.57}$, Nb_3B(?), Nb_2B(?), NbB, $NbB_{2\pm x}$, ZrB_2, TiB_2, CeB_4, and CeB_6. The molybdenum and tungsten borides were very high melting, but were not as stable toward reduction as the other borides. TaB and NbB appear to be the most promising refractory borides for highly reducing conditions. ZrB_2 and CeB_4 also show considerable promise. The tungsten borides, W_2B and $WB_{0.92-1.02}$, should be useful refractories when reducing conditions are not so severe. The molybdenum borides appear to be very similar in behavior to the tungsten borides except for somewhat lower melting points which may be an advantage under some circumstances due to the difficulty in sintering tungsten borides except at very high temperatures.

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