superficial since the metallic appearance of the substances indicates that the bonding is by no means ionic. It may serve, however, as a working hypothesis in the preparation of analogous compounds of the transition metals.

BROOKLYN, N. Y. RECEIVED APRIL 27, 1951

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE COLLEGE OF ENGINEERING OF THE OHIO STATE UNIVERSITY

High-temperature Reactions in the System Titanium Carbide–Boron Carbide[1]

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Titanium carbide and boron carbide are shown to react at temperature above 1920° to produce titanium diboride, carbon and a higher boride of titanium of unknown composition.

With the development of interest in metal-impregnated refractory carbides as structural materials for jet engines, reactions in the solid state at high temperatures in such systems have assumed ever increasing importance. Whereas various indications that carbon may be removed from the initial carbide body by the impregnating metal phase to form new carbides have been observed, nothing as yet has been published which would indicate that two carbides may react with one another at high temperatures to form a new compound and free carbon. During our investigation of the binary system titanium carbide–boron carbide (TiC–B_4C) we have observed such a phenomenon. We have found that in this system at temperatures of the order of 2000° the reaction represented by the following equation takes place

$$2TiC + B_4C \longrightarrow 2TiB_2 + 3C$$

Preparation of Materials.—Titanium carbide (TiC), 325 mesh, was obtained from Titanium Alloy, Mfg. Division of the National Lead Company. It analyzed Ti, 76.0; C, 20.0; Fe, 1.5; minor impurities 2.5%. Boron carbide (B_4C) #99, 400 grit, was obtained from the Norton Company. It analyzed, B, 78.0; C, 20.0; minor impurities 2.0%.

Five-hundred-gram lots of the crude carbides were wet-milled for 65 hr. in one-quart capacity hardened steel ball mills using steel balls. Methanol was used as the liquid medium. The milled carbides were dried in air and leached with 6 *N* hydrochloric acid. They were then washed with distilled water until free of acid and chloride, washed with methanol, dried in air and granulated through a 200 mesh screen. Particle size distributions in the finished products are given in Table I.

TABLE I

Particle size range, microns	Weight, % TiC	Weight, % B_4C
>20	0.5	3.7
20—10	2.0	2.3
10—5	10.9	26.5
5—1.6	63.2	60.6
<1.6	23.4	6.9

The moisture contents of the processed carbides were TiC, 0.05%, and B_4C, 0.06%. The titanium carbide contained no impurities detectable by X-ray diffraction. The boron carbide contained traces of graphite and FeC solid solution.[2]

Procedure.—Binary mixtures of the two carbides were prepared at 10% weight intervals. The proper weights of the carbides were wet-mixed for 12 hours in liquid methanol in small bottles packed in ball mills. The separate mixtures were then dried in air and granulated through a 32 mesh screen. The granulated powders were pressed in a two-punch cylindrical steel die at 850 kg./cm.^{2} The cylindrical specimens thus formed were approximately 1.25 cm. in diameter by approximately 0.75 cm. thick and weighed approximately 2.8 g. These samples were placed in rubber bags, the bags evacuated and the samples repressed hydrostatically at 2400 kg./cm.^{2}.

The pressed specimens were placed on thin discs of the same composition, then placed on graphite pedestals after which the assemblies were packed in a graphite crucible. The crucible and contents were placed in a vacuum desiccator which was then evacuated and flushed with argon, the cycle being repeated at least three times. The crucible was then removed and quickly placed in an induction furnace. The firing was carried out in a lamp-grade argon atmosphere using a seven-hour firing schedule. The maximum temperature was attained within six hours at a rate of increase of 350° per hour. All firings were held at the maximum temperature for one hour. Maximum firing temperature ranged from 1920 to 2150°.

To identify the phases present in the first specimens, X-ray diffraction analyses by the powder method were carried out. Molybdenum K_α radiation with a zirconium filter was used at 50 kv. and 20 ma. employing a 114.6 mm. Debye–Scherrer camera. Six hour exposures were used and intensities were estimated visually.

Results and Discussion.—In samples containing less than 60 weight per cent. of TiC, no TiC remained after firing. In samples containing less than 70 weight per cent. of B_4C no lines for that compound could be found for the fired specimen. Except in the case of pure TiC, carbon was found to be present in all fired specimens. The carbon was identified by its X-ray diffraction pattern. The 002 reflection was quite sharp and had an interplanar spacing of 3.36 Å. This seems to indicate that the carbon present was definitely crystalline.

With the exception of the interplanar spacings for TiC, B_4C and C, the interplanar spacings and their estimated intensities for eight fired binary mixtures are tabulated and available on microfilm.[3] The majority of these "d" spacings can be grouped into two categories: (a) those whose intensities reach a maximum at about 60 to 70 weight per cent. of TiC, and (b) those whose intensities reach a maximum at about 30 weight per cent. TiC. The first category is designated as "II" in the table and the second as "X." Spacings of the "II" group correspond to titanium diboride, TiB_2. It is believed that the "X" spacings correspond to a boride TiB_x in which, judging from the B/Ti ratio, x has a value of the order of 10.

The structure of TiB_2 has been reported as being

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[1] This investigation was carried out under USAF Contract No. 33 (038)-16911 between the Air Materiel Command and The Ohio State University Research Foundation.

[2] Konobejewski, *Z. Krist.*, **72**, 386 (1929).

[3] Order Document 3307 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C. remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

hexagonal, belonging to the space group $C6/mmm$-D^1_{6h} with a_0 = 3.028 Å. and C_0 = 3.228 Å.[4] The positions of the atoms are: Ti at 0,0,0; B at $^1/_3$, $^2/_3$, $^1/_2$ and at $^2/_3$, $^1/_3$, $^1/_2$.

The first eight interplanar spacings with the designation II listed in the microfilmed table are those given by Norton[5] for the compound TiB_2. The remainder of the spacings which we have attributed to TiB_2 and designated by "II" do not disagree with Norton's spacings but supplement them. These supplementary spacings are all smaller than the smallest given by Norton indicating that his spectrometer probably did not scan the region yielding the smaller interplanar spacings or else he used a target material which placed the spacings out of the instrument's range. A table of all the interplanar spacings for TiB_2 as determined in this Laboratory is available on microfilm.[3]

The photomicrograph in Fig. 1 was taken of the reaction product between TiC and B_4C with the former in excess. TiB_2 was the only new phase formed, and appears in the photomicrograph as the light, well-defined phase. The gray phase is TiC and the very dark irregular shapes are voids.

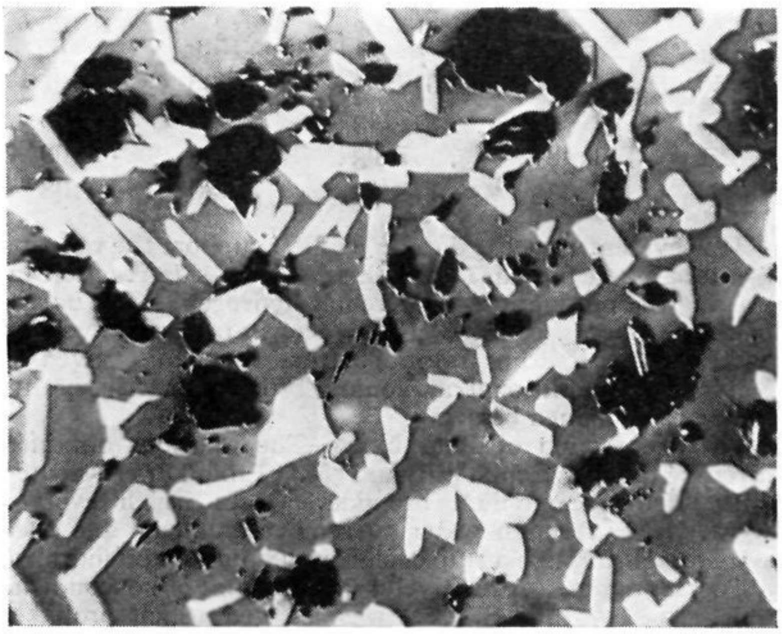

Fig. 1.—1500× unetched. Gray matrix is TiC. White areas are TiB_2. Black areas are void.

Figure 2 is a photomicrograph of the reaction product between TiC and B_4C where all of the carbide has reacted to give TiB_2, TiB_x and C. Two phases are seen in this photograph, both of which are light. The lightest, best-defined phase is TiB_2 and the other is TiB_x. Again, the very dark irregular shapes are voids. TiB_x could not be mistaken for a carbide because of the former's higher reflectivity. This can be seen by comparing the TiB_x of Fig. 2 with the TiC of Fig. 1.

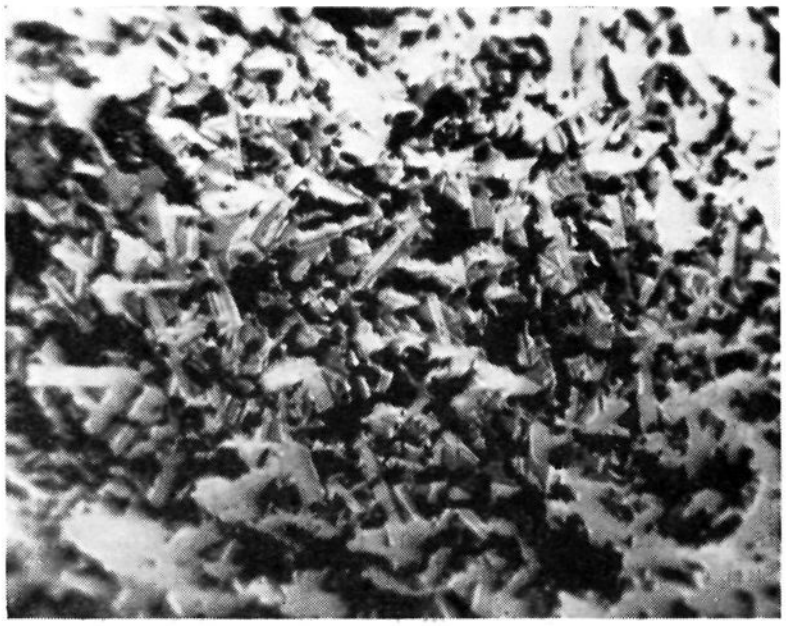

Fig. 2.—1500× unetched. Lightest, best defined phase is TiB_2 and the other is TiB_x. Black areas are voids.

As of the time of this communication, the identification of the TiB_x compound has not been accomplished. Because of the similarity of TiB_2 and AlB_2, the authors considered the possibility of TiB_x being TiB_{12}, an isomorph of AlB_{12}.[6] X-Ray evidence, however, failed to support this consideration.

It is not certain in which of the two classifications, TiB_2 or TiB_x, the two spacings designated as "O" in the microfilmed table belong, or if they arise from a new structure. However, as a result of the intensity distribution, the authors feel that these spacings, 0.73 Å., and 0.71 Å., belong to TiB_2.

The authors wish to thank Thomas S. Shevlin and Clinton C. McBride for their technical assistance, and Dr. George A. Bole, under whose direction research on USAF Contract No. 33(038)-16911 is being carried out.

COLUMBUS, OHIO RECEIVED APRIL 18, 1951

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(4) Norton, Blumenthal and Sindeband, *J. Metals*, **I**, No. 10 Trans. 749 (1949).

(5) J. T. Norton, private communication, November, 1950, from Massachusetts Institute of Technology.

(6) Halla and Weil, *Z. Krist.*, **101**, 435 (1939).