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Preparation of single crystals of MoB_2 by the aluminium-flux technique and some of their properties

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Crystal growth of MoB_2 ($R\bar{3}m$; $a_{hex.} = 0.30136(6)$ nm, $c_{hex.} = 2.0961(4)$ nm) from high-temperature aluminium solutions (1000 to 1500° C) has been investigated, and the optimum conditions for obtaining single crystals of this compound were examined. Starting with about 33 to 53 g of a mixture of molybdenum, boron and aluminium, in which the atomic ratio is 1 : 2.5 : 53.3 to 88.9, MoB_2 single crystals of about 1.5 mm in size were grown without being accompanied by any other crystal phases. The stoichiometry and the crystal structure were corroborated by chemical analysis and single-crystal X-ray diffractometry. The Vickers microhardness measured in the (0 0 1) plane is in the range 2170 to 2470 kg mm^{-2}. The oxidation of the crystal in air is examined by thermogravimetric and differential thermal analyses up to 1200° C.

1. Introduction

Borides of transition metals have various unique properties which in many cases are of great importance from technological viewpoints. Among their attractive properties are high thermal and chemical stability, high electrical and thermal conductivity, and high hardness and high mechanical stiffness [1].

Recently we have reported the crystal structure of MoB_2 [2] which had been grown from a high-temperature aluminium solution [3]. This boride compound was at first considered to be of the Mo_2B_5-type structure (rhombohedral, $R\bar{3}m$; $a_{hex.} = 0.3011$ nm, $c_{hex.} = 2.093$ nm) [4, 5] from preliminary X-ray diffraction work. Chemical analysis and an accurate structure determination by single-crystal diffractometry showed, however, that this material has the ideal chemical composition MoB_2 [2].

In this paper, we report experimental conditions for growing MoB_2 crystals as well as some of their properties, corroborating the MoB_2-type structure by single-crystal diffractometry. The crystal growth and stoichiometry of the related compound WB_2 [6] are also discussed.

The crystal of MoB_2 investigated in the present work is quite different from that designated MoB_2 in an earlier paper [7]. The latter is of the AlB_2-type structure (hexagonal, P6/mmm; $a = 0.305$ nm, $c = 0.3113$ nm [7]). On the other hand, the structure of the present crystal (hereafter called simply MoB_2 or rhombohedral MoB_2) is similar to that proposed for Mo_2B_5 [4]. Between these two, however, there is an essential difference in one of the two kinds of boron network constituting them, and the difference necessarily results in a difference in the stoichiometry.

2. Experimental details

2.1. Preparation of crystals

A vertical alumina tube furnace equipped with silicon carbide resistors was used. The starting materials were powdery molybdenum metal (average particle size, 3.5 μm; purity 99.5%), crystalline boron (– 115 mesh; purity, 99.5%) and aluminium metal chips (purity, 99.99%). Various mixtures of these materials in various atomic ratios were placed in an alumina crucible and heated in an argon atmosphere. The furnace was raised to a prescribed temperature at a rate of 300° C h^{-1}, maintained at that temperature for a fixed time, cooled to 900° C at the rate of 50° C h^{-1} and then allowed to cool to room temperature. The starting materials were heated to a temperature not exceeding 1500° C, because the furnace tube and the crucible made of alumina did not keep their refractory properties at higher temperatures. The crystals grown in the reaction mixtures were separated by dissolving the excess metals in hydrochloric acid.

2.2. X-ray and chemical analyses

The crystals obtained were examined by powder X-ray diffractometry or oscillation, Weissenberg and precession methods. The relative amount of each phase in the product of each experiment was estimated roughly in terms of the relative X-ray intensity, as observed from powder X-ray diffractometer charts. Crystals for chemical analysis were selected under a binocular microscope. A number of crystals were put into a ZrO_2 crucible, treated with $NaOH$–Na_2O_2 mixture at 600° C, and then analysed by inductively coupled plasma emission spectroscopy [8].

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2.3. Structure determination by single-crystal diffractometry

For intensity measurements an approximately spherical specimen of MoB_2 (average diameter, 0.08 mm) was selected from the fragments obtained by crushing relatively large single crystals. The lattice constants were determined by the same diffractometer that was used for the intensity measurements; the wavelength employed was 0.071073 nm for Mo*Kα* radiation. The reflections ($0 \leqslant h \leqslant 6, 0 \leqslant k \leqslant 6, -50 \leqslant l \leqslant 50$; $2\theta < 120°$) were measured by a Rigaku automated four-circle diffractometer, with graphite-monochromatized Mo*Kα* radiation. The ω ($2\theta \leqslant 30°$) or $\omega - 2\theta$ ($30° < 2\theta < 120°$) scan mode was used at a rate of $2\,\text{deg}\,\text{min}^{-1}$ in ω. Background counts of 10 sec duration were measured on each side of the scanning width, $\Delta\omega = 1.2 + 1.5 \tan\theta$. Three standard reflections were examined after every 100 reflections and no significant variations were observed. A total of 735 reflections with F_o values greater than 2.5 times the standard deviations was collected. They were corrected for Lorentz, polarization, and absorption effects. Anisotropic secondary extinction effects were corrected experimentally during the last least-squares refinement of the structure.

Starting from the structural data of MB_2, published in our previous paper [2], the structure was refined by the full-matrix least-squares program RADIEL [9], with anisotropic thermal parameters for molybdenum, isotropic for boron atoms and with anomalous-dispersion correction. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weights w were $1/\sigma_F^2$. Experimental anisotropic extinction parameters were also included in the final stage of the refinements. Final R values are: $R = \Sigma w(|F_o| - |F_c|)/\Sigma w|F_o| = 0.028$ and $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2} = 0.037$ for 14 parameters and 735 reflections of which 371 were unique. The final difference Fourier synthesis showed no significant residual peak. The calculations for the structure analysis other than the least-squares refinement were performed by using the program UNICS-III [10]. The atomic scattering factors and the anomalous dispersion correction factors were taken from International Tables [11].

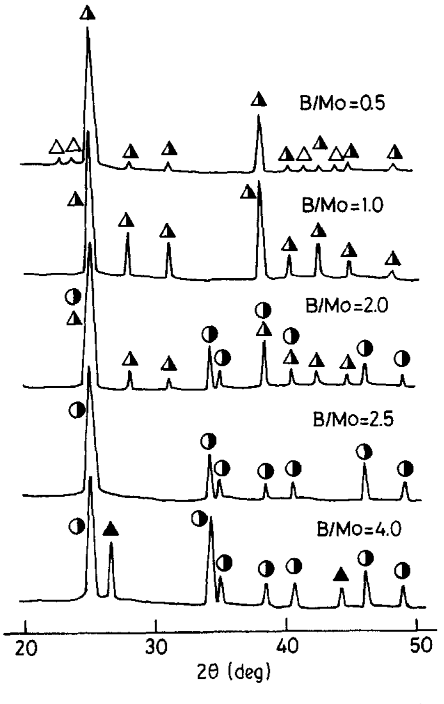

Figure 1 Powder X-ray patterns (Cu*Kα* radiation) of the products obtained from several starting materials with various compositions. The atomic ratio Al/Mo of the starting materials is fixed at 53.3. The starting materials are heated at 1500° C for 10 h. (◑) MoB_2, (**△**) MoAlB, (△) Unknown 1, (▲) Unknown 2.

2.4. Properties

2.4.1. Hardness

The hardness of the MoB_2 single crystals was measured with a Vickers diamond indenter. A load of 100 g was applied for 15 sec at about 10 positions on the (0 0 1) plane of each crystal, and the values obtained were averaged. Altogether 15 single crystals were used for the hardness measurement.

2.4.2. Oxidation in air

Thermogravimetric and differential thermal analyses were made up to 1200° C. α-Al_2O_3 was used as a standard material for differential thermal analysis. The specimens of about 30 mg were heated at a rate of $10°\,\text{C}\,\text{min}^{-1}$. The sizes of the crystals were in the range 25 to 36 mesh.

3. Results and discussion

3.1. Optimum conditions for the preparation of MoB_2 single crystals

Adjustable parameters for growing crystals in the present experiment are heating temperature and the mixing ratio in the starting materials. Since the amount of molybdenum in the starting material was fixed at 2 g throughout all the experiments, actual adjustable parameters concerning the composition of the starting material are the atomic ratios B/Mo and Al/Mo. The experiment for the preparation of MoB_2 crystals consists of four series.

In the first series (Table I, Run No. 1-13) the effect of changing B/Mo ratio in the starting material was examined. In this series a total of four crystal phases (MoB_2, MoAlB, Unknown Phase 1, Unknown Phase 2) was identified from powder X-ray diffraction diagrams. In each run of Table I, the product crystals are presented from the left to the right according to the order of their yield. From the starting materials containing a very small amount of boron (B/Mo = 0.3, 0.5) MoAlB and Unknown Phase 1 were grown.

From the starting materials with B/Mo = 0.8 to 1.2 only the ternary compound MoAlB [3, 12] was grown. With an increase of boron content from B/Mo = 1.5 to 2.2, MoB_2 was grown in addition to the ternary phase. From the starting materials with B/Mo = 2.4 and 2.5 only MoB_2 was obtained, but from those of higher boron content (B/Mo = 2.6 to 4.0) Unknown Phase 2 appears together with MoB_2.

The powder X-ray diffraction diagrams of product crystals obtained in the experiments of the first series are presented in Fig. 1. The relative amount of each phase in the product of each experiment is given roughly in terms of the relative X-ray intensity (Fig. 2), which was calculated by measuring the intensities of the representative reflections: I_{011}, MoB_2; I_{150},

TABLE I Preparation conditions of MoB_2

Series	Run No.	Composition of raw material (atomic ratio)*			Temperature (° C)	Time (h)	Phases identified
		Mo	B	Al			
I	1	1	0.3	53.3	1500	10	Unknown 1, MoAlB
	2	1	0.5	53.3	1500	10	MoAlB, Unknown 1
	3	1	0.8	53.3	1500	10	MoAlB
	4	1	1.0	53.3	1500	10	MoAlB
	5	1	1.2	53.3	1500	10	MoAlB
	6	1	1.5	53.3	1500	10	MoAlB, MoB_2
	7	1	2.0	53.3	1500	10	MoB_2, MoAlB
	8	1	2.2	53.3	1500	10	MoB_2, MoAlB
	9	1	2.4	53.3	1500	10	MoB_2
	10	1	2.5	53.3	1500	10	MoB_2
	11	1	2.6	53.3	1500	10	MoB_2, Unknown 2
	12	1	3.0	53.3	1500	10	MoB_2, Unknown 2
	13	1	4.0	53.3	1500	10	MoB_2, Unknown 2
II	14	1	2.5	53.3	1000	10	MoAlB, Unknown 3
	15	1	2.5	53.3	1100	10	MoB_2
	16	1	2.5	53.3	1200	10	MoB_2
	17	1	2.5	53.3	1300	10	MoB_2
	18	1	2.5	53.3	1400	10	MoB_2
	19	1	2.5	53.3	1500	10	MoB_2
III	20	1	2.5	53.3	1500	5	MoB_2
	21	1	2.5	53.3	1500	20	MoB_2
	22	1	2.5	53.3	1500	50	MoB_2
IV	23	1	2.5	17.8	1500	10	MoB_2
	24	1	2.5	35.6	1500	10	MoB_2
	25	1	2.5	53.3	1500	10	MoB_2
	26	1	2.5	71.1	1500	10	MoB_2
	27	1	2.5	88.9	1500	10	MoB_2
	28	1	2.5	106.7	1500	10	MoB_2, MoAlB

*The raw materials for Series I (Run Nos 1 to 13) consist of 2.00 g Mo, 0.06 to 0.90 g B and 30.00 g Al; the raw materials for Series II, III and IV (Run Nos 14 to 28) consist of 2.00 g Mo, 0.56 g B and 10.0 to 60.0 g Al.

MoAlB; $I_{(2\theta=41.7°)}$, Unknown Phase 1; and $I_{(2\theta=26.9°)}$, Unknown Phase 2. Thus, the relative X-ray intensity of the ith phase in a product containing n phases is defined as

$$I_i(\text{rel.}) = I_i \Big/ \sum_{j=1}^{n} I_j$$

From Run No. 1-13 in Table I, the most favourable B/Mo ratio for obtaining MoB_2 is 2.4 or 2.5, at which only MoB_2 single crystals are produced.

In experiments of the second series (Run Nos 14 to 19 in Table I) the maximum temperature at which the sample was maintained is varied in every 100° C interval from 1000 to 1500° C. The results of the powder X-ray analysis of the product samples are presented in Fig. 3 in the same manner as in Fig. 2. The composition of the starting material is fixed at Mo : B : Al = 1 : 2.5 : 53.3, which is acertained to be optimum in the experiments of Series I. At 1000° C MoB_2 does not grow but MoAlB is accompanied by a third unknown phase (Unknown 3), which shows the strongest X-ray intensity at $2\theta = 34.5°$. Between 1100 and 1500° C the product samples contain only MoB_2, which exhibits a larger size as the growth temperature increases. At 1500° C MoB_2 single crystals, as large as about 1.5 mm at least in one direction, are obtained as plate-like crystals with well-developed {0 0 1} faces.

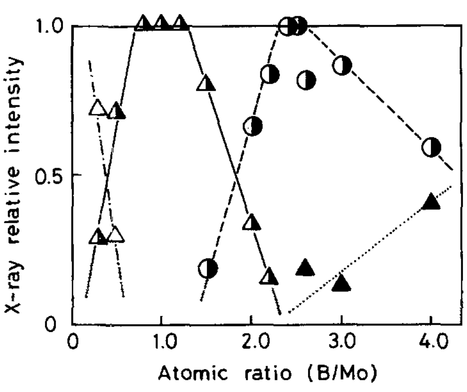

Figure 2 Relative X-ray intensity of each phase in the products whose X-ray patterns are presented in Fig. 1. (◑) MoB_2, (◭) MoAlB, (△) Unknown 1, (▲) Unknown 2.

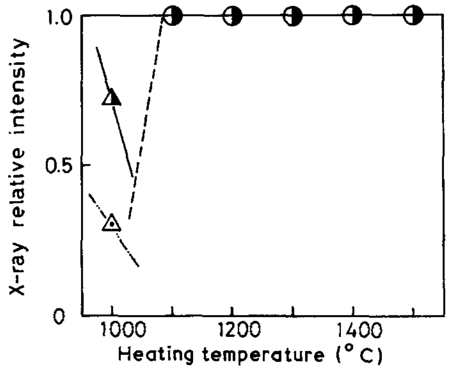

Figure 3 Relative X-ray intensity of each phase in the products obtained by heating the starting materials at various temperatures for 10 h. The composition of the starting materials is fixed at Mo : B : Al = 1 : 2.5 : 53.3 (atomic ratios). (◑) MoB_2, (◭) MoAlB, (△) Unknown 3.

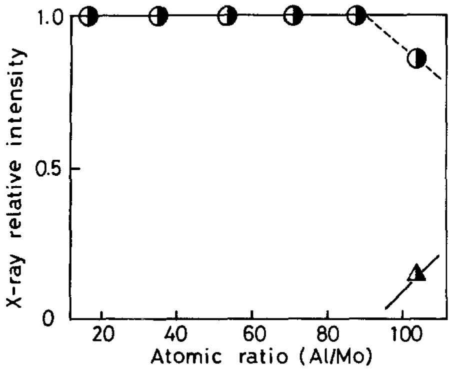

Figure 4 Relative X-ray intensity of each phase in the products obtained from several starting materials with various aluminium contents. The atomic ratio B/Mo is fixed at 2.5. The starting materials are heated at 1500° C for 10 h. (◑) MoB_2, (▲) MoAlB.

The time for which the starting materials was kept at the maximum temperature (1500° C) is not so important (third series; Run Nos 20 to 22 in Table I), because the extension of the time beyond 10 h did not improve the result in obtaining larger crystals. Thus, the optimum temperature was found to be 1500° C with a maintaining time of 10 h.

In experiments of the fourth series (Run Nos 23 to 28 in Table I) the amount of aluminium flux in the starting material is changed. The results of the powder X-ray analysis of the product samples are presented in Fig. 4. At aluminium contents ranging from Al/Mo = 17.8 to 88.9 only MoB_2 crystals were obtained; on the other hand at Al/Mo = 106.7 MoB_2 was obtained accompanied by MoAlB phase. With an increase of the aluminium flux content, the MoB_2 single crystals tend to grow to a larger size. For example, at a lower content of aluminium flux with the atomic ratio of Al/Mo = 17.8 to 35.6 the crystals obtained were very small, having sizes below 0.1 mm, while the crystals grown from starting materials with the atomic ratio Al/Mo > 53.3 showed a larger size, attaining at least 1.5 mm in one dimension. They are mostly obtained as hexagonal plate-like crystals with well-developed {0 0 1} planes. Single crystals having the typical crystal form are shown in Fig. 5.

From the results thus far described, it is concluded that the optimum conditions for growing MoB_2 single crystals by using the aluminium flux technique are with the atomic ratios of the starting materials B/Mo = 2.5 and Al/Mo = 53.3 to 88.9, and the maximum heating temperature 1500° C (10 h).

3.2. Crystal structure

Since a paper on Mo_2B_5 was published [4], the Mo_2B_5-type structure has been acknowledged as being real, and no publication concerning the rhombohedral MoB_2 has thus far been made except for our recent paper [2]. Therefore, we have reinvestigated the structure of the present crystal by single-crystal X-ray diffractometry, and special attention was paid to the structure of the boron network in order to see whether it is the same as the counterpart in the similar compound Mo_2B_5 or not. The specimen chosen for the structure analysis was that grown under the optimum conditions described above; the atomic ratio B/Mo in the starting material was 2.5, which corresponds to the stoichiometry of Mo_2B_5.

TABLE II Crystal data of MoB_2

Formula unit	MoB_2
Crystal system	Rhombohedral
$a_{hex.}$ (nm)	0.30136 (6)
$c_{hex.}$ (nm)	2.0961 (4)
Space group	R$\bar{3}$m
$d_m(cm^{-3})$	7.1
$d_x(cm^{-3})$	7.103
Z(in hexagonal cell)	6

The crystal data are given in Table II and atomic coordinates and temperature factors in Table III. The structure of the present crystal is exactly the same as that of MoB_2 published in our recent paper [2]. The correctness of the structure of MoB_2 in the present work as well as in the previous one [2] is based on a low *R* value, a featureless final difference Fourier map, and normal values of the thermal parameters for all atoms.

Although the structure of MoB_2 has been described in detail in the previous paper [2], a brief description will be given here to facilitate discussion. The arrangement of molybdenum atoms in the crystal is the same as that of Mo_2B_5 [4]. The stacking sequence of the molybdenum layers in the *c* axis direction can be described as AABBCCAABBCC . . . (Fig. 6). The mode of stacking is similar to that of the well-known sequence of layers ABCABC . . . in the ⟨1 1 1⟩ direction of the cubic closest packing structure. There are two kinds of hexagonal boron network, H and K′ (Fig. 6). The H type is an almost planar network and is sandwiched in the molybdenum double layers of AA or BB or CC. Thus the triple layers AHA or BHB or CHC are partial structures of the AlB_2-type structure. Between the sets of triple layers is another type of boron network K′. Unlike the H type, which is an almost planar network, the K′ type is a puckered network: the molybdenum trigonal pyramids, being centred by boron atoms of the K′ type, are pointing alternately upwards and downwards so that the boron atoms necessarily have two different *z* coordinates

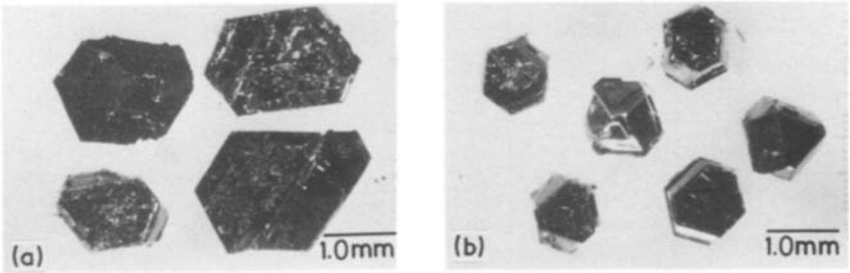

Figure 5 Microphotographs of MoB_2 single crystals with well-developed {0 0 1} planes. (a) Thin plate-like crystals; (b) thick plate-like crystals.

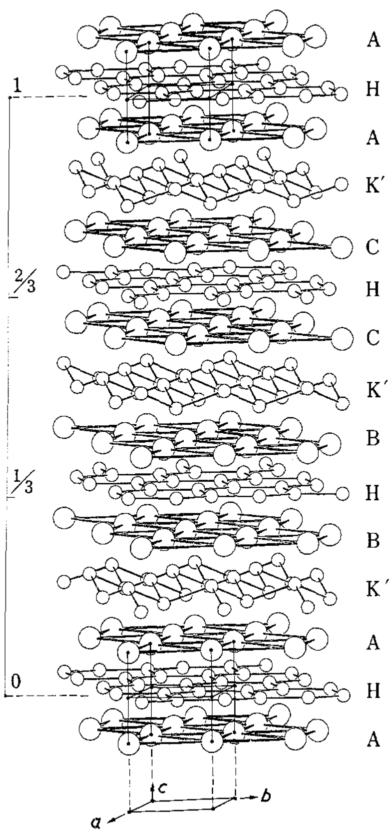

Figure 6 Perspective drawing of the structure of MoB_2.

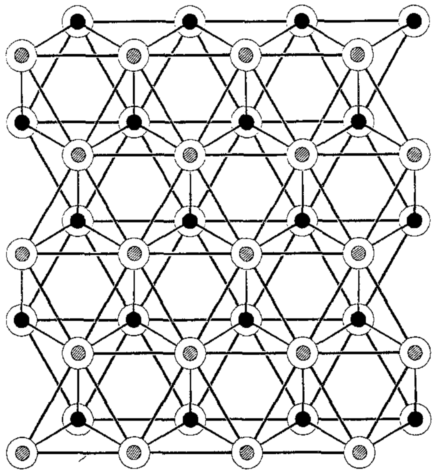

Figure 7 A partial structure (BK′C-layers in Fig. 6) of MoB_2 as seen along the c axis. (○) Mo, $z = \frac{1}{2} \pm 0.0910$ (± 0.1907 nm); (◉) B, $z = \frac{1}{2} + 0.015$ ($+0.031$ nm); (●) B, $z = \frac{1}{2} - 0.015$ (-0.031 nm).

($\Delta z = 0.062$ nm) according to the direction of the apex of the pyramid (Fig. 7). Consequently the full structure of MoB_2 can be described with the stacking sequence AHAK′BHBK′CHCK′AHA . . . Interatomic distances in MoB_2 are given in Table IV.

In the earlier investigation on the Mo_2B_5 [4], the molybdenum arrangement was determined from a powder X-ray diffraction photograph. The positions of the boron atoms were, however, assumed from an approximate chemical composition and space-filling considerations. Thus in the earlier investigation H-type and K-type boron networks as well as an ideal stoichiometry Mo_2B_5 were proposed without experimental evidence; the H-type network is the same as the present one, and the K-type network is that which can be derived by adding boron atoms placed inside the molybdenum trigonal anti-prism (Fig. 7) to the K′ type network; the trigonal anti-prism in the present crystal is confirmed to be empty from a difference synthesis as in the case of our previous crystal [2].

The present work indicates that it is impossible to prepare boride phases containing boron atoms beyond the content corresponding to the stoichiometry MoB_2; even by the use of the starting mixtures which contained an excess amount of boron (B/Mo = 2.5, 3.0, 4.0), crystals having the stoichiometry MoB_n with $n > 2$ are not obtained (Table V). Since the occurrence of the K-type network has never been corroborated experimentally [13], the existence of the Mo_2B_5-type structure is questionable.

A similar feature is reported for the W_2B_5 phase (hexagonal, P6/mmc; $a = 0.2982$ nm, $c = 1.387$ nm) [4] by Lundström [6], who found in this phase the K′ layer instead of the K layer, suggesting that the ideal stoichiometry of this phase should be WB_2. Therefore, we have reinvestigated the stoichiometry of the W_2B_5 phase which had been prepared by the aluminium flux technique [14]. The chemical analysis of the single crystals was made by using the same method as for the MoB_2 crystals in the present work, and no chemical composition with a boron content exceeding that corresponding to stoichiometric WB_2 was found. The results of the chemical analysis are presented in Table V together with those obtained for the MoB_2 crystals. As in the case of MoB_2, even by starting from mixtures containing an excess amount of boron, the crystals obtained always showed compositions with a boron content not exceeding that corresponding to WB_2.

3.3. Properties

3.3.1. *Hardness*

The Vickers microhardness of single crystals of MoB_2

TABLE III Final atomic coordinates (in hexagonal lattice) and temperature factors

Atom	Site	x		y	z		B(nm^2)
Mo	6(c)	0		0	0.07571(1)		*
B(1)†	6(c)	0		0	0.3323(1)		0.0023(1)
B(2)†	6(c)	0		0	0.1819(1)		0.0024(1)
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq} (nm^2)†
Mo	348(8)	(U_{11})	323(6)	($\frac{1}{2}U_{11}$)	0	0	0.0039(1)

*Anisotropic temperature factors. The expression is $\exp[-10^{-5} \times 2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^* + U_{33}l^2c^* + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

†B(1) belongs to the H type network and B(2) the K′ type network.

TABLE IV Interatomic distances in MoB_2 (nm)

Mo–3B(1)	0.2340(1)	Mo–6Mo	0.30136(4)
Mo–3B(1)	0.2370(1)	Mo–1Mo	0.31739(7)
Mo–1B(2)	0.2226(2)	B(1)–3B(1)	0.17404(4)
Mo–3B(2)	0.2355(1)	B(2)–3B(2)	0.1853(1)

measured in the $(0\,0\,1)_{\text{hex.}}$ plane ranged from 2170 to 2470 kg mm^{-2}, in good agreement with the value of 2350 kg mm^{-1} published for Mo_2B_5 [15]. These values are also comparable with the value of 2090 to 2260 kg mm^{-2} measured for the relevant compound WB_2 of which some description is given in the previous section. In Table VI the Vickers microhardness values of MoB_2 and WB_2 are compared with those of refractory metal diborides of the AlB_2-type structure. With the exception of TiB_2, the diborides of the metals which belong to the same group in the periodic table show nearly the same level of microhardness. It is of interest to note that although the structures of MoB_2 (Fig. 1) and WB_2 [5] are partially very different from that of the AlB_2-type, the hardness is approximately the same as that observed for CrB_2.

3.3.2. Oxidation in air

The oxidation of MoB_2 crystals was examined by thermogravimetric (TG) and differential thermal analyses (DTA). The results are shown in Fig. 8, being compared with those of WB_2. The TG curve shows that the reaction began at about 500° C and became prominent as the temperature rose. On the other hand, in the DTA curve there is no exothermic nor endothermic feature. On the whole, the nature of the oxidation of both MoB_2 and WB_2 is, from the shapes of the DTA and TG curves, considered to be the same.

The crystals of MoB_2 were heated for 30 min at every 50° C temperature interval between 400 and 1250° C, and the surface states of the crystals were observed by a scanning electron microscope. As the heating temperature rose, the oxide products on the surfaces of the crystals increased. At temperatures above 1000° C the oxide products melted, so that each crystal was covered with the melt and fused with neighbouring crystals via its melted surface oxide. This phenomenon is consistent with the TG curve at temperatures above 1000° C, where the slope of the curve is less steep than that at about 900° C, because the oxidation reaction may become less prominent even at higher temperature when the crystals are covered with melted oxide product. In the oxidation product obtained at 1250° C, MoO_3 was identified by powder X-ray diffractometry; the oxidation products at temperatures below 1250° C could not be examined because of the low yield.

TABLE V Chemical compositions of MoB_2 single crystals prepared from starting materials with various mixing ratios of molybdenum, boron and aluminium. Data for the relevant compound WB_2 prepared by the same technique are also given

Composition of raw material (atomic ratio)			Temperature (° C)	Time (h)	Composition of MoB_2 or WB_2 phase
Mo or W	B	Al			
1	2	54	1500	10	$MoB_{1.92}$*
1	2.5	53.3	1500	10	$MoB_{1.91}$
1	3.0	53.3	1500	10	$MoB_{2.00}$
1	4.0	53.3	1500	10	$MoB_{1.98}$
1	2.5	102.2	1500	10	$WB_{1.71}$
1	2.7	102.2	1500	10	$WB_{1.85}$
1	3.0	102.2	1500	10	$WB_{1.87}$
1	4.0	102.2	1500	10	$WB_{1.84}$

*The composition is obtained for the crystal published in our previous paper [2].

TABLE VI Comparison of Vickers microhardness* of transition metal diborides†

Compound	H_V (kg mm^{-2})	Reference
TiB_2	2700 to 3900	[16]
ZrB_2	2000 to 2600	[16]
HfB_2	2000 to 2500	[16]
VB_2	2670 to 2930	[17]
NbB_2	2440 to 3000	[18]
TaB_2	2950 to 3080	[18]
CrB_2	2070 to 2290	[19]
MoB_2	2170 to 2470	Present work
WB_2	2090 to 2260	Present work

*The microhardness is measured in the (0 0 1) plane except for VB_2, on which the value seems to be obtained from a polycrystalline specimen.

†All the diborides other than MoB_2 and WB_2 are of the AlB_2-type structure.

4. Conclusions

1. Optimum conditions for the preparation of single crystals of MoB_2 from a high-temperature molten aluminium solution has been established. By using 33 to 53 g of starting mixtures of molybdenum, boron and aluminium, in which atomic ratios are 1 : 2.5 : 53.3 to 88.9, MoB_2 single crystals with maximum dimension of about 1.5 mm were prepared without being accompanied by any other crystal phases.

2. The ideal stoichiometry MoB_2 and the crystal structure of MoB_2-type were corroborated by chemical analysis and single-crystal X-ray diffractometry. One of the two kinds of boron network in the crystal was confirmed to be different from the counterpart of

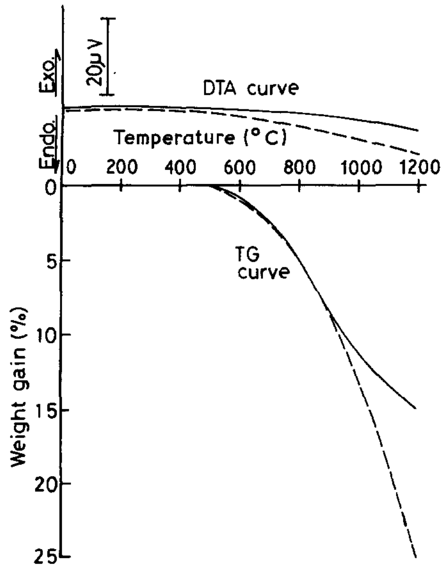

Figure 8 Thermogravimetric and differential thermal analysis of MoB_2 and WB_2. (——) MoB_2, (– – –) WB_2.

the proposed structure of the Mo_2B_5 phase. It was indicated that the existence of Mo_2B_5 is questionable.

3. The Vickers microhardness of single crystals of MoB_2 measured on the (0 0 1) plane was in the range 2170 to 2470 kg mm^{-2}. The oxidation of the crystal in air began at 500° C and became prominent as the temperature rose. At a temperature of about 1000° C, the oxidation products melted and covered the surfaces of the crystals so that the oxidation reaction was somewhat suppressed.

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