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Aluminium-Flux Growth and Properties Measurements of VB, V₅B₆, V₃B₄, V₂B₃ and VB₂ Single Crystals

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Single crystals of VB, V_5B_6 , V_3B_4 , V_2B_3 and VB_2 of size 0.06-3.20 mm were prepared by the high-temperature Al solution method. The orthorhombic VB, V_5B_6 , V_3B_4 , and V_2B_3 crystals grew in the forms of plates or columns or prisms. The hexagonal VB₂ crystals were obtained as thick platelets with well-developed (0001) planes. The Vickers microhardness of as-grown VB, V_3B_4 and V_2B_3 single crystals measured on the (010) planes ranges from 21.9(±0.5) to 23.2(±1.0) GPa, and that on the (0001) planes of as-grown VB₂ is 28.0(±0.13) GPa. The electrical resistivity of VB, V_3B_4 , V_2B_3 and VB_2 single crystals ranges from 0.36×10⁻³ to 212.9×10⁻³ $\Omega \cdot cm$. The oxidation of VB, V_3B_4 , V_2B_3 and VB₂ crystals begins to proceed with a measurable rate in the temperature range 530-570 °C. The final oxidation products were V_2O_5 , V_2O_4 and B_2O_3 .

KEYWORDS: vanadium borides, aluminium-flux, morphology, microhardness, electrical resistivity, oxidation

1. Introduction

Vanadium borides 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 melting points, high electrical and thermal conductivity, high hardness, high mechanical stiffness and wear resistance^{1,2)}. In the vanadium-boron system the intermediate phases V_3B_2 , VB, V_5B_6 , V_3B_4 , V_2B_3 and VB_2 have so far been reported ²⁻⁴). Recently, we have prepared single crystals of VB, V_3B_4 and $VB_2^{(5)}$ or $V_2B_3^{(6)}$ by the high-temperature aluminium solution method. In the present work we present the experimental conditions for the growth of relatively large VB, V_5B_6 , V_3B_4 , V_2B_3 and VB₂ single crystals using the same method. The crystals were examined by X-ray and chemical analyses. Densities, Vickers microhardness and electrical resistivity of the crystals were measured, and oxidation at high temperature in air was studied.

2. Experimental details

2.1. Preparation of vanadium boride crystals

The starting materials were vanadium metal chips (purity, 99.9%), crystalline boron powder (purity, 99.8%) and aluminium metal chips (purity, 99.996%). Mixtures of these materials in various atomic ratios were placed in an alumina crucible and heated in a tantalum-resistance furnace under an argon atmosphere. The amount of vanadium in the starting materials was fixed at 2.00 g throughout all the experiments. The temperature of the furnace was raised at a rate of 300 °C/h, maintained at prescribed temperature (1400 -1700 °C) for 5 h, and then cooled slowly to room tempe-

rature. The crystals grown in the reaction mixtures were separated from the solidified matrix by dissolving the excess metal in the 6 mol/dm³ hydrochloric acid. The average size and morphology of the as-grown crystals were examined by binocular optical microscope and a scanning electron microscope (SEM).

2.2. X-ray analysis

X-ray analysis of crystals was made by using a powder Xray diffractometer with monochromatic CuK α radiation (λ =1.54183 Å) or a Guinier-Hägg camera with strictly monochromatic CrK α 1 radiation (λ =2.289753 Å) and silicon powder (purity, 99.9999%, *a*=5.431065 Å) as an internal standard. The X-ray diffraction films were explored on a scanning microdensitometer (Line Scanner Model LS-18)⁷). Unit cell dimensions were refined with the aid of the local least-squares program CELLKANT.

2.3. Properties

2.3.1. Microhardness

The microhardness of as-grown single crystals was measured by using a Vickers diamond indenter at room temperature in air. A load of 200 g was applied for 15 seconds at 7 to 10 points of each crystal, and the values obtained were averaged.

2.3.2. Electrical resistivity

The electrical resistivity of as-grown VB, V_3B_4 , V_2B_3 and VB₂ single crystals were measured by direct current four probe technique at room temperature in air.

2.3.3. Oxidation in air

Thermogravimetric (TG) analysis and differential thermal analysis (DTA) were performed up to 1200 $^{\circ}$ C to study the oxidation of crystals in air. Specimens of about 25 mg were

heated at a rate of 10° C/min. The oxidation products were analyzed with a powder X-ray diffractometer.

3. Results and discussions

- 3.1. Crystal growth of vanadium borides from molten aluminium solutions
- 3.1.1. Preliminary search for optimum conditions of crystal growth

The experiments were initially performed under constant conditions of the Al/V atomic ratio of 28.32, heating rate of 300 °C/h, soaking temperature 1500 °C, soaking time 5 h and cooling rate of 50 °C/h, with the atomic ratio B/V in the starting materials being varied from 0.50 to 3.00. The results of phase analysis of the reaction products obtained under these initial conditions (Run. No. 1-17) are given in Table 1, together with results of next three series of experiments (Run. No. 18-22, 23-29, 30-33). As seen from the results of initial experiments, five kinds of vanadium borides VB, V₅B₆, V₃B₄, V₂B₃ and VB₂ are formed within the B/V range 0.50-3.00. It is shown that with increase of boron concentration in the starting materials more boronrich phases form as in the cases of the Ta-B⁸), Nb-B⁹) and Cr-B^{10, 11} phases.

3.1.2. Growth conditions of VB crystals

The optimum atomic ratios of the starting materials were B/V=0.70 and A1/V=28.32-37.76. VB single crystals were generally obtained as the needles elongated in the $\langle 100 \rangle$ or $\langle 001 \rangle$ directions (Fig. 1). The crystals show grayish metallic luster.

3.1.3. Growth conditions of V_5B_6 crystals

 V_5B_6 crystals were invariably obtained as a mixture of phases (with VB or V_3B_4). The shape of the V_5B_6 crystals was mostly irregular (Fig. 2). The V_5B_6 crystals are grayish, having metallic luster. The largest V_5B_6 crystals had maximum dimensions of about 0.05 mm \times 0.06 mm \times 0.08 mm.

3.1.4. Growth conditions of V_3B_4 crystals

When mixtures having the atomic ratios B/V=1.20 and Al/V=28.32-47.20 were used, the V_3B_4 phase formed without being accompanied by any other crystalline phases. The optimum atomic ratios of the starting materials were B/V=1.20 and Al/V=28.32 (Run. No. 22). The single crystals of V_3B_4 were columns enclosed with two (010) faces, two small (100) faces and two small (041) faces (Fig. 3), or thin plate-like crystals prepared in the present work attained maximum dimensions of about 0.40 mm×0.50 mm×1.20 mm.

3.1.5. Growth conditions of V_2B_3 crystals

In the first series of experiments, the optimum conditions were found to be those of Run. No. 8. Consequently, further search for the optimum conditions for growth of V_2B_3 was

Table 1. Preparation conditions of VB, V_2B_3 , V_3B_4 , V_5B_6 and VB₂ from molten aluminium solution

Composition of starting material						
Run (atomic ratio) Temp. ⁴ Phases						
<u>No.</u>	1	′ B	AI	(Ċ)	identified	
1	1	0.50	28.32	1500	VB	
2	1	0.70	28.32	1500	VB	
3	1	1.00	28.32	1500	VB, V_3B_4	
4	1	1.10	28.32	1500	V ₃ B ₄ , VB	
5	I	1.20	28.32	1500	V ₃ B ₄	
6	1	1.33	28.32	1500	$V_{3}B_{4}, V_{2}B_{3}$	
7	1	1.40	28.32	1500	$V_{2}B_{3}, V_{3}B_{4}$	
. 8	1	1.45	28.32	1500	$V_2 B_3, V B_2$	
9	1	1.50	28.32	1500	V ₂ B ₃ , VB ₂	
10	1	1.55	28.32	1500	$V_{2}B_{3}$, VB_{2}	
11	1	1.60	28.32	1500	VB_2 , V_2B_1	
12	1	1.70	28.32	1500	VB_2, V_2B_3	
13	1	1.80	28.32	1500	$VB_{2}, V_{2}B_{3}$	
14	1	2.00	28.32	1500	VB ₂	
15	1	2.20	28.32	1500	VB ₂	
16	1	2.50	28.32	1500	VB ₂	
17	i	3.00	28.32	1500	VB ₂	
18	1	1.20	0.94	1500	V_3B_4 , V_5B_6	
19	1	1.20	2.36	1500	$VB, V_{3}B_{4}, V_{5}B_{6}$	
20	1	1.20	4.72	1500	$VB, V_{3}B_{4}, V_{5}B_{6}$	
21	1	1.20	9.44	1500	V_3B_4 , VB, V_5B_6	
22	1	1.20	28.32	1500	V ₃ B ₄	
23	1	1.45	0.94	1500	$VB_2, V_3B_4, VB, V_5B_6, V_2B_3$	
24	I	1.45	2.36	1500	$V_{3}B_{4}, VB_{2}, V_{2}B_{3}$	
25	1	1.45	4.72	1500	$V_{3}B_{4}, VB_{2}, V_{2}B_{3}$	
26	1	1.45	9.44	1500	V_2B_3, V_3B_4, VB_2	
27	1	1.45	14.16	1500	V_2B_3, V_3B_4, VB_2	
28	1	1.45	28.32	1500	V_2B_3, VB_2	
29	I	1.45	47.20	1500	V_2B_3, VB_2	
30	I	1.45	28.32	1400	V_2B_3, VB_2, V_3B_4	
31	1	1.45	28.32	1500	V_2B_3 , VB_2	
32	1	1.45	28.32	1600	V_2B_3, VB_2	
3.5	1	1.45	28.32	1700	$v_2 B_3$, $V B_2$	

^a The time for which the raw material was kept at this temperature was 5 h in all cases.



Fig. 1. Stereomicroscope photographs of VB single crystals.



Fig. 2. SEM photograph of V_5B_6 single crystals.

134 JJAP Series 10

made using the starting materials with the B/V ratio 1.45 and the Al/V ratios being varied from 0.94 to 47.20 (Run. No. 23-29). The V_2B_3 crystals were always obtained together with other phases. Therefore, next series of experiments were carried out to examine the influence of the soaking temperature (from 1400 to 1700 °C) using the starting materials with B/V=1.45 and Al/V=28.32. The size of the V_2B_3 crystals increases with soaking temperature and at 1600 °C the crystals obtained had the maximum dimensions of about 0.20 mm×0.20 mm×0.40 mm. The crystal is characterized by two small faces of each of the crystallographic forms (010), (100), (001) and (061). The crystals are shown in Fig. 4. The V_2B_3 crystals are grayish, showing a metallic luster.



Fig. 3. SEM photograph of V_3B_4 single crystal.



Fig. 4. SEM photograph of V_2B_3 single crystal. 3.1.6. Growth conditions of VB_2 crystals

Considering the results of the first series of experiments, further search for the optimum starting material was made, and the mixture with B/V=2.20 and Al/V=28.32 was found



Fig. 5. SEM photograph of VB_2 single crystals.

to be optimum. The single crystals of VB₂ are obtained as nearly hexagonal polyhedral crystals enclosed with (0001), (1011), (1101), (1010) and (1100) faces (Fig. 5). The maximum size of VB₂ crystals obtained was about 0.10 mm $\times 0.14 \text{ mm} \times 0.14 \text{ mm}.$

3.1.7. X-ray and chemical analyses

The results of X-ray and chemical analyses are listed in Table 2. The cell dimensions of the crystals are in good agreement with previously published data^{4,12)}. The measured densities and chemical compositions are all close to the X-ray densities and stoichiometric compositions, respectively. A small amount of Al impurity from the Al solvent was detected in each of obtained crystal phases. The balances (Table 2) between the total wt% and 100% are ascribable to the incorporation of very fine Al₂O₃ fragments from the alumina crucible. In Table 3, the powder X-ray data of V₅B₆ obtained by Guinier-Hägg method are presented together with calculated *d*-spacings and intensities. The

Table 2. The X-ray and chemical analysis data of VB, V_5B_6 , V_3B_4 , V, B, and VB.

້າວາສ	NI VD ₂				
Formula unit	VB	V ₅ B ₆	V ₃ B ₄	V ₂ B ₃	VB ₂
Crystal system	orth.	orth.	orth.	orth.	hexa.
a (Å)	3.0595(8)	3.063(1)	3.058(1)	3.0595(3)	2.9981(1)
b (Å)	8.0503(12)	21.248(4)	13.224(2)	18.428(3)	-
c (Å)	2.9719(8)	2.979(1)	2.980(1)	2.9836(8)	3.0590(1)
$V(\dot{A}^3)$	73.20(3)	193.88(9)	120.51(2)	168.23(5)	23.81(1)
Space group	Cmcm	Cmmm	Immm	Cmcm	P6/mmm
$dm(g \cdot cm^{-3})$	5.54(5)	-	5.35(4)	5.27(5)	5.03(4)
$dx(g \cdot cm^{-3})$	5.603(2)	5.474(3)	5.402(4)	5.303(2)	5.061(1)
Z	4	2	2	4	1
B (wt%)	15.4	-	21.7	23.4	28.0
V (wi%)	72.5	-	75.3	74.1	68.9
AI (wi%)	1.4	-	0.28	0.43	0.79
Total (wt%) ^a	89.3	-	97.28	97.93	97.69
Chemical composition	VB _{1.00}	-	$V_{3}B_{4.07}$	V ₂ B _{2.98}	VB _{1.92}
			Contraction of the second s	THE OWNER WATCHING TO THE OWNER WATCHING TOW	

^a The balance between the total wt% and 100% was ascribed to the incorporation of very fine Al₂O₃ fragments from the crucible.

Table 3. Powder X-ray diffraction data of V_5B_6

		and the second se	and the second se	the second s
hkl	dcalc(Å)	dobs(Å)	Icalc	lobs
020	10.625	-	0.2	-
040	5.313	-	0.4	-
060	3.542	3.545	1.6	1.8
100	3.058	3.064	1.3	1.8
011	2.945	-	0.1	-
120	2.939	2.944	22.8	29.7
031	2.742	-	0.4	-
080	2.656	-	1.0	-
140	2.650	2.653	4.8	6.7
051	2.437	2.439	68.4	62.2
160	2.315	-	1.6	-
(0 10 0)				
\071/	2.125	2.125	23.2	27.6
1 1 1	2.121	-	8.7	-
131	2.042	2.043	100.0	100.0
180	2.005	2.006	68.2	84.4
151	1.906	1.908	4.9	5.2
091	1.849	-	2.8	-
0120	1.771	1.771	2.2	4.9
(1 10 0)				
(171)	1.745	1.747	20.9	15.8

JJAP Series 10

observed data are in excellent agreement with the calculated data.

3.2. Properties

3.2.1. Microhardness

The Vickers microhardness of as-grown VB, V_3B_4 and V_2B_3 crystals were measured on the (010) planes, and the values ranging from $21.9(\pm 0.5)$ to $23.2(\pm 1.0)$ GPa were obtained. The microhardness value on the (0001) planes of VB₂ crystals was found to be Hv= $28.0(\pm 0.13)$ GPa, in good agreement with the value $27.5(\pm 0.1)$ GPa published in the literature²). All the microhardness data are given in Table 4.

3.2.2. Electrical resistivity

The electrical resistivity of as-grown VB, V_3B_4 and V_2B_3 crystals were measured on the (010) planes, and that of VB₂ crystals measured on the (0001) planes. The obtained data are listed in Table 5, together with previously published data¹³).

Table 4.	Vickers	microhardnes	s a	of	VB,	V_2B_3
						~ ~ ~

V_3B_4 and	l VB ₂ sing	gle crystals	
Inc	dentation	Microhardness	
Compound	plane	Hv (GPa)	
VB	(010)	22.8 (±0.5)	
V ₅ B ₆	-	-	
V ₃ B ₄	(010)	21.9 (±0.5)	
V_2B_3	(010)	23.2 (±1.0)	
VB ₂	(0001)	28.0 (±0.13)	
Data of reference	e^{2} : V ₃ B ₄	23.0 GPa; VB ₂ , 27	.5

(±0.1) GPa

6

Table 5. Electrical r	esistivity a of VB, V ₂ B ₃ ,
V_3B_4 and	VB ₂ single crystals
Compound	Electrical resistivity
	(room temp.)
	$\rho (\Omega \cdot cm)$
VB	0.36×10^{-3}
V ₅ B ₆	-
V ₃ B ₄	14.6×10^{-3}
V ₂ B ₃	212.9×10^{-3}
VB ₂	22.70×10^{-3}
a Data of reference	¹³⁾ : VB, $35 \times 10^{-3} \Omega$ · cm
(20 ℃) VB ₂ , 38>	<10 ⁻³ Ω · cm (20 ℃); 70.8×
$10^{-3} \Omega \cdot cm (102)$	27 ℃)

3.2.3. Oxidation in air

The oxidation reaction of the crystals in air has been traced by DTA and TG (Fig. 6). The TG curves show that the reaction began at about 530 °C for VB₂, and at about 570 °C for VB, V₃B₄ and V₂B₃. On the other hand, a large exothermic peak of the DTA curve was found at 630-640 °C for VB, V₃B₄ and V₂B₃, and about 610 °C for VB₂. The crystals were heated for 30 min at 1200 °C, and in each case the oxidation products identified were V₂O₅, V₂O₄ and B₂O₃ phases.



Fig. 6. DTA and TG curves of the oxidation of $VB_1V_3B_4$, V_2B_3 and VB_2 in air.

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