JOURNAL OF SOLID STATE CHEMISTRY **133,** 113–116 (1997)
ARTICLE NO. SC977325

Microhardness of Czochralski-Grown Single Crystals of VB_2

C. Bulfon,* A. Leithe-Jasper,† H. Sassik,* and P. Rogl†

*Institut für Experimentalphysik, TU Wien, Wiedner Hauptstraße 8-10, A-1040 Wien, Austria; and †Institut für Physikalische Chemie, Universität Wien, Währingerstraße 42, A-1090 Wien, Austria

Received January 16, 1997; accepted February 6, 1997

Single crystals of congruent melting hexagonal VB_2 were grown using a triarc furnace applying the Czochralski technique. Orientation dependent microhardness measurements on a single crystal reveal quasi similar hardness in the crystallographic directions $\langle 00.1 \rangle$ and $\langle 10.0 \rangle$, whereas the $\langle 10.1 \rangle$ shows slightly lower values.

1. INTRODUCTION

The transition metal borides are promising candidates in hard materials applications due to their high hardness, high melting point, good electrical and thermal conductivity, and wear resistance and oxidation resistance. Optimization of the mechanical behavior in these ceramics essentially depends on a profound knowledge of the elastic properties of the single phase components. Whereas for TiB_2 specific details have been established, analogous data for the corresponding diboride VB_2 hitherto are scarce. Thus, the present paper is devoted to the production of sizeable single crystals of VB_2 for microhardness measurements as a function of crystallographic orientation.

2. EXPERIMENTAL

2.1. Sample Preparation

Master alloys of VB_2 (hexagonal AlB_2 type, space group P6/mmm; see Fig. 1) with a total weight of 10 g were synthesized by arc melting V ingots (99.99 wt.%) and B powder (99.8 wt.%, crystalline powder < 60 mesh, Ventron GmbH, Germany) which was compacted into pellets without using any lubricants. For the crystal growth experiments specimens of about 3–5 g with the nominal composition of 30 at.% V and 70 at.% B were melted in a modified triarc furnace. The melting or crystal growth process was carried out under a slight overpressure of titanium gettered Ar employing a CENTORR Series 3 crystal puller. Details of the experimental setup are given in a previous publication (1).

2.2. Crystal Growth

Alloys with a weight of about 4 g were completely melted at a current of 160 amperes. A tungsten electrode figured as a seed crystal. The VB_2 compound allows a high pulling speed of about 30 mm/h. By varying the current—thus controlling the temperature of the molten alloy button —a "neck" could be produced in order to favor a single growth front. After having reached a diameter of about 2–3 mm the crystal growth proceeded constantly for about 10 mm (single crystal part of the grown specimen). Due to severe evaporation during the triarc melting a premature ending of the experiment was enforced. The crystal was then cut perpendicular to the growth direction in several slices which were subject of extensive metallographic investigations in order to prove single crystallinity. Laue backscatter technique (Mo radiation) was employed to determine the orientation and quality of the crystals. A piece cut from a single crystal is shown in Fig. 2.

2.3. Microhardness

Throughout all the crystal growth experiments a first cut perpendicular to the direction of growth established the crystallographic $\langle 10.1 \rangle$-axis as the direction of crystal growth, although sometimes the crystals happened to grow inclined up to 15° from this axis. A small piece of this single crystal was powdered in a Co bonded WC mortar and subject to powder X ray analysis employing Guinier Huber diffraction technique ($CuK\alpha_1$; $\lambda = 0.154056$ nm; internal standard, $a_{Ge} = 0.565791$ nm). The refined lattice paremeters of the single crystal subject to all microhardness measurements are $a = 0.29997(1)$ nm and $c = 0.30604(1)$ nm. For hardness measurements on the various crystal faces the specimens were mounted in STRUERS Epofix resin and were cut with a STRUERS Accutom diamond wheel. A microhardness tester MHT-4 equipped with a Vickers diamond tip was used in connection with an optical Reichert Polyvar Met microscope. The hardness data were obtained in a load range between 5 and 65 *p*. All indentations have been formed with constant load increase and

0022-4596/97 $25.00

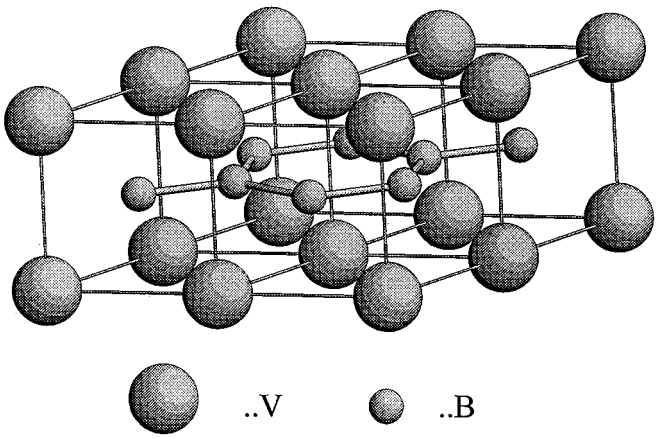

FIG. 1. The crystal structure of VB_2 (AlB_2 type of structure, space group P6/mmm).

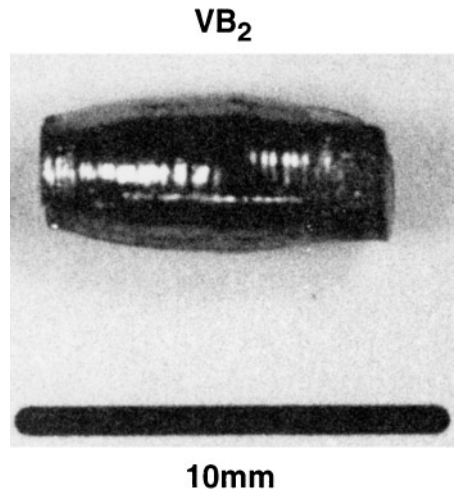

FIG. 2. VB_2 single crystal.

dwell time (5 *p*/s; 5 s). The microscopic image was transferred via a dual reflex module to a video screen. The indentation diameter was then measured by movable bars generated by a digital eyepiece. The bar distance is read into the control and evaluation unit of the tester. In connection with the testing parameters, the hardness value is calculated and displayed in HV. Each indentation was measured three times in order to improve reliability. For each load five indentations were made, except for 20 *p*, where 25 indentations were performed, as these are the data with the best statistics.

3. RESULTS AND DISCUSSION

The results of the microhardness measurements are summarized in Table 1 and Fig. 3. Indentations in {00.1} sometimes showed cracks from the edges starting at a load of about 25 *p* and in {10.1} at a load of about 35 *p*. In the {10.0} crystallographic face measurements up to a load of 65 *p* could be achieved without the appearance of cracks. In Figs. 4a and 4b indentations on the {10.0} and {10.1}

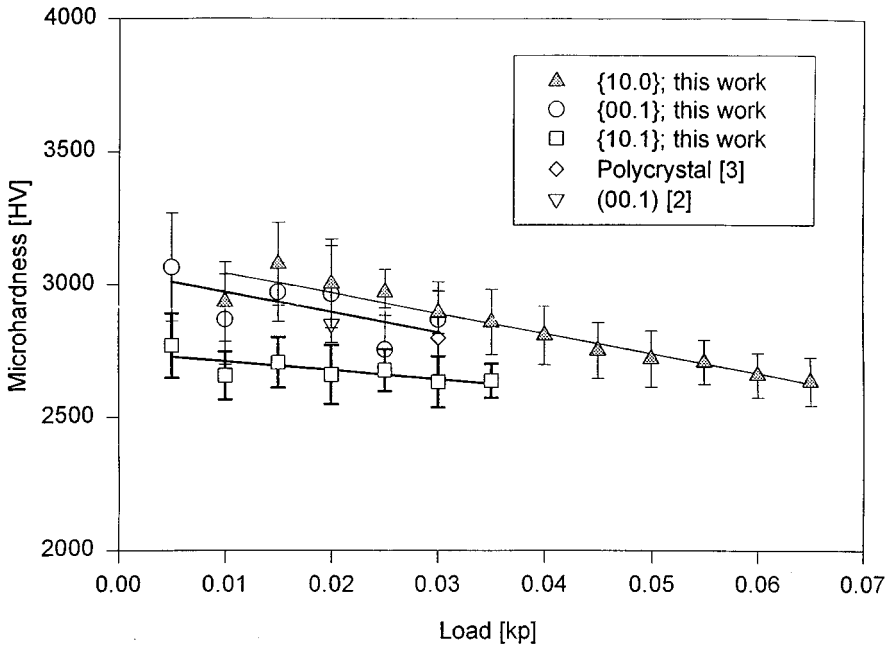

FIG. 3. Microhardness of VB_2 for various crystallographic faces.

TABLE 1
Vickers Hardness of VB_2 for Various Crystallographic Faces and Comparison with Data from Literature

Orientation	HV 0.02	HV 0.02 (2)	HV 0.03 (3)
Polycrystal			2800 ± 13
{10.0}	3000 ± 170		
{00.1}	2960 ± 180	2850 ± 13	
{10.1}	2660 ± 100		

Note. E.g., 3000 HV 0.02 stands for 3000 kp/mm^2 (= 30.6 GPa; conversion factor 98.1) measured at a load of 0.02 kp (1 kp = 9.81 *N*).

crystallographic faces for various loads (starting at the top with 10 to 100 *p* in steps of 10 *p*, read from right to left) are shown. Comparison of the two pictures reveals a significant difference in the brittleness of the two crystallographic faces. As can be seen out of Table 1 and Fig. 3 the microhardness measurements in the {10.0} direction show slightly higher values than the other directions which seems convincing considering the strong B–B bonds in the basal plane of the AlB_2 structure.

Data in literature are available only for the (00.1)-orientation (2) and with a value of 2850 HV 0.02 measured on

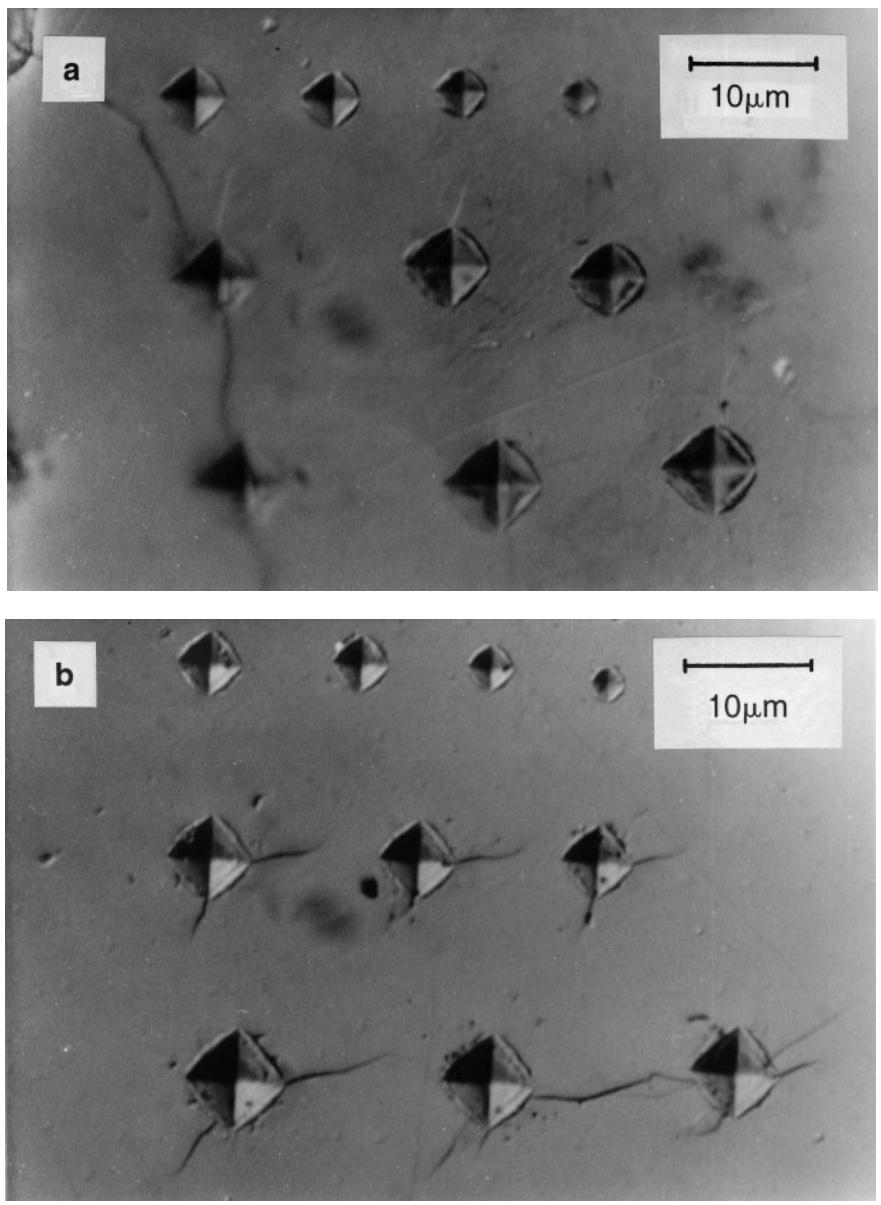

FIG. 4. (a) Indentations on the {10.0} crystallographic face for various loads (10–100 *p*) (b) Indentations on the {10.1} crystallographic face for various loads (10–100 *p*).

relatively small Al-flux grown crystals ($0.1 \times 0.14 \times 0.14$ mm); they are in good agreement with the present data set (see Table 1). Comparison with results obtained from supposedly polycrystalline material (3) is convincing as well.

ACKNOWLEDGMENTS

This research has been sponsored by the Austrian FFWF under Grant S5605. Thanks are due to Dr. H. Bangert for kind assistance in the microhardness measurements, Ings. S. Mielniczek, and P. Hundegger in metallography and FI. M. Gitschthaler for photodocumentary work.

REFERENCES

1. C. Bulfon, A. Leithe-Jasper, H. Sassik, and P. Rogl, "Thermal Expansion and Hardness of Czochralski Grown Single Crystals of W_2B_{5-x} (WB_2)," Proceedings, Werkstoffwoche '96, Stuttgart, Germany 1996. [to be published in Keramische Berichte, 1997]
2. S. Okada, K. Kudou, I. Higashi, and T. Lundström, "Aluminium-Flux Growth and Properties Measurements of VB, V_5B_6, V_3B_4 and VB_2 Single Crystals," Proceedings, 11th International Symposium on Boron, Borides and Related Compounds, Tsukuba, Japan, 1993. *Jpn. J. Appl. Phys. Series* **10** 132–135 (1994).
3. G. V. Samsonov and I. M. Vinitskii, "Handbook of Refractory Compounds," Chap. 5, p. 293. IFI/Plenum, New York, 1980.