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Letter to the Editor

High-temperature hardness of ReB_2 single crystals

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ABSTRACT

Vickers micro-hardness was measured on the (0 0 0 1) and (1 0 - 1 0) planes of ReB_2 single crystals. By increasing the temperature from 20 to 1000 °C, the hardness decreased from 30.8 to 19.8 GPa and from 35.8 to 14.3 GPa, respectively. ReB_2 was found to have the highest hardness among refractory borides, but exhibited deliquescence.

1. Introduction

Hardness measurement is a simple method of examining mechanical properties. We have used hardness, especially high-temperature hardness, to estimate the quality of refractory crystals prepared by the floating zone method [1–3]. ReB_2, one of refractory borides, was recently reported to have high hardness, 48 GPa under a load of 0.49 N, and to leave scratch marks on a diamond surface, as well as to have possible applications in cutting because it was synthesized under ambient pressure without using a high-pressure technique [4]. However, Dubrovinskaia et al. [5] commented that the hardness should be 30 GPa in a range of no load dependence and that it was not high enough to scratch a diamond surface. In response to the comment, AFM (Atomic Force Microscopy) data were presented to show that ReB_2 scratched diamond, making a groove 2.4 μm wide and 0.23 μm deep [6]. It is not yet clear how the diamond was scratched. The ReB_2 samples were polycrystalline and the orientation was not clearly identified. In this report, using single crystals, the hardness was examined and compared with other refractory crystals.

2. Experimental procedure

ReB_2 was synthesized from rhenium and amorphous boron powders by means of self-propagation high-temperature reaction (SHS reaction) [7]. The product was ground into powder using a silicon nitride mortar and pestle. The powder was mixed with a small amount of polyvinylbutyral ethanol solution as binder, and then isostatically pressed in a rubber bag at 200 MPa. The pressed rod was sintered in vacuum at 1800 °C. Single crystals of ReB_2 were prepared in 0.5 MPa of ambient argon gas by the floating zone method [7]. The crystal orientation was examined by X-ray using the Laue back-reflection method. The crystals were cut into rectangular blocks, 5 mm × 5 mm × 10 mm, so that the large planes would be the (0 0 0 1) and (1 0 - 1 0) planes of the hexagonal lattice. The planes were mirror-like polished using 2 μm diamond paste, after coarsely grinding the crystal planes with B_4C abrasive.

Hardness measurement was carried out from 20 °C, room temperature, to 1000 °C in a vacuum <10^{-3} Pa, using a micro-hardness tester (QM-12, Nikon Ltd.) and a diamond Vickers indenter. The load was 0.98 N (100 g) and 1.96 N (200 g) for 10 s. Hardness was obtained from the average value of more than ten measurements because of experimental errors due to the small indentation.

3. Results and discussion

Rhenium diboride, ReB_2, which congruently melts at 2400 °C [8], was easily synthesized as a single phase by controlling the mixing ratio of Re and B, as speculated from the ease of synthesis of borides, such as LaB_6 and YB_4, which congruently melt. Single crystals 1 cm in diameter were prepared from feed rods with a little excess boron, 67–68 at% of B, using the floating zone method [7].

The hardness of the (0 0 0 1) plane of ReB_2 crystal was 29.8(±2.4) and 30.8(±1.5) GPa under a load of 0.98 and 1.96 N, respectively, at room temperature. The values are within experimental error, ±6%. Accordingly, the load was determined to be 1.96 N. The measured hardness on the (0 0 0 1) and (1 0 - 1 0) planes was 30.8(±1.5) and 35.8(±1.0) GPa at room temperature, respectively, as shown in Fig. 1. The reported hardness at 48 GPa under a load of 0.49 N decreased to 30–34 GPa under a load higher than 1.96 N [4], which is consistent with our data reported above. Therefore, ReB_2 was found to have high hardness among the borides, as shown in Table 1, but not as high as superhard materials such as c-BN at ∼72 GPa and B_6O at ∼59 GPa.

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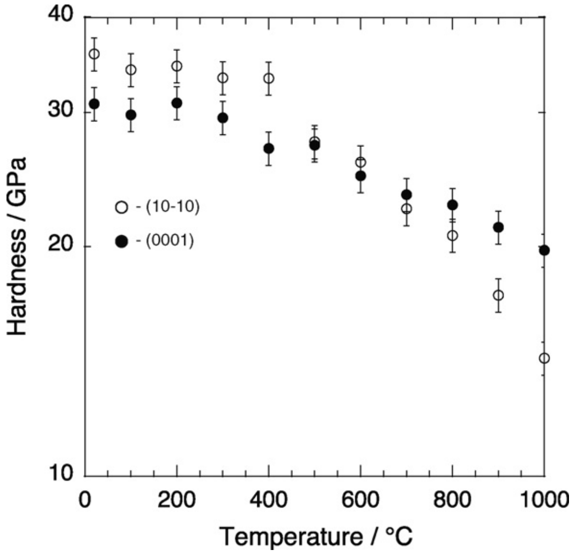

Fig. 1. Vickers micro-hardness of ReB_2 crystal.

Table 1
Vickers micro-hardness of some refractory borides and carbides as measured on single crystals [2,9].

	m.p. (°C)	Hardness (GPa)			
		20 °C		1000 °C	
		(0 0 0 1)	(1 0 - 1 0)	(0 0 0 1)	(1 0 - 1 0)
ReB_2	(2400)	30.8	35.8	19.8	14.3
WB_2	(2365)	20.4	19.4	9.3	13.3
TaB_2	(3037)	29.2	22.2	14.2	11.9
HfB_2	(3380)	17.8	24.5	16.4	8.8
ZrB_2	(3220)	22.2	19.5	7.8	5.5
YB_4	(2800)	13.2^{+}	17.1^{++}	9.6^{+}	11.9^{++}
LaB_6	(2715)	18.9*	–	8.4*	
TiC	(3067)	25.7*	–	2.5*	

$^{+}$, $^{++}$: On the (0 0 1) and (1 0 0) planes of the tetragonal lattice, respectively.
*: On the (1 0 0) plane of the cubic lattice.

In the process of finishing mirror-like planes for the hardness measurement, the (0 0 0 1) plane was not easily ground by the green silicon carbide, ∼28 GPa, but was easily ground by the B_4C abrasive, ∼33 GPa. Accordingly, the hardness of ReB_2 was between these two values, corresponding well with the above hardness data. The finish of the mirror-like planes was achieved by polishing with a cloth using 2 μm diamond paste.

The mirror-like (0 0 0 1) and (1 0 - 1 0) planes of the ReB_2 crystals were easily scratched with the tip of the diamond indenter by hand, which was easily determined since the hardness was measured with a diamond indenter. However, the diamond plane, one of four side-planes of the tip of the diamond indenter, could not be scratched by the edge of the (0 0 0 1) and (1 0 - 1 0) planes of the ReB_2 crystal. The ReB_2 crystal merely slipped on the diamond surface while being pushed. Although ReB_2 was reported to scratch the diamond plane [4], this was not reproduced in our experiments.

Fig. 1 also shows the dependence of hardness on the temperature. Relatively high hardness was maintained during the process of raising the temperature: 19.8(±1.4) and 14.3(±0.6) GPa on the (0 0 0 1) and (1 0 - 1 0) planes, respectively, at 1000 °C. High-quality refractory crystals without subgrain boundaries are generally grown by the floating zone method, in cases where the hardness is higher than 5 GPa at 40% of the melting point [2], ∼800 °C in the case of ReB_2. This empirical rule was found to apply to the crystal growth of ReB_2, too [7]. Table 1 shows a comparison of hardness with other refractory materials at 1000 °C [2,9]. ReB_2 was found to have the highest hardness even at 1000 °C, although the 2400 °C melting point of ReB_2 is not high among refractory borides.

In summary, ReB_2 was found to be one of the hardest borides, but not as hard as superhard materials such as c-BN and B_6O. A severe problem exhibited by ReB_2 is deliquescence, that is, it absorbs water in the air and becomes covered with a viscous solution within a few months. In addition, rhenium is an expensive element. Therefore, it is not easy to use ReB_2 as a material for cutting tools.

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