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Borides of the transition metals have been the subject of several recent research studies (refs. 1 to 5) primarily because of their high melting temperatures and relatively good oxidation resistance. The experiments reported herein were conducted to determine the hardness of several borides at as high temperatures as possible with the available equipment (1625° C).

The tested materials, which were obtained from commercial sources, are listed in table I. For the zone melted borides, a plane perpendicular to the rod axis was metallographically prepared for hardness measurements. Hardness tests were conducted at room temperature using a standard microhardness tester with the Vickers (136° apex square-base pyramid) diamond indenter and a load of 50 grams. Hot hardness was measured at 1625° C on a commercial tester in a vacuum of 5×10^{-5} millimeter of mercury with a polycrystalline boron carbide indenter. Hot pressed boron carbide of 98 to 99 percent theoretical density, ground and lapped to the Vickers configuration was employed after indenters of sapphire and 90 percent theoretical-density polycrystalline titanium diboride were found to be too soft and too fragile, respectively, at 1625° C. The boron carbide indenters produced distinct hardness impressions and suffered no observable deformation or cracking. A 2500-gram load and

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a dwell time of 15 seconds were used for the hot-hardness tests. The indentations made at 1625° C were measured at room temperature on standard equipment.

The hardness values obtained are recorded in table I and plotted in figure 1. The room-temperature values are the results of ten impressions on each material. With the exception of the fine-grain-size holmium tetraboride (HoB_4), no impressions made at room temperature encountered grain boundaries or second-phase particles. Lanthanum hexaboride (LaB_6), with a hardness of 2520 kilograms-per-square-millimeter, was the hardest material tested at room temperature. The remaining four borides were significantly softer with hardnesses in the 2140 to 2230 kilograms-per-square-millimeter range. Literature hardness values for zone-melted zirconium diboride (ZrB_2) and niobium diboride (NbB_2)(ref. 6) compare well with the values measured here in the 2130 to 2280 kilograms-per-square-millimeter hardness range. However, two considerably different hardness values for hafnium diboride (HfB_2) determined on different testers (ref. 7), are significantly higher than the value measured here (see fig. 1).

Because of the small sample diameter ($\approx$ 1/4-in.-diam by 0.150-in.-thick) and the operating characteristics of the hot hardness tester, only one impression was possible on each material at 1625° C. While more impressions would have been desirable, those obtained here are believed to be reliable and to give a comparison of materials because of the use of the relatively high loading force. This high loading force minimizes the total reading error for measuring the diagonals of the impression and essentially eliminates any elastic recovery effect (refs. 8 and 9).

The impressions made at 1625° C on ZrB_2 and LaB_6 did not encounter any grain boundaries or second-phase particles. Similar impressions for HfB_2 and NbB_2 did encounter some particles of the second phase. For HfB_2, ZrB_2, and NbB_2, the single grain penetrated in the hot hardness test was large enough to allow Laue back-reflection X-ray patterns to be obtained. These showed the polished plane to be very close to $\{11\bar{2}0\}$ for all cases.

As shown in figure 1, HfB_2 exhibited a significantly higher hardness at 1625° C than did the other borides, while HoB_4 was by far the softest. Also plotted in figure 1 are the reported hardnesses of zone-melted ZrB_2 and HfB_2 on $\{10\bar{1}0\}$ planes determined with diamond indenters at temperatures up to 1000° C (ref. 7). Extrapolations of these plots to the 1625° C hardness values were made disregarding the unexplained anomalous hardness values of reference 7 above 760° C. While the extrapolations appear reasonable, they must be viewed in the light of some qualifications. The hardness values of reference 7 were obtained on $\{10\bar{1}0\}$ planes with loads of 160 to 190 grams while the hardness values reported here are for $\{11\bar{2}0\}$ planes with a load of 2500 grams. However, reference 7 has demonstrated that, for these borides, loads above 500 grams have no effect on the measured hardness values at room temperature, and that, in the case of ZrB_2 only a 10 percent measured-hardness decrease was noted by increasing the load from 160 to 500 grams. No such study has been conducted at elevated temperatures. The reference 7 hardness values were obtained with diamond indenters, which are reported to undergo graphitization in vacuum above 900° C (ref. 8) and to react with boron above 900° C (ref. 10). Whether either or both of these reactions occurred is not known, but their occurrence might explain the anomalous results for temperatures above 760° C as reported in reference 7. However, such anomalies were not observed for polycrystalline ZrB_2 and HfB_2 in reference 7.

In the HfB_2, ZrB_2 and NbB_2 samples, some slip lines were noted near the hot-hardness impressions. In all cases, these traces were parallel to the [0001] direction which suggests that the active slip plane is a plane of the [0001] zone, that is, a plane of the type {hki0}.

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TABLE I. - MATERIALS TESTED AND HARDNESS VALUES

Boride and crystal structures	Fabrication technique	Measured density, gm/cc	Theoretical density,(1) percent	Grain size	Metallography	Hardness-Kg/sq mm		
						Room temperature		1625° C
						50 gram load	Standard deviation	2500-gram load
Hafnium diboride, hexagonal	Induction zone-melted	10.87	97.1	≈1/8 in.	Lamellar HfB second phase	2230	200	569
Zirconium diboride, hexagonal	↓	6.18	99.7	≈1/8 in.	Lamellar ZrB second phase	2170	130	312
Niobium diboride, hexagonal	↓	6.87	95.3	≈5/16 in.	Random unidentified second phase	2140	120	302
Lanthanum hexaboride cubic	↓	4.72	99.4	0.025 in.	Single phase	2520	220	371
Holmium tetraboride, tetragonal	Hot pressed	6.42	94.7	11 μ	Random unidentified second phase	2220	220	155

(1) Based upon X-ray densities. No account taken of second phases present.

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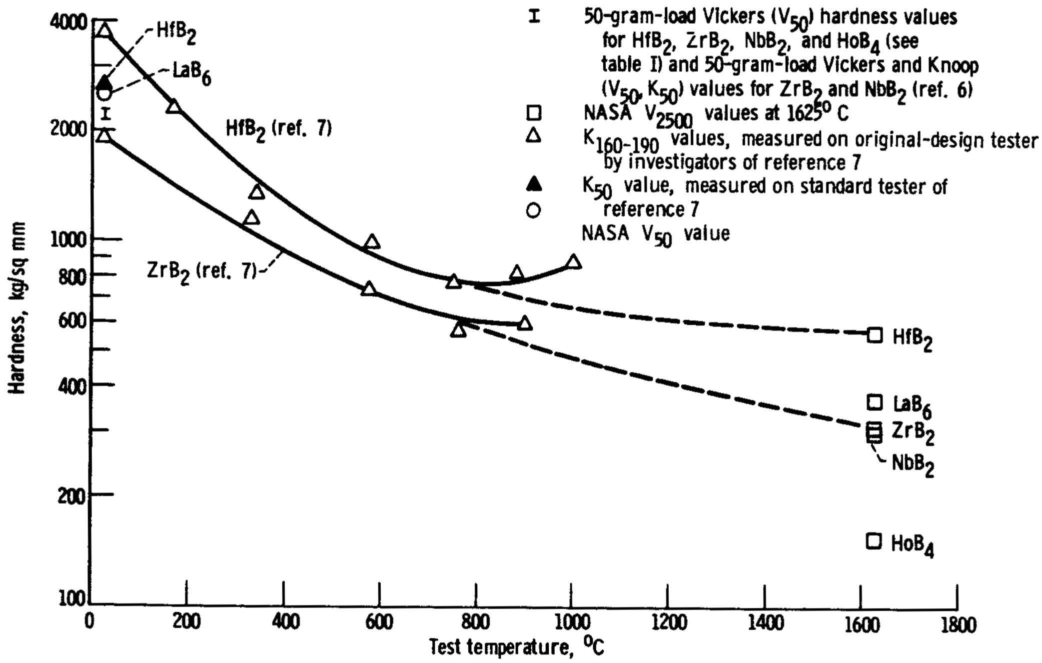

Figure 1. - Hardness of borides as function of temperature.