EFFECTS OF WATER DESORPTION ON INDENTATION MICROHARDNESS ANISOTROPY IN MINERALS

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Abstract

Water adsorption from ambient air is shown to affect significantly the relative values of the indentation microhardness as measured on different crystal planes of various minerals. Specific types of minerals studied include oxides, silicates, sulfides, fluorides, carbides, and carbonates.

Frequent use is made of the indentation microhardness technique to assess the mechanical anisotropy of refractory compounds. Based upon the well established correlations between hardness data and macro-mechanical properties, the indentation technique affords the opportunity of obtaining reliable data on very brittle materials, on very tiny crystals and in a minimum time. The first explicit studies of anisotropy with the indentation technique were measurements on aluminum crystals by O'Neill in 1923. Since then many authors have explored anisotropic effects in a wide variety of materials using indenters of Vickers, Knoop, cone and double cone geometries. Summaries of these findings have been published in monographs by Tertsch (1949) and Mott (1956).

The discovery by Jorgensen and Westbrook (1964) that the microhardness of synthetic corundum was significantly lowered by water adsorbed from the air led them also to demonstrate (1965) that such softening was commonly experienced by a wide variety of nonmetallic materials (although not by metallic substances). They further showed (1965) that adsorbed water was the causative agent for the unusual time dependence of microhardness, so-called "anomalous indentation creep", previously observed in nonmetallic materials by Mitsche and Onitsch (1948) and by Walker and Demer (1964). The attribution of microhardness anisotropies in nonmetallic crystals to intrinsic structural factors is thus brought into question. That is, to what degree do the observed differences in microhardness instead reflect differences in water adsorption or the mechanical response to water adsorption? In the particular case of the antipodal faces of non-centrosymmetric compounds, Westbrook and Hanneman (1965) found that the commonly reported hardness differences between these faces were eliminated, in all cases examined, by the removal of adsorbed water, *i.e.*, no intrinsic mechanical difference existed. All of these effects of adsorbed water have

been summarized in somewhat more detail in a review paper by West-brook (1967).

Previous work in this laboratory by Jorgensen and Westbrook has demonstrated that other common vapor species in the air are not responsible for the softening effects observed following air exposure of desorbed crystals. In these experiments, dried oxygen, nitrogen and hydrogen were each bubbled individually over the surfaces of specimens which had been thermally desorbed, quenched into anhydrous toluene, and kept immersed in that medium during test. None of these gases brought about any hardness change relative to the "dry" values obtained in toluene. However, interposition of a water bubbler between the dried gas source and the toluene bath caused a rapid decrease in hardness, independent of the nature of the carrier gas. Quenching baths of other common reagents, less polar than water, including carbon tetrachloride, ethyl alcohol, methyl alcohol, and mineral oil also gave results corresponding to the "dry" condition *when in scrupulously anhydrous form.* These reagents, however, were easily contaminated with water by short air exposure and were then found to soften various specimens which had previously been desorbed.

Adsorption induced softening has been shown to be related to the effects of environment on dislocation mobility as revealed by etching up the dislocation rosettes produced by indenting in different media, West-brook (1967), Hanneman and Westbrook (1968), Westwood (1962; 1967; 1968). This procedure has been used to assess the activity of environments. Among the active media which have been found in addition to water are various aqueous solutions containing highly charged ions (either $+$ or $-$) and highly polar non-aqueous substances, *e.g.*, ammonia, dimethyl formamide (DMF), dimethyl-sulfoxide (DMSO), nitrobenzene, chlorobenzene, etc. Certain of these media have been found to be several times as efficacious as water in promoting near-surface dislocation mobility in crystals of non-metals and instances have even been found of impairment of dislocation mobility.

Because of the ubiquitous presence of water in ordinary atmospheres, it is this adsorbate which will ordinarily confound microhardness measurements. The purpose of the present investigation was therefore simply to examine the extent to which water adsorption affects the apparent anisotropy of micro-indentation hardness in a variety of minerals.

<h2 style="text-align:center">PROCEDURES</h2>

The materials tested were large single crystals of either synthetic or natural origin. The corundum, bromelite, periclase, rutile and alpha silicon carbide were synthetic and all others were natural. The natural faces of well developed euhedral crystals were tested

when possible. Other test faces were developed by diamond cutting and polishing (0.5 μ abrasive). Orientation was determined by habit, cleavage, or Laue X-ray diffraction.

Hardness measurements were made with a Vickers diamond indenter in a Kentron microhardness tester using a 50-g load (except in the case of calcite (25 g) and galena (10 g) and a 15-second loading time. The load was chosen so as to make indentations shallow enough to reveal adsorption effects, Westbrook and Jorgensen (1965), but large enough to permit accurate measurements and not so large as to lead to cracking. No attempt was made to align the indenter axes relative to crystallographic direction within the crystal face tested. However, a few cursory tests failed to reveal any substantial effect of this variable as was perhaps to be expected for the symmetrical indenter geometry employed. Indentations were measured with a 70X oil immersion objective or a 50X dry objective depending on the optical characteristics of the test material.

At least five hardness measurements on a given face were made and averaged for each of two conditions: "dry"-desorbed by heating two hours in dry argon at 300°C, quenched into fresh anhydrous toluene at room temperature and tested while under this toluene; and "wet"-as-received or as-polished. It was found that "dry" surfaces, when desired, could be returned to the "wet" condition with a reproducible hardness value by exposure to laboratory air of 40 percent R.H. (several hours), water immersion (few minutes) or exposure to steam from an open beaker of boiling water (few seconds). Although the data populations for a given crystallographic face and test condition were too few to permit a statistical analysis, we believe from considerable experience in this laboratory in microhardness testing of ceramic and mineral samples that differences in average hardness in excess of ± 3 percent represent real differences in properties.

RESULTS

The principal results of this study are shown in Tables 1, 2 and 3. It will be noted that almost every face examined of every crystal studied softened appreciably (up to 32%) when adsorbed water was present. The effects observed are believed to be due to adsorbed water as such and not due to hydrate or hydroxide formation for two reasons: (1) analogous results were obtained for all species tested yet only a very few, *e.g.*, BeO and MgO, are readily susceptible to hydroxide formation near room temperature, and (2) the same desorption treatment was effective in removing the effects of water in all cases. In all cases the relative hardness of the faces of a given crystal was different for the "wet" condition than for the "dry" condition. In several cases, periclase, topaz, corundum, and galena, this change was just sufficient to alter the hardness rank of the faces tested. Thus, only hardness data obtained under "dry" conditions can be thought of as indicative of the intrinsic or structural mechanical anisotropy of the crystal, and the ordinary hardness values in humid air are the resultant of the superposition of a chemical (*i.e.*, adsorptive) anisotropy.

It must be emphasized that the quantitative aspects of these results must be related to the particular depth of indentation (*i.e.*, load) used; for shallower depths the difference between "wet" and "dry" will be expected to increase, and for greater depths to decrease and ultimately

TABLE 1. VICKERS HARDNESS (KG/MM^2), OXIDES

Bromellite (synthetic)

Crystal plane	VHN wet	Rel. to {0001}	VHN dry	Rel. to {000$\bar{1}$}	$\Delta H\left(\dfrac{dry\text{-}wet}{dry}\right)\%$
{000$\bar{1}$}[a]	1140	1.00	1370	1.00	17
{10$\bar{1}\bar{1}$}[a]	885	.78	935	.68	5
{10$\bar{1}$0}[a]	790	.69	915	.67	14

Corundum

		Rel. to {0001}		Rel. to {0001}	
{0001}	2630	1.00	3070	1.00	14
{10$\bar{1}$0}	2350	.89	2600	.85	10
{11$\bar{2}$0}	2320	.88	2680	.87	13

Periclase

		Rel. to {100}		Rel. to {100}	
{100}[b]	615	1.00	845	1.00	27
{110}	725	1.18	830	0.98	13
{111}	690	1.12	845	1.00	18

Quartz

		Rel. to {10$\bar{1}$0}		Rel. to {10$\bar{1}$0}	
{10$\bar{1}$0} (m)[a]	870	1.00	1140	1.00	21
{10$\bar{1}$1} (r)[a]	935	1.08	1240	1.09	25
{01$\bar{1}$1} (z)[a]	1020	1.17	1245	1.09	18

Rutile

		Rel. to (001)		Rel. to (001)	
(001)[a]	735	1.00	970	1.00	24
(100)[a]	850	1.15	965	0.99	12
(110)	875	1.19	965	0.99	9

[a] Natural face.
[b] Cleavage face.

TABLE 2. VICKERS HARDNESS (KG/MM²), SILICATES

Kyanite

Crystal plane	VHN wet	Rel. to (100)	VHN dry	Rel. to (100)	$\Delta H\left(\dfrac{\text{dry-wet}}{\text{dry}}\right)\%$
(100)[b]	700	1.00	828	1.00	15
(010)[b]	639	.91	675	.82	5
(001)[b]	975	1.39	1270	1.53	23

Topaz

		Rel. to (001)		Rel. to (001)	
(001) (c)[a]	1170	1.00	1290	1.00	9
(110) (m)[a]	1330	1.14	1510	1.17	12
(120) (l)[a]	1440	1.23	1510	1.17	5
(221) (o)[a]	1150	.98	1270	.98	9
(111) (u)[a]	1090	.93	1185	.92	8
(041) (y)[a]	1200	1.03	1360	1.05	12
(201) (d)[a]	1430	1.22	1550	1.20	8
(021) (f)[a]	1390	1.19	1550	1.20	10

Tourmaline

		Rel. to (0001)		Rel. to (0001)	
(0001) (c)[a]	1000	1.00	1090	1.00	8
(02$\bar{2}$1) (o)[a]	1210	1.21	1320	1.21	8
(10$\bar{1}$1) (r)[a]	1020	1.02	1150	1.05	11
(21$\bar{3}$4) (t)[a]	1150	1.15	1260	1.16	9
(11$\bar{2}$0) (a)[a]	985	.99	1090	1.00	10
(10$\bar{1}$0) (m)[a]	980	.98	1110	1.02	12

[a] Natural face.

[b] Cleavage face.

to disappear. For example, in the case of {100} periclase, reduction of the load from 50 g to 5 g causes the %ΔH(dry−wet/dry) to increase from 27 to 40 percent, while at 100 g the adsorption effect has disappeared. Thus these results are in accord with previous findings, Westbrook (1965), (1967), that the adsorbate affected mechanical properties are confined to a region not more than 3μ from the free surface, *i.e.*, microhardness but not macrohardness is affected. It must also be pointed out that the "dry" values reported here may still not represent

TABLE 3. VICKERS HARDNESS (KG/MM²); SULFIDES, FLUORIDES, CARBIDES, CARBONATES

Fluorite

Crystal plane	VHN wet	Rel. to {111}	VHN dry	Rel. to {111}	$\Delta H\left(\dfrac{\text{dry-wet}}{\text{dry}}\right)\%$
{111}[b]	189	1.00	213	1.00	11
{110}	181	.96	189	.89	4
{100}	157	.83	171	.80	8

Sphalerite

		Rel. to {110}		Rel. to {110}	
{110}	161	1.00	181	1.00	11
{111}[b]	187	1.16	203	1.12	8
{100}	132	.82	146	.81	10

Galena

		Rel. to {100}		Rel. to {100}	
{100}[b]	50	1.00	60	1.00	17
{110}	61	1.22	66	1.10	8
{111}	57	1.14	58	.97	2

Calcite

		Rel. to $(10\bar{1}1)$		Rel. to $(10\bar{1}1)$	
$(10\bar{1}1)$ (r)[b]	126	1.00	135	1.00	7
$(21\bar{3}1)$ (v)[a]	146	1.16	147	1.09	<1
$(10\bar{1}0)$ (m)	131	1.04	145	1.07	10

Silicon carbide

		Rel. to {0001}		Rel. to {0001}	
{0001}[a]	2850	1.00	3270	1.00	13
{000$\bar{1}$}[a]	2780	.98	3250	1.00	14
{10$\bar{1}$0}	1860	.65	2730	.83	32
{11$\bar{2}$0}	2240	.78	2740	.84	18

[a] Natural face.
[b] Cleavage face.

intrinsic behavior since either the cleavage process or surface flow during polishing may in some cases have increased the hardness value over that expected for undisturbed material.

It is apparent that this previously unrecognized variable, adsorption, may be in part the cause of discrepancies between several types of sets of indentation hardness data on non-metallic materials: differences between investigators, differences between freshly cleaved versus polished faces, differences between other types of surface preparation treatments, or differences in heat treatment—in short anything which might alter the extent or nature of the surface adsorption. The present results also present a particular caveat to those wishing to employ microhardness, see Uytenbogaardt (1951), Pudovkina (1957), Bowie and Taylor (1958), and Povarennykh (1963), or microhardness anisotropy, Lebedva (1961), as a mineral or phase identification tool. To be soundly based, such reference tables and comparisons should be in terms of hardness values obtained under desorbed or anhydrous conditions. In addition to the possible effect which adsorbed water may have on the hardness values themselves, it can also alter the tendency to crack under load or the time dependence of hardness, both of which have been suggested as further definitive identification criteria for minerals, Ribalko (1964) and Young and Millman (1964).

DISCUSSION

There is scanty information in the literature with which to compare the data of the present study. Some specific comments may be made on each crystal species, however. Unless otherwise noted, comparison is made between literature hardness values and our "wet" data.

Bromellite. Hanneman and Westbrook (1968) reported Vickers hardness for $\{0001\}$ and $\{000\bar{1}\}$ surfaces under "dry" and "wet" conditions. Their values of 1400 kg/mm² for a "dry" $\{000\bar{1}\}$ surface and 1100 kg/mm² for the same surface under "wet" conditions are in excellent agreement with the values found in the present study.

Corundum. Young and Millman (1964), using a 100-g load, report $\{10\bar{1}0\}$ harder than $\{0001\}$ which is opposite to the findings of this study, while Albrecht (1954) reports the Vickers hardness for 50-g load on a plane parallel to the c axis less than the hardness on a plane perpendicular to the c axis in conformity with the present results. Albrecht's numerical values of 1960 kg/mm² for the parallel orientation and 2100 kg/mm² for the perpendicular orientation are quite far from the values reported here, although load and indenter geometry are the same.

Periclase. The fact that little anisotropy was found for the "wet" or "dry" condition may perhaps be associated with the cubic NaCl structure. No prior data on indentation hardness of individual crystal planes could be found.

Quartz. Winchell's Knoop measurements (1945) showed $\{10\overline{1}0\}$ harder than $\{10\overline{1}1\}$ and $\{01\overline{1}1\}$, and Taylor's Vickers data (1949) showed $\{10\overline{1}0\} > \{0001\}$, Young and Millman's Vickers data also showed $\{10\overline{1}0\} > \{0001\}$. No explanation is apparent for the opposite findings of Winchell and the present study; a comparison cannot be made with Taylor's or Young and Millman's data. It is worthy of note that the positive and negative rhombohedral faces, r $\{10\overline{1}1\}$ and z $\{01\overline{1}1\}$ respectively, show the same "dry" hardness although z is harder than r when "wet". Although it is recognized that penetration twinning, especially of Dauphiné type, is to be expected in quartz crystals, Frondell (1962), no evidence for this was sought or found in this study. Typically a so-called "r" face on a given crystal might contain large regions of polar twin in the "z" orientation. No suggestion of this was found in any bimodal distribution of the hardness values in these faces. However, the test indentations were perhaps confined to an area too limited to detect such a circumstance.

Rutile. Young and Millman (1964) report Vickers hardness measurements on $\{001\}$ and $\{111\}$ planes using 25- and 100-g loads. No conclusions could be drawn from their work because of overlapping ranges of hardness values. It is interesting to note from the present data that this tetragonal crystal, which exhibits considerable hardness anisotropy in the "wet" condition, is essentially isotropic in the desorbed or "dry" condition.

Kyanite. Vickers hardness has been reported by Young and Millman (1964) for $\{001\}$, $\{010\}$ and $\{100\}$. Their 100-g load hardness values are considerably higher than those reported in this study, and the hardness order of their various faces is difficult to assess due to the wide ranges of hardness values reported.

Topaz. Young and Millman (1964) report overlapping ranges of hardness values for $\{001\}$, $\{010\}$ and $\{100\}$ between 1478–2012 kg/mm² for loads of 100 g. Winkler (1955) also lists hardness values for various planes on topaz. Interpolation of his data to 50-g loads yielded the values 1740, 1490, 1475 and 1180 kg/mm² respectively for the following planes $\{001\}$, $\{110\}$, $\{011\}$, and $\{120\}$. It should be noted that the

order of hardness is not the same as found in this study and the hardness values of the {001} and {120} planes are not in agreement with the numbers reported here.

Tourmaline. Young and Millman (1964) found the {10$\bar{1}$0} plane of tourmaline slightly harder than the {0001} plane, while essentially no difference was found for these planes on the tourmaline crystal used in this investigation.

Fluorite. Young and Millman (1964) using a 100 g load report Vickers hardness for {100} equal to 174–181 kg/mm² and for {111} a value of 174–203. Neglecting the effect of load these values are in good agreement with the hardness found for fluorite in this study.

Sphalerite. Henriques (1957) found hardness in sphalerite was a function of the iron content. His empirical equations for three faces are

$$H_{\{100\}} = 165 + 16 \log C$$
$$H_{\{011\}} = 187 + 18 \log C$$
$$H_{\{111\}} = 193 + 19 \log C$$

where C is the wt% of iron in sphalerite. Hence for a given iron concentration the hardness order for the above listed planes is {111}, {011} and {001}. This order is identical to the one found in the present study.

Galena. Young and Millman (1964) report overlapping hardness ranges for the {100}, {110} and {111} planes. Considering the midpoint of these ranges, a hardness order of {100} > {110} > {111} can be established. This order of hardness does not correspond to the order found in the present investigations under either "wet" or "dry" surface conditions.

Calcite. Taylor (1949) measured the Vickers hardness on the major cleavage surface of calcite and also on planes perpendicular and parallel to the optic axis. The values obtained were 136 kg/mm², 105 kg/mm² and 145 kg/mm², respectively. The hardness value on the cleavage plane {10$\bar{1}$1} corresponds very well with the hardness values measured in this study. Gottardi (1951) measured the Vickers hardness of various planes of calcite as a function of load and reported values in terms of the hardness corresponding to a 10 μ diagonal. He found the hardness for {21$\bar{3}$1} > {13$\bar{4}$1} > {10$\bar{1}$1}. The hardness ratio of the {21$\bar{3}$1} and {10$\bar{1}$1} planes was in close agreement with that reported here although

the hardness values were not. Teremetskaya *et al.* (1962) have also investigated the Vickers hardness anisotropy of calcite for five different planes. Using a 50-g load, they found $\{21\bar{3}1\} > \{10\bar{1}0\} > \{10\bar{1}2\} > \{10\bar{1}1\} \approx \{0001\}$. The hardness ratios for the three planes common with those studied here are in good agreement but the hardness numbers differ from those of the other three investigations.

Alpha silicon carbide. Shaffer (1964) studied the Knoop 100-g hardness of αSiC and examined not only the values for different surfaces but also the effects of indenter orientation. If his values for each surface are averaged, the Knoop hardnesses fall in the order $(0001) > (11\bar{2}0) > (10\bar{1}0)$ in the ratio $1:00:0.876:0.832$. This is the same order of rank as found here for the "wet condition" although the ratios are not the same. Exact correspondence could not be expected because of differences in depth of indenter penetration and amount of adsorbed water.

Conclusions

The previously reported softening effects of adsorbed water on minerals are confirmed. Adsorbed water is further found to alter the apparent anisotropy of hardness of the different crystallographic surfaces in such compounds. It is now recognized that this variable must be controlled for purposes of reproducibility or identification.

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