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Knoop microhardness of single crystal sulphur

HONG LI
Materials Engineering Department, Rensselaer Polytechnic Institute, Troy, NY 12180-3950, USA

YOUNG H. HAN, R. C. BRADT
Department of Chemical and Metallurgical Engineering, Mackay School of Mines, University of Nevada-Reno, Reno, NV 89557-0136, USA

The Knoop microhardness of single crystal sulphur was measured as a function of crystallographic orientation and applied test load on the (1 1 0) and (1 1 1) planes. Microhardnesses were determined to be in the range of 25–35 kg mm^{-2}. Anisotropy of the microhardness and a normal indentation size effect (ISE) were observed. The ISE was addressed by the application of the traditional power law and the proportional specimen resistance model (PSR) of Li and Bradt. The load-independent hardness was determined, from which it was concluded that the (1 1 1) plane is harder than the (1 1 0) plane and also that the (1 1 1) plane is more anisotropic in microhardness.

1. Introduction

It is well established that for the measurement of the microhardness of solids there exists a dependence of the apparent microhardness on the applied test load. The phenomenon is known as the indentation size effect, or ISE. The ISE is usually reported to be of the form that the apparent microhardness increases with a decreasing applied indentation test load (decreasing indentation size). Although numerous mechanisms have been proposed to explain this phenomenon, most appear to be applicable only for specific situations [1–11]. Recently Li and Bradt [12] developed a general model: proportional specimen resistance (PSR) that describes the ISE. In the PSR model, the two contributing factors to the increase in microhardness are the friction between the indenter facets and the test specimen, and the elastic resistance of the test specimen. Both of these decrease the magnitude of the effective applied load on the specimen during indentation loading. The form of the PSR has a general (1/indentation size) functionality and has been demonstrated to describe accurately the ISE in numerous ceramics [13], glasses [14], metals [15] and also for single crystal diamond [16].

There are also several published reports of an inverse type of indentation size effect, where the apparent microhardness decreases with a decreasing applied indentation test load. It is prominent for Si, Ge, GaP, GaAs, InP [17, 18], S [19], and the chalcogenides of antimony, arsenic and bismuth [20]. The phenomenon is not understood. A possible explanation relates to the work hardening of the test specimen during indenter loading. Larger indentations require a greater amount of plastic flow, greater work hardening and hence exhibit a higher hardness. For brittle materials, another possibility may come from the source of indentation induced specimen cracking during indenter loading. Feltham and Banerjee [17, 18] suggest that the inverse trend of the ISE may be related to the applied energy loss as the result of specimen chipping surrounding the indentation. However, quantitative measures of the effect of indentation cracking on the apparent microhardness remain to the determined.

Single crystal sulphur has previously been reported to exhibit an inverse ISE. This paper addresses the ISE in sulphur and reports measurements of the Knoop microhardness and the related microhardness anisotropy as a function of the indentation test load. The observed ISE is further analysed using both the PSR model and the traditional power law approach.

2. Experimental procedure

Natural single crystals of sulphur were obtained for this study from Steamboat Springs, NV, USA. The sulphur was a bright yellow colour and the crystals were in the form of a small viburnum cluster. Sulphur has an orthorhombic crystal structure with the space group $2/m\ 2/m\ 2/m$ [21]. Specimens exhibiting large flat surface areas, about 10×5 mm^2, of natural crystal faces for the (1 1 0) and (1 1 1) planes were extracted from the cluster. These crystal planes were then confirmed using X-ray diffraction and compared with the JCPDS file [22]. The $\langle 1\,1\,0 \rangle$ was identified as a reference direction for both the (1 1 0) and the (1 1 1) planes of the natural crystals.

To prepare the individual single crystals for the microhardness measurements, specimens were mounted in epoxy and cured, then successively polished using Al_2O_3 slurries with particle sizes of 15, 5, 3 and 1 μm in sequence. Finally, a 0.3 μm alumina slurry was used in an automatic polisher. Knoop indentations were made on the (1 1 0) and the (1 1 1) planes for systematic indenter orientations, as specified by the

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long diagonal of the Knoop indenter. The crystallographic directions were from the [0 0 1] to the [1 $\bar{1}$ 0] on the (1 1 0) plane, and from the [1 $\bar{1}$ 0] to the [$\bar{1}$ $\bar{1}$ 2] on the (1 1 1) plane. These angular ranges are sufficient for the symmetry of sulphur. Microhardness measurements were made at room temperature for applied test loads varying from 25 to 100 g at an indentation rate of 0.017 mm s^{-1} for a dwell time of 15 s. A Shimadzu microindenter was used and the indentation dimension measurements were completed immediately after each unloading. The values of the Knoop microhardness (KHN) were calculated from

$$\mathrm{KHN} = 14.299\frac{P}{d^2}\ (\mathrm{kg\ mm^{-2}}) \quad (1)$$

where P is the applied indentation test load (kilograms) and d is the long diagonal of the Knoop impression (millimetres). Knoop microhardnesses are reported as the averages for 20 individual indentations. Occasionally, indentation induced microcracking was observed, particularly at the 100 g applied test load and those results were discarded from the final microhardness calculations. No slip traces were observed in the vicinity of indentations.

3. Results and discussion

Figs 1 and 2 illustrate the Knoop microhardness profiles as a function of the applied test load for the (1 1 0) and the (1 1 1) planes, respectively. Error bars representing the 95% confidence intervals based on the t-distribution are also presented, but only for the 25 g measurements to preserve clarity. Sulphur is quite soft, only 25–35 kg mm^{-2}. However, the orientation dependences of the Knoop microhardness is evident on both crystal planes. For the (1 1 0) plane, the microhardness decreases from the [0 0 1] to the [1 $\bar{1}$ 0]; while for the (1 1 1) plane, the hardness increases from the [1 $\bar{1}$ 0] to the [$\bar{1}$ $\bar{1}$ 2]. For the same indentation orientation, the ⟨1 1 0⟩, there are both similarities and differences in the microhardnesses on the two crystal planes. This is related to the anisotropy of the plastic deformation of the specimens, since the effective resolved shear stress on the operating slip systems varies with indenter orientation [23–27]. Unfortunately, the slip systems of sulphur are not known and the complexity of the orthorhombic crystal structure precludes the application of trial and error methods to analyse the microhardness anisotropy.

The Knoop microhardness of the two sulphur single crystals on both the (1 1 0) and (1 1 1) planes decreases with an increase in the applied indentation test load. This trend is in agreement with the normal ISE which has been reported for numerous other materials. It is, however, the opposite to the previously reported Vickers microhardness trends for sulphur by Srebrodolski

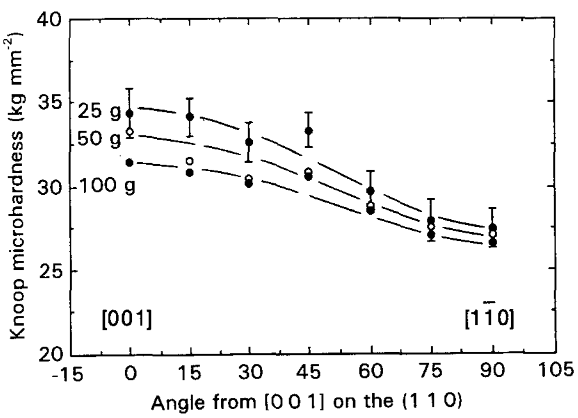

Figure 1 Knoop microhardness as a function of indentation test load and crystallographic orientation on the (1 1 0) plane for single crystal sulphur.

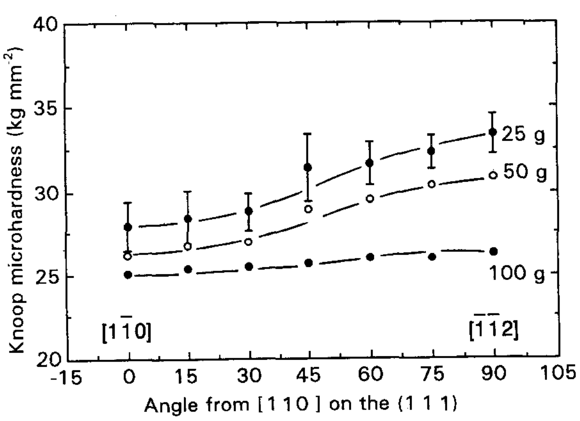

Figure 2 Knoop microhardness as a function of indentation test load and crystallographic orientation on the (1 1 1) plane for single crystal sulphur.

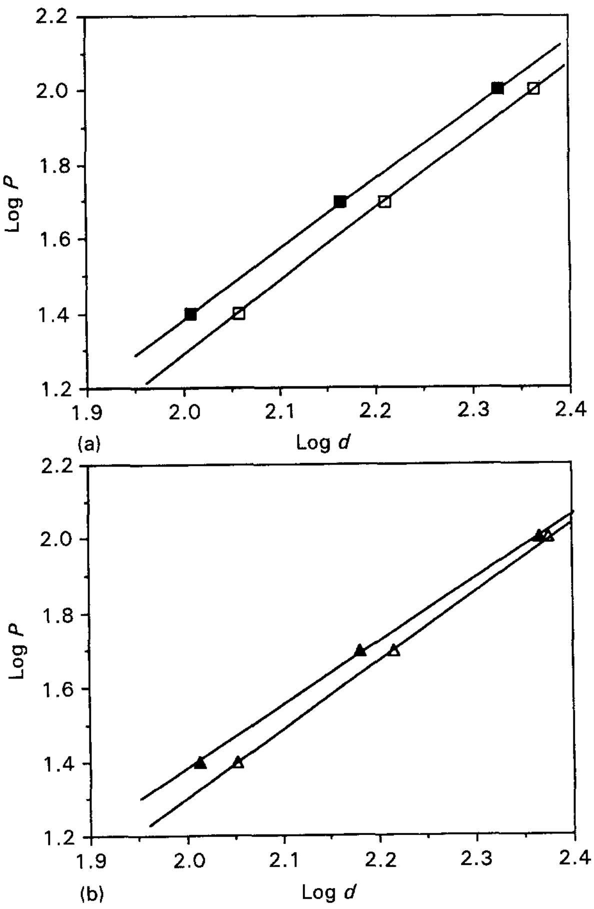

Figure 3 Application of the power law to indentation load–size relationship for major crystallographic orientations of single crystal sulphur on (a) the (1 1 0) and (b) the (1 1 1) plane. For (a): (■) [0 0 1], $n = 1.88$, (□) [1 $\bar{1}$ 0], $n = 1.95$. For (b): (▲) [$\bar{1}$ $\bar{1}$ 2], $n = 1.70$; and (△) [1 $\bar{1}$ 0], $n = 1.86$.

and Yushkin [19]. As the Vickers indenter is much sharper than the Knoop, perhaps the results of the two studies are expected to be different. Certainly the Vickers indentations are more prone to cracking [19].

Traditionally, the ISE has been described utilizing the power law relationship [1, 7]

$$P = Ad^n \quad (2)$$

where P and d are as previously defined. The extent of the ISE is hence assessed by the n value, i.e. its deviation from two, $(2 - n)$. Fig. 3a, b illustrates the logarithmic plots of the indentation load–size relationship, confirming their applicability to the ISE. However, as has been discussed at length elsewhere [27], Equation 2 lacks physical meaning, for the n values provide no insight to the mechanism of the ISE, neither does the A value. For the major crystallographic orientations on the two crystal planes for sulphur, linear regression analyses yield n values varying from 1.70 to 1.95, as summarized in Table I. These n values less than two confirm that a normal power law relationship exists for the ISE of the Knoop microhardness of sulphur.

The PSR model of Li and Bradt describes two distinctive regimes of microhardness: (i) the indentation load-dependent, or ISE, regime; and (ii) the indentation load-independent one. In the ISE regime, the indentation test load, P, is related to the corresponding indentation size, d, by the load-independent hardness, (H_o/geometrical factor, ψ), or (P_c/d_o^2) as [12]

$$P = a_1 d + a_2 d^2 = a_1 d + \left(\frac{P_c}{d_o^2}\right) d^2 \quad (3)$$

In Equation 3, the a_1 coefficient is the PSR contribution to the apparent microhardness and the a_2 coefficient relates to the load–independent microhardness, which is equal to (P_c/d_o^2). Here P_c is the critical applied indentation test load above which the hardness is load-independent and d_o is the corresponding characteristic indentation size [27]. The load-independent microhardness is readily obtained from the slope of the linear plot of

$$\left(\frac{P}{d}\right) = a_1 + \left(\frac{P_c}{d_o^2}\right) d \quad (3a)$$

It is equal to (P_c/d_o^2) times the geometric conversion factor, 14.229, for the Knoop indenter as described by the standard Knoop microhardness formula [12–14].

Fig. 4a, b illustrates the plots of (P/d) versus d for two of the major crystallographic orientations on each of the (1 1 0) and the (1 1 1) planes of single crystal sulphur. These plots confirm the validity of the linear relationship (cf. Equation 3a) for single crystal sulphur. Table II summarizes the PSR parameters, a_1 and a_2 or (P_c/d_o^2), on both planes for the major crystallographic directions. Both the load-dependent and the load-independent Knoop microhardnesses are also listed for comparison. It is evident that the ISE on the apparent microhardness is significant, higher by 65% in the case of the (1 1 1) $[\bar{1}\,\bar{1}\,2]$. As a result of the magnitude of the ISE, it is uncertain which crystal plane is actually harder (cf. Table II). However, when the load-independent microhardnesses are compared, it is evident that the (1 1 0) plane is harder than the (1 1 1) plane.

TABLE I The power law parameters for single crystal sulphur

(*hkl*) [*uvw*]	A value (g μm^{-n})	n value	r^2
(1 1 0) $[1\,\bar{1}\,0]$	2.42×10^{-3}	1.95	> 0.99
(1 1 0) [0 0 1]	4.20×10^{-3}	1.88	> 0.99
(1 1 1) $[1\,\bar{1}\,0]$	3.81×10^{-3}	1.86	> 0.99
(1 1 1) $[\bar{1}\,\bar{1}\,2]$	9.46×10^{-3}	1.70	> 0.99

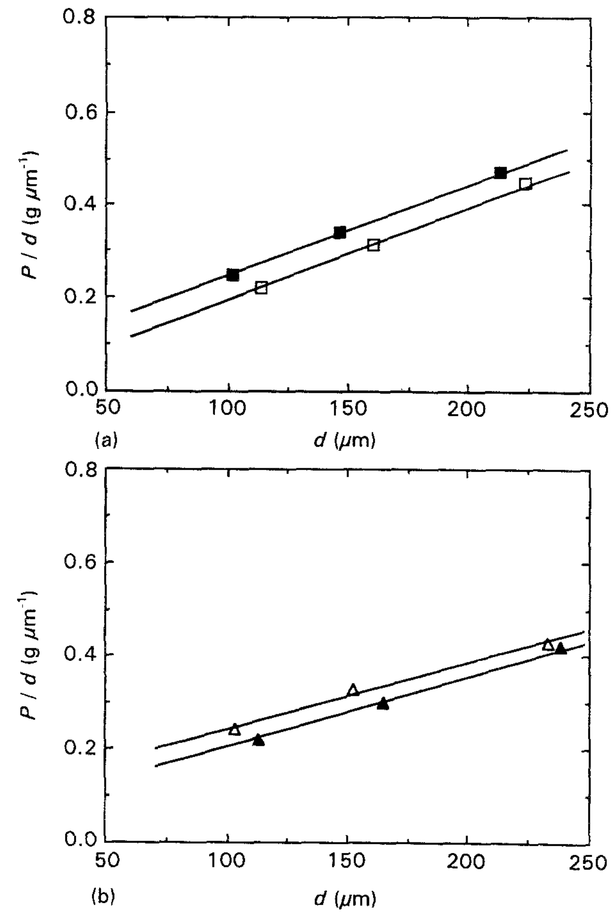

Figure 4 Application of the PSR model to indentation load–size relationship for major crystallographic orientations of single crystal sulphur on (a) the (1 1 0) and (b) the (1 1 1) plane. For (a): (■) [0 0 1], (□) $[1\,\bar{1}\,0]$. For b: (△) $[\bar{1}\,\bar{1}\,2]$, and (▲) $[1\,\bar{1}\,0]$.

In the PSR model, the a_1 value relates to both the friction and the elastic resistance of the test specimen. For the long diagonal of the Knoop indenter parallel to the ⟨1 1 0⟩ orientations on the (1 1 0) and (1 1 1), the Young's moduli are equal; thus the observed differences in the a_1 values may be expected to be primarily from the differences in the effect of friction [12, 15] for those test orientations. The load-independent hardness, H_o, for the (1 1 0) $[1\,\bar{1}\,0]$ is greater than that for the (1 1 1) $[1\,\bar{1}\,0]$ and the a_1 value of the (1 1 0) $[1\,\bar{1}\,0]$ is less than that for the (1 1 1) $[1\,\bar{1}\,0]$ as summarized in Table II. For the (1 1 0) $[1\,\bar{1}\,0]$, the ISE effect at the lowest indentation load level is only about 7% based on $(H_{25\,g} - H_o)/H_o$. For the (1 1 1) $[1\,\bar{1}\,0]$, however, it is about 23% when estimated on the same basis. This indicates that the contribution of the frictional resistance from the test specimen to the ISE also varies with

TABLE II Load-dependent Knoop microhardness, PSR parameters and estimated load-independent hardnesses for single crystal sulphur

(hkl) [uvw]	P (g)	H_k ($kg\,mm^{-2}$)	a_1 ($g\,\mu m^{-1}$)	P_c/d_o^2 ($g\,\mu m^{-2}$)	r^2	H_o[a] ($kg\,mm^{-2}$)
(1 1 0) [1 $\bar{1}$ 0]	25	27.4				
	50	27.0	0.014	0.0018	> 0.99	25.7
	100	26.5				
(1 1 0) [0 0 1]	25	34.3				
	50	33.3	0.042	0.0020	> 0.99	28.8
	100	31.5				
(1 1 1) [1 $\bar{1}$ 0]	25	27.9				
	50	26.1	0.041	0.0016	> 0.99	22.7
	100	25.1				
(1 1 1) [$\bar{1}$ $\bar{1}$ 2]	25	33.4				
	50	30.8	0.102	0.0014	0.98	20.2
	100	26.2				

[a] $H_o = 14\,229\ (P_c/d_o^2)$, where a_2 is equal to P_c/d_o^2 (see References [12–14])

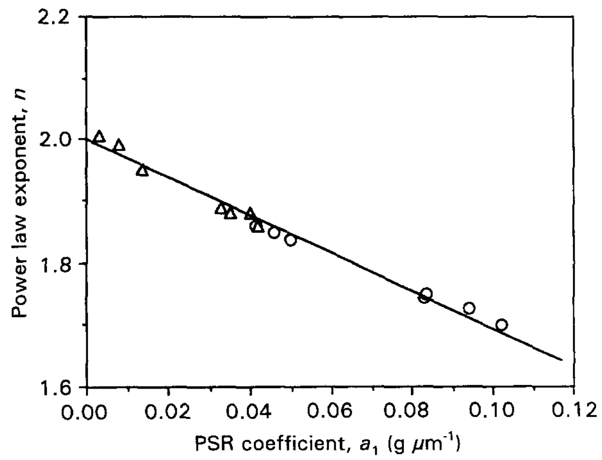

Figure 5 Correlation between the power law exponent, n value, and the PSR factor, a_1, for single crystal sulphur, confirming that the ISE, or the n value, less than 2, originates from the PSR: (△) (1 1 0) [hkl]. (○) (1 1 1) [hkl].

crystal plane and orientation. This leads to the conclusion that the ISE for single crystal sulphur is anisotropic, that is directionally dependent, the same as the Knoop microhardness.

For the (1 1 0) plane, the load-independent microhardness, H_o, is a minimum, 25.7 $kg\,mm^{-2}$, in the [1 $\bar{1}$ 0] and a maximum, 28.8 $kg\,mm^{-2}$, in the [0 0 1]. For the (1 1 1) plane, the maximum is 22.7 $kg\,mm^{-2}$ in the [1 $\bar{1}$ 0] and minimum is 20.2 $kg\,mm^{-2}$ in the [$\bar{1}$ $\bar{1}$ 2]. If the microhardness anisotropy is evaluated by the ratio of the two extremes, applying the load-independent microhardness values, it is about 1.12 for both crystal planes. If this ratio is estimated from the load-dependent microhardness values, it is only about 5% greater. On the basis of these two comparisons, it appears that the anisotropy of the microhardness is nearly load-independent, even though the apparent microhardnesses are highly load-dependent.

In the power law analysis, the n value was treated as indicative of the magnitude of the ISE: the larger the difference $(2 - n)$, the greater the ISE. The physical meaning of that interpretation can now be explained by comparison with the PSR model, as previously reported for other materials [12–14]. The n values are related to the a_1 values of the PSR model as shown in Fig. 5. It presents the n values versus the a_1 values for all of the orientations measured for the single crystals of sulphur, confirming that the n value is related to the a_1 value with a linear regression coefficient of 0.99. This is clearly shown in Fig. 5, as the lower n values correspond to the higher PSR coefficients, a_1 values. Furthermore, it is evident that once the a_1 value approaches zero, the power law exponent approaches two, signifying the presence of the load-independent microhardness. The results shown in Fig. 5 are in excellent agreement with expectations of the PSR model for the ISE.

4. Summary and conclusions

The Knoop microhardness of natural single crystal sulphur was studied on the (0 1 1) and the (1 1 1) crystal planes. Crystallographic and indentation load dependencies of microhardness were observed. These are well described with the approach of the proportional specimen resistance (PSR) model. The Knoop microhardnesses decrease with an increase of the applied indentation load. This is a normal ISE, not the inverse form which has been previously reported for Vickers microhardnesses for single crystal sulphur. The n value of the power law was confirmed to be directly related to the a_1 value of the PSR model.

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