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NOTE ON THE HARDNESS OF HEXAGONAL PYRRHOTITE AND A METHOD FOR MEASURING THE ABRASION DEPTH IN SULFIDES

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ABSTRACT

Hardness tests carried out on hexagonal pyrrhotite from the Silberberg mine at Bodenmais, Bavaria indicate that (0001) is the hardest crystallographic plane in low-temperature, ordered pyrrhotite. The mixing of two pyrrhotite phases, namely. the *4C* and *5C* types, commonly observed in the parting plane of this material, does not influence this result. The Vickers hardness measured on a Shimadzu microhardness tester is $VH_{50} = 349$ (16) kg mm^{-2}. Below 240°C, temperature has no significant effect on hardness. At this temperature, the hardness increases abruptly to 371 kg mm^{-2}, presumably as a result of the transformation from an ordered to a disordered distribution of vacancies. With the aid of a microhardness tester, the abrasion depth D in sulfides can be calculated by means of the formula $D = (d_o - d_1)\ [2\sqrt{2}\tan(\theta/2)]^{-1}$ where d_o and d_1 are the lengths of the indentation diagonals before and after abrasion, respectively, and θ is the angular opening of the indentation diamond.

Keywords: hexagonal pyrrhotite, Vickers hardness, sulfides, abrasion depth, (0001) parting, Bodenmais, Germany.

SOMMAIRE

On a étudié la dureté de la pyrrhotine hexagonale d'un échantillon de la mine Silberberg (Bodenmais, Bavière). C'est sur (0001) qu'elle est la plus élevée pour la pyrrhotine complètement ordonnée, de basse température. La coexistence des deux formes polytypiques *4C* et *5C*, communément observée sur le plan de séparation n'affecte pas la dureté. Mesurée au moyen de l'appareil Shimadzu, la dureté Vickers VH_{50} est de 349(16) kg mm^{-2}. Sous 240°C, la température n'exerce aucune influence sur la dureté; à 240°C, la dureté atteint soudainement 371 kg mm^{-2}, ce qui marquerait la transition à une forme à lacunes désordonnées. On calcule la profondeur de l'abrasion D dans les sulfures par la formule $(d_o - d_1)\ [2\sqrt{2}\tan(\theta/2)]^{-1}$; d_o et d_1 sont les longueurs des diagonales de l'indentation avant et après l'abrasion et θ est l'angle d'ouverture du diamant d'indentation.

(Traduit par la Rédaction)

Mots-clés: pyrrhotine hexagonale, dureté Vickers, sulfures, profondeur de l'abrasion, plan de séparation (0001), Bodenmais, Allemagne.

INTRODUCTION

Like all crystalline materials, pyrrhotite shows varying physical properties along different crystallographic planes. One of these properties is hardness, as defined by the Vickers or related methods. The Vickers hardness (*VH*) for pyrrhotite thus varies between 210 and 360 kg mm^{-2}, but higher values have been reported (Bowie 1967, Uytenbogaardt 1967).

In this investigation the (0001) parting of hexagonal (*5C*) pyrrhotite was analyzed with respect to its Vickers hardness. A large, monocrystalline piece of pyrrhotite from the Silberberg mine near Bodenmais in Bavaria, with perfectly developed parting along (0001), provided the samples for the test. The specimen was kindly placed at the author's disposal by the Mineralogical Museum of the Geological Institute, University of Uppsala.

X-ray examination showed that the parting planes do not contain pure hexagonal pyrrhotite. The outermost regions near the surface consist of a mixture with monoclinic pyrrhotite, in proportions that change parallel to the c axis according to the equation $Y = \mathrm{Exp}(aX+b)$, where Y is the fraction of monoclinic pyrrhotite expressed as a percentage of the total, X is the depth in μm and a and b are constants. In this way the pyrrhotite changes continuously from 100% monoclinic to 100% hexagonal type (Kübler, *in prep.*). An attempt was made to relate the Vickers hardness to this compositional gradient. In addition, a test was carried out to check the effect to temperature up to 350°C on the Vickers hardness in the (0001) parting.

EXPERIMENTAL METHODS

The hardness was tested with a Shimadzu

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microhardness tester with an automatic indentation-time control. A few final tests were carried out on a Leitz Durimet instrument. After identification of the (0001) plane by X-ray analyses, each surface was tested at times with 5, but mostly with 10 to 20 indentations, depending on the surface area of the sample. In general, a 50 gram load was used, but occasionally 100 gram tests were performed. Diagonals were measured twice and a mean value was calculated. Finally, the mean and standard deviation of all indentations made on the surface were computed. A typical sample surface had the dimensions 2 x 3 mm.

Then the sample surface was polished with MgO in H_2O until a layer of 0.5 to 1.5 μm had been removed. For the estimation of abrasion depth, the old impressions were used. The diagonals of these cut indentations were measured again; the new value d_1, together with the original value d_o, were inserted into the following formula to give the depth of abrasion D:

$$D = \frac{d_o - d_1}{2\sqrt{2\tan(\theta/2)}}$$

The angle θ corresponds to the angular opening of the indentation diamond which, for the Vickers method, is 136°.

This method gives a fairly accurate value of abrasion depth if all parameters influencing the normal hardness-testing procedure are carefully considered. Commonly, these parameters are described in handbooks supplied with hardness-testing instruments but are also found in several more comprehensive investigations of relations between physical factors, indentation mechanism and hardness values (Bückle 1954, Pärnamaa 1963, Bowie 1967). There is one main factor limiting the use of this method for accurate measurements of depth. The volume deficit caused by the indentation pyramid is compensated by a volume uptake in its surroundings, leading to a piling up; the material is more or less pushed aside, aided by existing slip systems (Bückle 1954). A measurement of the diagonal, in this case, gives a false depth.

The effect is dependent on the plastic properties of the material. Bückle (1954) showed very convincingly that arched edges of the indentation square are evidence of either "sinking in" (arch pointing inward) or "piling up" (arch pointing outward) of the material surface in the immediate vicinity of the impression. In the first case, the slope of the pile-up descends below the level of the original surface in the middle of the edge; in the second case, the edge cuts the pile-up above the original surface. Straight edges are formed either because no volume transfer to the surroundings compensated for the indentation, which is very unlikely, or because the piling-up effect was spread over a larger area, thus suppressing the arching.

Sphalerite and chalcopyrite, for example, generally show a pronounced sinking-in of the indentation edges. Pyrrhotite, however, is free of this, and all indentations made during this investigation on (0001) had more or less straight edges. Bückle also showed that the height of the pile-up ridge is directly proportional to the length of the diagonal (and thus to the test load) only when d_0 exceeds 40 μm. For $d_0 < 20$ μm the ridge height increases very slightly in relation to d_0. The example given by Bückle indicates a total ridge-height of 0.25 μm under prevailing circumstances, *i.e.*, when strong sinking-in occurred at the indentation edges.

In the present investigation it was possible to make a reasonably precise estimation of the piling-up around the indentations in pyrrhotite, as the volume transfer, under certain circumstances, obviously used the (0001) plane for slip and material transport. This occurred when the bonding forces between the (0001) parting planes were weakened owing to delayed relaxation of stresses built up during deformation. The area affected by the indentation force then bulged up sufficiently to be observed under the microscope. The ridge height calculated in this way was 0.16 μm (mean). However, a comparison between 50-gram- and 100-gram-load indentations revealed that the error in abrasion depth caused by ridge formation did not exceed ± 0.1 μm.

Annealing of the samples up to 240°C was carried out in air and above 240°C in evacuated glass tubes. Temperature was measured with a chromel–alumel thermocouple to within ± 5°C. For the X-ray analyses, Ni-filtered Cu $K\alpha$ radiation at 40 kV and 25 mA was used. Goniometer speed was kept at 0.125° min^{-1}.

RESULTS

Hardness-vs.-depth series

Two complete series of hardness-*vs.*-depth tests were carried out. An initial test made on three successive planes in pure pyrrhotite gave a mean value of $VH_{50} = 356$ kg mm^{-2} [upper limit, $VH(u.l.) = 367$ kg mm^{-2}; lower limit, $VH(l.l.) = 346$ kg mm^{-2}, 12 indentations]. Tests in series S–1 were carried out on a sample selected

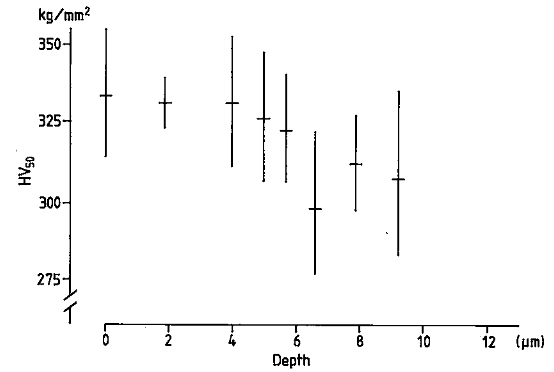

FIG. 1. The change in Vickers hardness, VH_{50} (in kg/mm²), with depth (in µm) from the parting surface (0001) in pyrrhotite from Bodenmais. Sample S–1. Only undisturbed indentations were used for mean values.

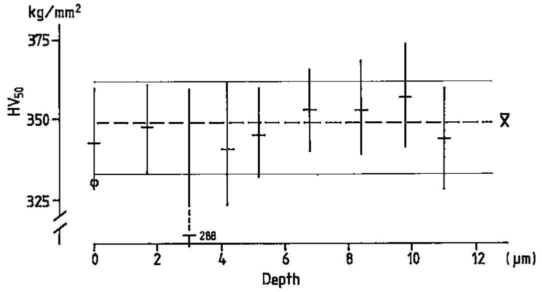

FIG. 2. The change in Vickers hardness with depth from the parting surface (0001) in pyrrhotite. Sample S–2. Dashed line: mean of all indentations made in this series. Upper and lower limit (limits of standard deviation) are indicated. Only undisturbed indentations were used for mean values. Circle indicates results of 100-gram tests.

from the near-surface parts of the museum specimen. The specimen was covered by a brownish layer of oxidation products characteristic of pyrrhotite exposed to air. This layer was removed until only a thin oxidized cover remained, indicated by pale interference colors. This plane was taken as the 0 level, and all other abrasion values were measured in relation to this plane. In general, sample S–1 showed rather high variations in hardness on all depth levels (Fig. 1). The mean value at the 0 level was $VH_{50} = 334$ kg mm^{-2} [$VH(u.l.) = 355$, $VH(l.l.) = 315$ kg mm^{-2}]; hardness decreases slightly with increasing depth. At $D = 6.4$ μm, the hardness abruptly decreased to $VH_{50} = 308$ kg mm^{-2}, but with a large standard deviation.

Series S–2 shows a completely different trend compared with S–1. The sample was cut out around 10 mm below the oxidized surface of the specimen. Natural parting planes had only very thin (and with the method described above, not measurable) oxidized layers, and one of these planes was used as the 0 level.

The measured hardness in this plane was $VH_{50} = 343$ kg mm^{-2} [$VH(u.l.) = 360$ kg mm^{-2}, $VH(l.l.) = 328$ kg mm^{-2}]. The probability that there is a significant difference with the S–1 results is greater than 60% but lower than 75%. If the 100-gram tests (carried out in both series at the 0 level) are taken into account, no significant difference is obtained. However, the hardness in series S–2 did not change until more than 4 μm of material was removed by abrasion (Fig. 2). From this depth on, a small increase in hardness was observed, reaching a maximum VH_{50} of 357 kg mm^{-2} at a depth of 10 μm from the surface. At this level the surface consisted of nearly pure hexagonal pyrrhotite. This final value of hardness is the same as that obtained in the initial test on (0001) planes in pure hexagonal pyrrhotite.

The mean value of all 111 indentations in S–2 corresponds to a hardness of $VH_{50} = 349$ kg mm^{-2} [$VH(u.l.) = 365$ kg mm^{-2}, $VH(l.l.) = 333$ kg mm^{-2}; dashed line in Fig. 2]. Excluded are the VH_{50} values from the plane at 3 μm. The 15 indentations made on this plane had a strongly heterogeneous distribution along the VH scale. About half of the measurements, however, fell well within the indicated interval of values characteristic for series S–2.

F tests were performed on the S–1 and S–2 results assuming that every hardness population follows a normal distribution. The tests revealed that the negative trend in S–1 is true to more than 99%, whereas the positive trend in S–2 has a probability of only 86%. Thus for S–2, the hypothesis that the hardness is the same on all levels cannot be rejected. Results of the 100-gram-load tests at $D = 0$ and $D = 2.0$ μm are slightly lower and fall within a range that seems characteristic for all 100-gram tests (circle in Fig. 2).

Hardness-vs.-temperature series

With respect to the hardness-*vs.*-temperature studies, only tentative results were obtained. In Figure 3 the hardness at higher temperatures is compared to the mean value of the S–2 series at room temperature. "Fresh" fragments from the same region in the interior of the pyrrhotite specimen were used in the experiments. Annealing at temperatures up to 240°C was

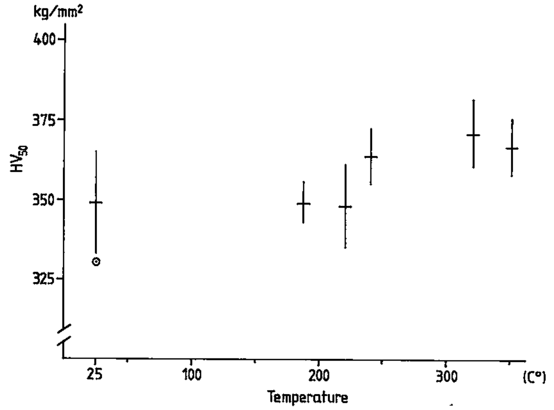

FIG. 3. The effect of annealing on the Vickers hardness in the parting surface (0001) in pyrrhotite. Circle: location of results from 100-gram-load tests. Only undisturbed indentations were used for mean values.

carried out in air. A bluish oxidized layer formed on the sample surfaces. After removal of this layer and testing with the 50-gram load, no change in hardness could be observed for the samples heated at temperatures below 240°C. The sample kept at 240°C showed a considerable increase in hardness; the difference ΔVH_{50} is $+16$ kg mm^{-2}. According to the *t* test, the significance of this difference has a probability near 90%. The two last samples, S–3 and S–5, were heated in evacuated glass tubes at 350°C for 1 hour and at 320°C for 2.5 minutes, respectively. The results at these two temperature levels do not deviate significantly from the hardness at 240°C.

X-ray-diffraction analyses revealed that annealing also effected crystal-structure changes. Between 25 and 220°C, these changes manifested themselves in a very small contraction of the unit cell parallel to the *c* axis ($\Delta c =$ -0.14% or 0.008 Å). Heating at 240°C caused no further change in the cell dimension parallel to *c* (hexagonal). After heating to 320°C for 2.5 minutes (S–5), the monoclinic phase disappeared and only the basal reflection of the hexagonal phase remained. However, after removal of about 4 μm of material, the monoclinic phase reappeared. No difference in the *c*-axis dimensions (hexagonal) of the near-surface homogeneous areas could be detected after heating.

At the highest temperature the experiment gave a completely homogenized sample. Only one basal reflection remained but at a lower Bragg angle; this observation suggests that in spite of the homogenization of the two-phase pyrrhotite, the *c* axis expanded from $c = 5.7326(5)$ to 5.7391(5) Å ($\Delta c = 0.11\%$). The trend of these changes in the *c* dimension is in agreement with the results of Taylor's (1970) investigation of the expansion of the pyrrhotite lattice with temperature.

DISCUSSION

The small but varying amounts of vacancies and the varying degrees of vacancy ordering in pyrrhotites have a pronounced influence on the physical properties of the mineral. Vaughan (1973) demonstrated a positive, linear relationship between number of vacancies and hardness of synthetic, disordered, high-temperature pyrrhotite. The series of tests S–1 and S–2 carried out in this investigation, relating hardness to depth, *i.e.*, to a compositional gradient parallel to the *c* axis in pyrrhotite, show quite different trends. The first series shows a decreasing hardness with depth, starting at the 0 level, to a lower value than in the second series. S–2, instead, seems to show no clear relation between hardness and depth. Hardness values deviating from the calculated mean value of the whole test-series are well within the region of standard deviation (Fig. 2). Thus, there is no evidence that the structural–compositional gradient influences hardness despite a variation from nearly 100% monoclinic to 100% hexagonal pyrrhotite. The pronounced X-ray line-broadening observed in the diffraction analyses on S–1 cleavage surfaces indicates that the low hardness in this series originates from a greater quantity of faults in the lattice rather than from a chemical gradient. The mean Vickers hardness obtained from series S–2 represents a value that is reproducible for all randomly chosen, freshly separated (0001) parting fragments. This value, $VH_{50} = 349 \pm 16$ kg mm^{-2}, thus seems to be the true one under prevailing conditions. Compared with hardness values obtained by other workers and with results of a large number of tests performed on polycrystalline pyrrhotite ore by the present author, the hardness in the (0001) plane obviously corresponds to the upper limit of the recorded range of hardness for low-temperature, ordered pyrrhotite.

The heating experiments revealed a sudden increase in hardness between 220 and 240°C. Such a distinct change in Vickers hardness in this temperature interval may be due to one of several structural rearrangements that occur in pyrrhotites between room temperature and about 320°C (Nakazawa & Morimoto 1971, Nakazawa *et al.* 1976). One of these rearrangements, the nonintegral repetition of the *a* *a*xis of the pyrrhotite superstructure, begins at 218°C as a progressive, continuous process. The coincidence of this structural transformation with the increase in hardness suggests that statistical disordering accounts for the higher mechanical resistance of the (0001) parting, *e.g.*, by blocking former glide planes of the ordered structure.

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