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Microhardness measurement on haematite crystals at temperatures up to 900° C

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The Vickers hardness of haematite crystals was measured at temperatures up to 900° C. In five different orientated specimens hardness decreases with increasing temperature, whereas the rate of decrease is more rapid up to 200 to 300° C than at higher temperatures. The scatter in values decreases with increasing temperature, which means that the effect of hardness anisotropy decreases at higher temperatures. Hot hardness testing promises to be very useful for geoscientific purposes and applicable to a wide range of experimental research.

1. Introduction

Data on the plasticity of crystalline solids cannot only be acquired by deformation experiments, but also by microhardness measurements. Tabor [1] pointed out the relation between shear stress, S_s, and Vickers hardness H_V

$$S_s = H_V/c$$

with $1 \leqslant c \leqslant 3$, depending on the material examined. Furthermore a strain rate of $10^{-2}\,\mathrm{sec}^{-1}$ for hardness data and a strain of 8% corresponding to the deformation of the indent can be assumed. Using this relation it is possible to plot hot-hardness data in the form of deformation-mechanism maps. To verify deformation-mechanism maps, Verral *et al.* [2] used hot-hardness data for LiF and NaCl, and Atkinson [3] used hot-hardness measurements for magnetite Fe_3O_4 [4]. Besides these, corundum Al_2O_3 [5] is the only known oxide mineral investigated by this method.

As Kollenberg and Siemes [6] pointed out, hot-hardness measurements are suitable for obtaining preliminary and supplementary information to three axial deformation experiments. The present hot-hardness data can be seen as supplementary to the experimental deformation of haematite crystals at 25, 200 and 400° C by Hennig-Michaeli and Siemes [7] and as a preliminary step before further experiments at selected temperatures.

2. Starting material

Haematite Fe_2O_3 is isostructural with corundum Al_2O_3. The haematite structure has been defined by Blake *et al.* [8]. Several crystallographic data are listed in Table I and the stereographic projection is shown in Fig. 1a.

Current knowledge of deformation characteristics has been reviewed by Siemes and Hennig-Michaeli [9]. The glide mechanisms at room-temperature are deformation twinning on $\{r\}$ and on (c) (see below). At 200° C prismatic slip $\{1\,1\,\bar{2}\,0\}\langle 1\,1\,0\,0\rangle$ becomes operative. For higher temperatures, Al_2O_3 data can be compared and it is suggested that (0 0 0 1) slip might be activated at temperatures not much higher than 400° C in Fe_2O_3.

One important advantage of microhardness testing, in general, is the possibility of using small samples and for hot-microhardness measurement – in particular, the possibility to use one specimen for a wide range of temperatures. For testing the microhardness at higher temperatures specimens should be large enough to accommodate a set of indents at several temperatures, but it also should be as small as possible to minimize heating time.

Five specimens (7 mm × 5 mm × 2 mm) with different orientations were cut from one haematite crystal from Minas Gerais, Brazil. The orientations (Fig. 1b) were checked by means of a pole figure goniometer [10]:

Specimen	Form	Index
1	r	$(0\,1\,\bar{1}\,2)$
2	e	$(1\,0\,\bar{1}\,4)$
3	$\bar{m}$	$(0\,1\,\bar{1}\,0)$
4	n	$(1\,1\,\bar{2}\,3)$
5	c	(0 0 0 1)

One plane of each specimen was polished and the surface quality was checked by interference contrast microscopy.

3. Apparatus and methods

The tests were performed at the National Physical Laboratory, Teddington, UK. The high temperature microhardness tester is designed for simultaneous viewing and has the capacity for positioning the indenter accurately on the desired regions of the specimen. The specimen can be moved between microscope and indenter, using a slide and independently by x–y shifts to position a region. It is also possible to rotate the specimen, but this cannot be done systematically. Specimen, indenter, furnaces and associated components are contained within a sealed vessel which is evacuated to protect the heated specimen, indenter and furnaces from oxidation. The two furnaces, indenter furnace and specimen furnace, are supplied with power independently by two solid state proportional controllers, normally pre-set to the same temperature. At the moment heating up to 1000° C is possible.

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TABLE I Crystallographic data of haematite [8]. Hexagonal unit cell: $a_0 = 0.504\,nm$; $c_0 = 1.377\,nm$. Space group R3c: iron 0, 0, z; $z = 0.355$; oxygen x, 0, 1/4; $x = 0.306$.

Forms	Miller–Bravais $c_0/a_0 = 2.733$	Angle to (0001) (deg)
c	(0001)	0
a	$\{11\bar{2}0\}$	90
m	$\{10\bar{1}0\}$	90
e	$\{10\bar{1}4\}$	38.3
r	$\{01\bar{1}2\}$	57.6
n	$\{11\bar{2}3\}$	61.2

The temperature of the specimen is measured by a thermocouple in direct contact with the polished surface. The indenter is driven down onto the sample by hand and the applied load is measured with a strain gauged load cell. The equipment is calibrated by comparison with indents made in a dead weight microhardness machine.

4. Experimental results

At every specimen the series of indentations started at room temperature, followed by 100° C in successive intervals of 100° C. The heating time between two temperature stages was about 30 min. At each stage at least three indents were made, which were checked by microscope. The highest temperature a haematite specimen was heated to was 900° C (Specimen 2) but it was no longer possible to produce measurable indents at this temperature.

Fig. 2 shows the Vickers hardness against temperature plots for the five different orientations. Each value represents the mean of three indents, which all have the same alignment. Anisotropy of hardness was not investigated by specimen rotation, because of the problems described above.

A load of 0.98 N was used for indentation, except in Samples 1 and 2 where 1.96 N load was applied up to 200° C. Because the hardness values at 200° C differ between 643, with a 1.96 N load applied, and 547, with a 0.98 N load applied, the subsequent series were started with a 0.98 N load, although the indents at room-temperature became small (about 13 μm diameter).

During testing specimen 3 the sample furnace broke and the test could not be continued above 400° C.

5. Discussion and conclusion

The results are summarized in Fig. 3. As expected the hardness decreases with increasing temperature, but also the scatter in data decreases at higher temperatures. These phenomena can be compared with the decreasing degree of anisotropy in hardness with increasing temperature for corundum crystal described by Burnand [5]. This is a common occurrence where the nature of anisotropy is maintained but the degree is reduced. For other materials, a reversal in the nature of hardness anisotropy, due to a change in the primary slip systems, is also known, i.e. metal carbides and rocksalt type crystals [11].

Plotting data on a logarithmic scale and comparing with other materials (Fig. 4) a typical change in the behaviour of plasticity at about 0.5 T/T_m is obvious. That is the region where diffusion-controlled processes become important. At lower temperatures, the rate-controlling mechanism is dislocation glide.

Plotting the ratio of the hardness to the shear modulus as a function of homologous temperature, Fig. 5 is obtained. Values of the shear modulus of haematite and its temperature dependence are given by Frost and Ashby [13]. Silicon is representative of covalent and copper of metallic crystals, whereas

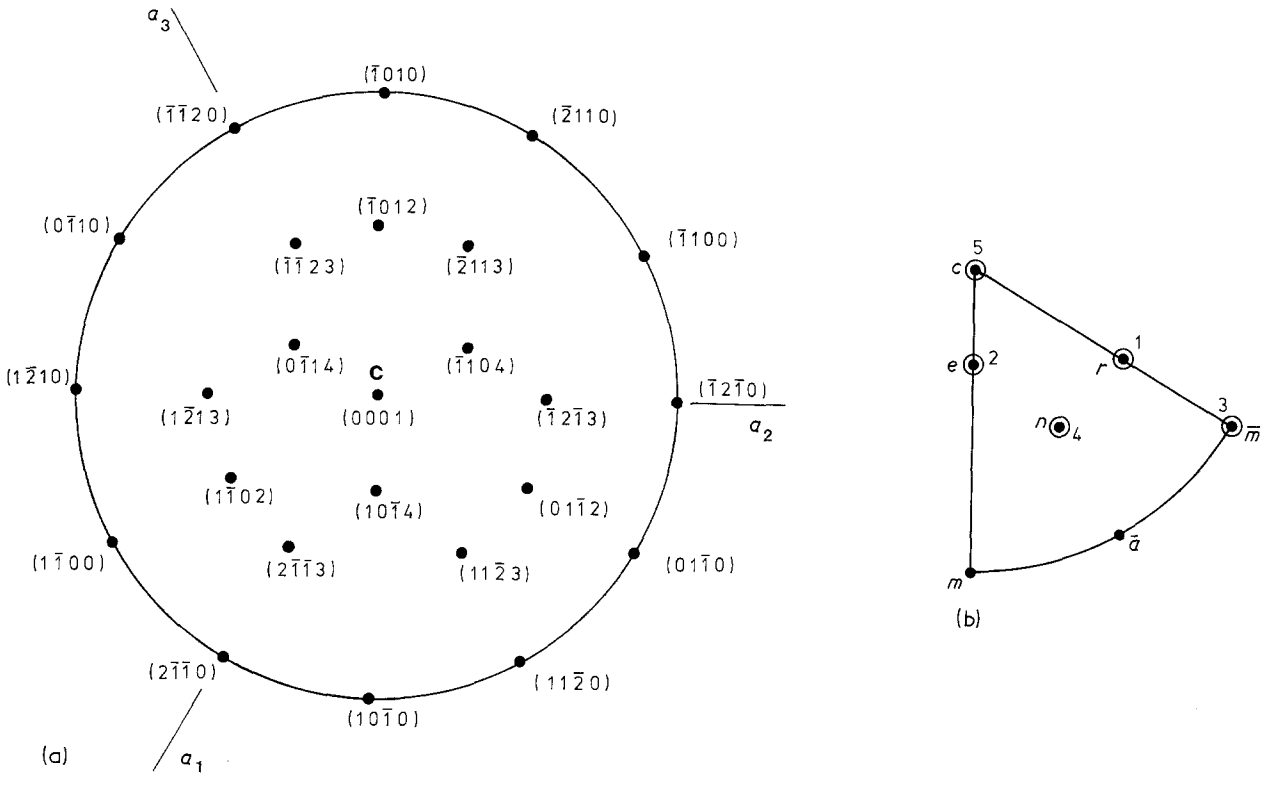

Figure 1 Stereographic projection of haematite. Upper hemisphere. (a) Structural indices. (b) Specimen orientations 1 to 5.

TiC and MgO change their behaviour at higher temperatures [14]. TiC changes from covalent at lower temperatures to metallic behaviour at higher temperatures. Ionic MgO is intermediate at low temperature, but also moves to metallic values. Haematite shows a trend similar to TiC.

This work was designed as a preliminary study of hot hardness testing for geoscientific purposes and the results show promise for a wide range of applications. For haematite, further investigations by mean of deformation experiments are necessary in the range 100 to 300° C and above 700° C.

An interpretation of operative deformation mechanisms during indentation could only be a theoretical

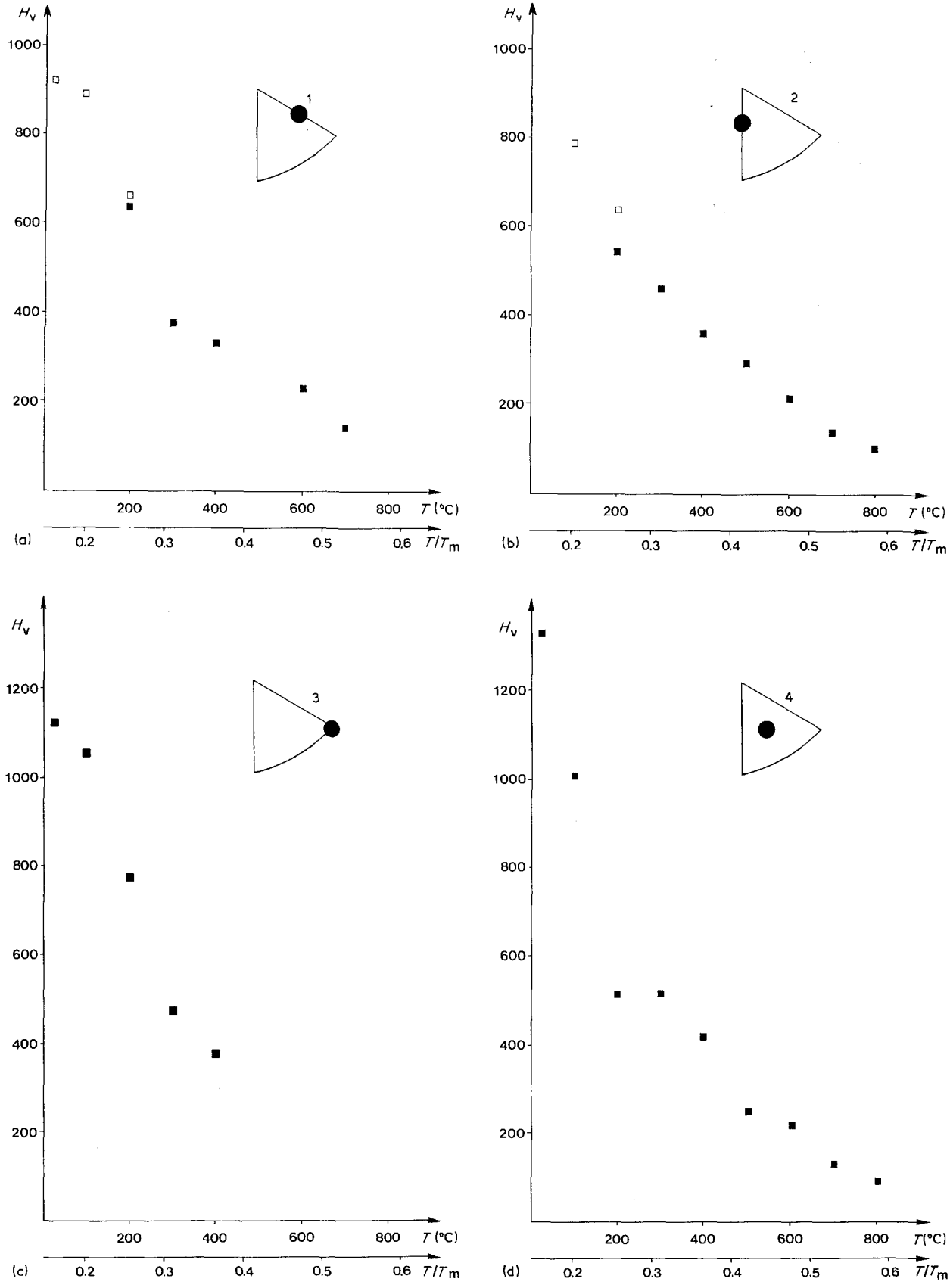

Figure 2 Plots of Vickers hardness against temperature for five investigated specimens of different orientations. (□) 0.98 N load applied, (■) 1.96 N load applied.

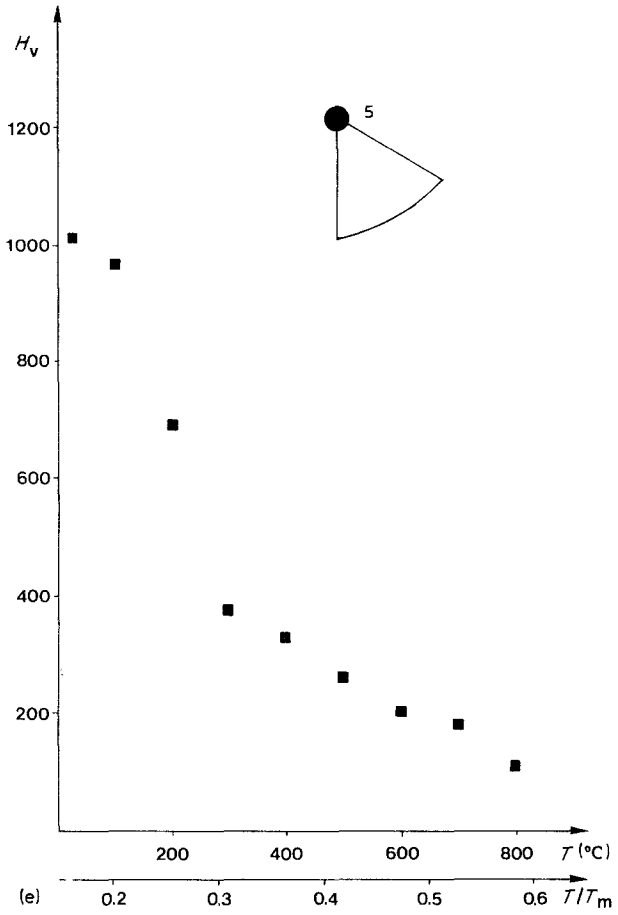

Figure 2 Continued.

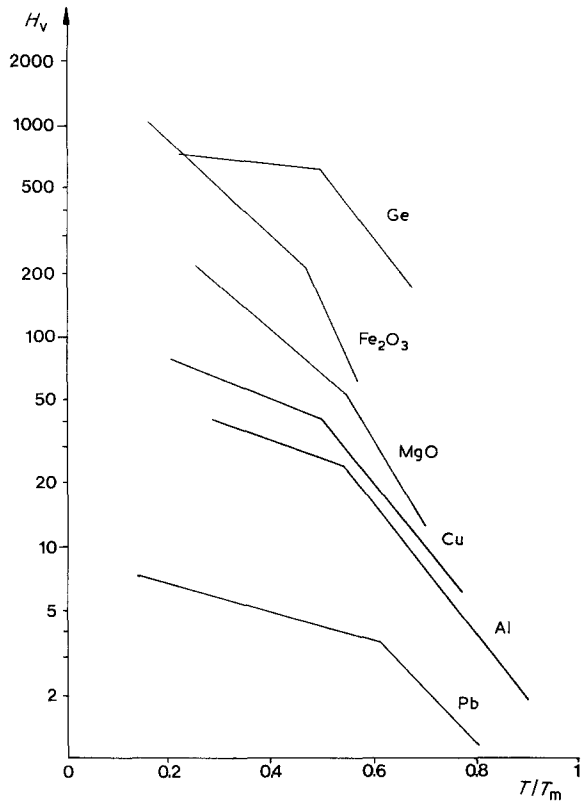

Figure 4 Effect of temperature on the indentation hardness of different materials. Results for Ge, MgO, Cu, Al and Pb referred by Atkins and Tabor [12].

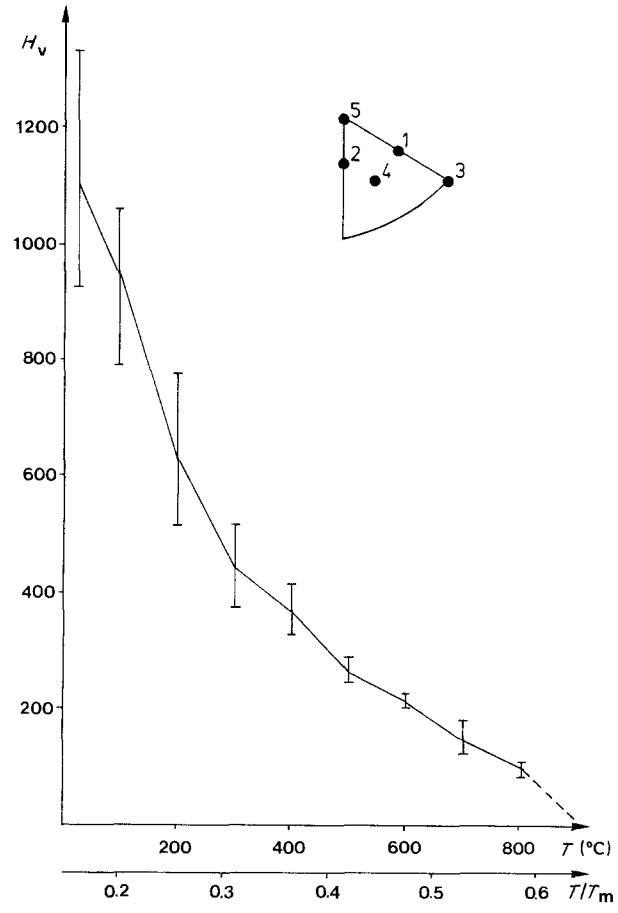

Figure 3 Mean Vickers hardness and scattering of data plotted against temperature for five investigated specimens of different orientations.

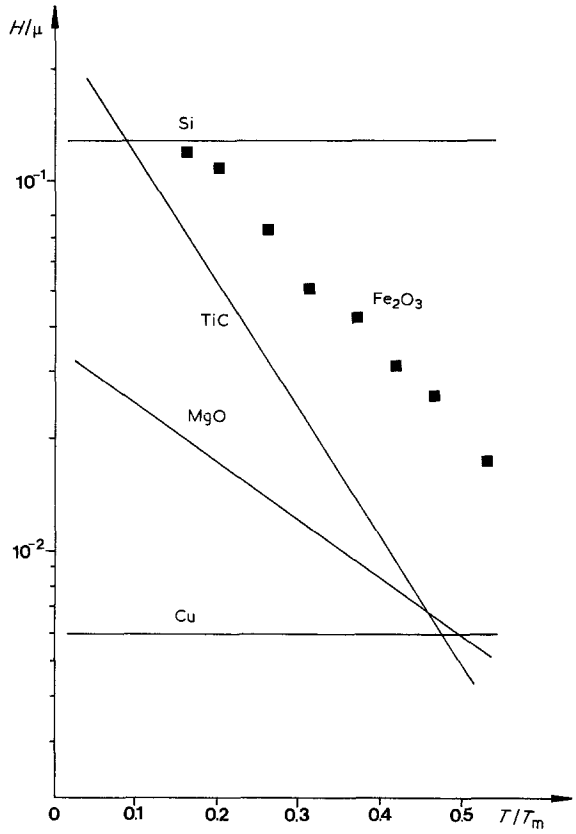

Figure 5 Ratio of hardness to shear modulus as a function of homologous temperature. Data for Si, TiC, MgO and Cu taken from Chin [14].

consideration and is therefore neglected in this study. Further investigations are designed to define the activated mechanisms more closely; the comparison to isostructural corundum, in particular, will be discussed in detail.

The effect of hardness anisotropy must also be studied using a KNOOP-indenter.

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