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Vickers Indentation Hardness of Stoichiometric and Reduced Single Crystal TiO_2 (Rutile) From 25 to 800 °C

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SUMMARY

The indentation microhardness of stoichiometric and reduced single crystal rutile (TiO_2) from 25 to 800 °C is presented in this paper. The results serve two main purposes. One is to assess the effect of rutile's stoichiometry on its hardness. The other is to test recently suggested theory on solid lubrication with sub-stoichiometric rutile in an effort to better understand shear controlled phenomenon.

Microhardness was measured using a Vickers diamond indentor on both vacuum and hydrogen reduced single crystal rutile from 25 to 800 °C. The results indicate that stoichiometry and temperature have a pronounced effect on rutile's hardness. The measured effects lend support to theory on solid lubrication by enhanced crystallographic slip which suggest that solid lubricant materials may be produced by careful atomic level tailoring (stoichiometry control).

INTRODUCTION

The identification and development of solid lubricants for high temperatures have been characterized by chance discovery through mostly trial and error testing. This serendipitous approach has produced many good lubricants for limited applications; products such as intercalated graphite, MoS_2, WS_2, PbO, and others (refs. 1 to 3). New technologies, however, have accentuated the need for better solid lubricants. For example, low heat rejection engines demand lubricants for temperatures up to 760 °C (ref. 4). Other national development programs such as the National AeroSpace Plane (NASP) require lubricants for airframe and engine seals capable of withstanding temperatures nearing 1000 °C (ref. 5). For these extreme environment applications, current solid lubricant technology is inadequate. None of the available lubricants are fully satisfactory and new ones must be identified and developed.

The development process, however, is hindered by our limited fundamental understanding of how and why solid lubricants function. Currently accepted theories suggest that plastic shearing of an interfacial layer between moving surfaces, a "third body," controls friction and wear. A good solid lubricant provides a low shear strength film that shears easily yet provides separation of moving surfaces to mitigate wear (refs. 6 and 7). Since a material's hardness is often related to its shear properties, hardness, especially at anticipated use temperature, can be used as a first order assessment of a materials lubricating properties.

An emerging theory on solid lubrication asserts that the shear strength of material can be controlled through its crystal structure. This implies that a material not normally considered a lubricant can be made into a lubricant by altering its atomic structure in such a way as to activate low shear strength slip planes (ref. 8). Demonstrating this effect may give insight regarding the nature of solid lubrication. Improved lubricants and lubricant development may also result from such understanding.

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In references 8 to 10, it was proposed by Gardos that TiO_2 (rutile) can be made to function as a solid lubricant if low shear strength slip planes are activated through anion vacancy creation. That is, nonstoichiometric rutile (TiO_{2-x}) can be made to have low shear strength and act as a solid lubricant. In addition, he proposed that certain stoichiometries may also have high shear strength and act as an abrasive. Testing this assertion requires that carefully prepared, various nonstoichiometric rutile be formulated and tribologically tested. However, typical friction and wear measurements can be exceedingly difficult to make and compounded by mitigating factors such as adsorbed surface contamination, counterface effects, and the potential for stoichiometry changes during testing especially in high temperature air. Therefore, a more controlled method to measure shear properties is required.

In references 8 and 9 a variable temperature vacuum tribometer integrated in an SEM was used to measure the effects of a reducing environment (high temperature vacuum) on the friction of rutile. Preliminary results suggested that the shear properties (friction coefficients) are affected by the environmental reduction. The results, however, were qualitative in nature because the stoichiometry of the tested rutile specimens was unknown.

Microindentation hardness is also suitable for the assessment of shear properties. Since indentation results in a permanent deformation of a thin surface layer, indentation hardness can be related to shear strength and, potentially, lubrication capabilities (refs. 11 and 12). Measuring the indentation hardness of rutile with various stoichiometries, thus, may be indicative of its potential to act as a solid lubricant.

The goal of this report, therefore, is to present data on the hardness of stoichiometric and nonstoichiometric rutile over a wide temperature range. The data may then be used to assess rutile's capability as a solid lubricant. To meet this objective, suitable rutile specimens were reduced in hydrogen gas and vacuum at temperatures to 900 °C for periods up to 40 hr. The reduced rutile samples were then hot-hardness tested from 25 to 800 °C. In addition to assessing the effect of rutile's stoichiometry on its hardness, the data helps test recently suggested theory on solid lubrication with substoichiometric rutile. Through this work, a better understanding of shear controlled phenomenon and solid lubrication may be developed.

MATERIALS

Commercially available single crystal rutile boules were diamond cut and polished into crystallographically oriented 5- by 5- by 10-mm bars. Hardness indentations were made into the (110) surface by a method described later in this report. Typical impurities in the specimens are given in table I. Figure 1 shows, schematically, the orientation of the samples as determined by Laue x-ray diffraction techniques.

APPARATUS/PROCEDURES

Hardness Measurement

High temperature hardness measurements were made using a commercial test machine equipped with a vacuum chamber and pumping system, separate Vickers pyramidal indenter and specimen furnaces with variable temperature set point controllers, an optical microscope indent measuring system, and an automatic indentation mechanism. The diamond tip was mechanically embedded in a high temperature tantalum alloy holder. This holder is threaded for attachment to the loading mechanism. The holder also contains a thermocouple for temperature measurements and thermal control of the indenter.

A typical measurement was made as follows: first, the 5- by 5- by 10-mm bar specimen was installed in the specimen furnace and then the chamber was evacuated to a pressure of 8×10^{-5} to 1×10^{-4} torr prior to being backfilled and purged with the helium at 2.5 psi. The specimens were heated to the maximum desired temperature and when this temperature was reached and maintained for 10 to 15 min, a series of five or more indents were made and the diagonals measured. The temperature was then lowered on each furnace and allowed to stabilize for 5 to 10 min and another set of indents was made. The hardness was determined for each set of indent diagonal measurements and the average hardness for all measurements was calculated and reported in units of kg/mm^2 (1 kg/mm^2 = 9.807 MPa). The standard deviation for each hardness set was then calculated. The temperature of the indenter was always kept within 5 °C of the specimen to minimize the influence of the indenter temperature on the specimen temperature. An indenter travel rate of 0.5 mm/sec, a dwell time of 10 sec and a load of 200 g (2.0 N) were used.

The single crystal rutile samples were rendered oxygen-deficient by reducing them in hydrogen gas or in a vacuum at elevated temperatures. The samples reduced in H_2 gas were placed in a controlled atmosphere tube furnace. The hydrogen reduction furnace was heated rapidly (10 °C/min) while purging with argon until the desired reduction temperature was reached. When the desired reduction temperature was reached, hydrogen gas was introduced into the furnace for various time periods ranging from 1 to 4 hr. For those samples reduced in vacuum, the rutile crystals were placed in the vacuum chamber of the hardness tester and simultaneously heated for the times indicated up to 40 hr, at approximately 10^{-5} torr. A liquid nitrogen cold trap helped prevent surface contamination by volatile condensibles.

Stoichiometry Measurement

The stoichiometry of the reduced rutile crystals was estimated using an Energy Dispersive X-ray Spectrometer integrated with a Scanning Electron Microscopy (SEM/EDS). The EDS system uses a windowless detector to be able to detect an average oxygen content to a depth of approximately 1 μm based upon the sample characteristics (e.g., sample atomic number and beam voltage).

RESULTS

The results of the hardness measurements are shown in figures 2 to 5. Figure 2 shows the indentation microhardness of H_2 reduced rutile as a function of stoichiometry (O/Ti ratio) at 25 to 500 °C. At an O/Ti ratio of 1.85, the data show a maximum hardness of 1500 kg/mm^2 at 25 °C and 1100 kg/mm^2 at 500 °C. It was observed during hydrogen reduction of the samples that specimens with O/Ti ratios greater than about 1.85 had a thin, visible noncontinuous precipitate phase on the surface. Those specimens with O/Ti ratios less than about 1.85 have a visible but thicker continuous precipitate phase on the surface. These surface phases may have had an effect on the hardness.

Figure 3 shows the hardness as a function temperature for fully stoichiometric and hydrogen reduced rutile at two stoichiometries, an O/Ti ratio of 1.85 and 1.91. For this limited stoichiometry range, the hardness decreases with temperature and O/Ti ratio.

Figure 4 is a plot of the hardness of a single rutile crystal specimen after vacuum reduction at 800 °C. The hardness values were made during the vacuum reduction at 800 °C.

Initially, the crystal was fully stoichiometric and was off-white and opaque in color. After 40 hr in vacuum ($\approx10^{-5}$ torr) at 800 °C the surface turned blue-black in color indicating that its stoichiometry (O/Ti ratio) was approximately 1.96 (ref. 8). The hardness of the sample initially increased during the

first 6 hr of reduction. After this point, however, the hardness remained more or less constant (within data scatter) for the rest of the test period.

Figure 5 shows the effect of indentor orientation with respect to the crystal specimen's C-axis on the room temperature hardness. There is a slight effect of indentor orientation on hardness. The hardness values at 0° and 90° are not exactly equivalent indicating that the pyramid indentor was not perfectly symmetrical. However, to minimize error, all of the hardness measurements reported in this paper were made with the same indentor orientation.

DISCUSSION

The data suggest that the hardness of rutile (and presumably its shear properties) is effected by the stoichiometry. Reduction of rutile, that is, the creation of oxygen vacancies, causes an increase in indentation hardness down to an O/Ti ratio of about 1.85. Stoichiometries (O/Ti ratio) lower than about 1.85 cause significant softening of the material. Therefore, control of rutile's shear properties necessitate careful tailoring and control of its stoichiometry.

The effect of temperature on hardness can be seen by examining figures 2 and 3. In each case, increasing temperature causes a commensurate decrease in hardness. This is likely due to the enhanced atomic mobility and active slip systems available for plastic deformation during indentation.

One clear finding of this work is that the stoichiometry of rutile is very sensitive to environmental factors. Indeed, it is this sensitivity that was capitalized upon to alter the stoichiometry using vacuum and hydrogen reduction. Figure 4 shows that even mild vacuum heating (10^{-5} torr) at 800 °C is sufficient to change the crystal hardness (and presumably stoichiometry). The data indicate that the hardness initially increases over the first 6 hr of reduction and then levels off. The stability reached in the measured hardness implies that the stoichiometry has also stabilized. This stabilization suggests that, under these conditions, an equilibrium is reached between vacancy creation (oxygen removal by the vacuum environment) at the surface and oxygen replenishment via transport (diffusion) from the fully stoichiometric bulk to the surface region. Therefore, it is reasonable to expect the hardness (stoichiometry) to level off under these conditions.

It is difficult to estimate specific shear strength values from the hardness data presented in this report. Several significant experimental uncertainties exist. One is the effect of indentor orientation depicted in figure 5. Because differing shear planes in rutile have differing shear strengths, it was expected that indentor orientation (since the indentor has a pyramidal shape) would have an effect on the measured hardness values. However, the observation that the hardness values at orthogonal indentor orientations (i.e., points A and D, 0° and 90° with respect to the crystal's C-axis respectively) are not equivalent suggests that the indentor is not perfectly symmetrical. It may also be true that the indentor surface features (e.g., roughness, imperfections, etc.) are not uniform. No attempts were made in this work to characterize the indentor. Nonetheless, this experimental uncertainty hinders the direct correlation of this data to shear strengths. Figure 3 further illustrates this point by showing that literature values for the hardness of fully stoichiometric rutile differ those measured here by about 20 percent. This, however, may be due to the nature of the specimens (the literatures values were from polycrystalline TiO_2).

Another experimental uncertainty arises from the nature of the reduced crystal surfaces. Rather than being comprised of a uniform surface region of reduced stoichiometry, the reduced crystals are more likely made up of a surface region with a stoichiometry gradient. The surface, due to the diffusion nature of the reduction, would be the most highly reduced while deeper into the crystal the O/Ti ratio is expected to

be stoichiometric. Compounding this uncertainty, both the microhardness indentor and the SEM's analytical electron beam penetrate into the bulk of the crystal to a differing extent. Based upon a "Monte Carlo" simulation, the estimated penetration depth of the electron beam (which is the basis for the stoichiometry analysis) is approximately 1.1 μm. The penetration depth of the microhardness indentor varies from about 3.5 to 7 μm depending on the crystal hardness. Therefore, both the stoichiometry measurement and the microhardness are "averaged" over different surface region layers in the specimen. These differing analysis depths make direct comparison of the measured stoichiometry and hardness difficult.

These points are important to consider when interpreting the results of this work. Notwithstanding, the trends measured here, for example, hardness decreasing with temperature and increasing with reduction (down to O/Ti ratios of $\approx$1.85) may give guidance to understanding the nature of shear and solid lubrication.

CONCLUSIONS

1. The stoichiometry of single crystal rutile has a pronounced affect on its microindentation hardness. This measured effect lends support to the theory by Gardos and aids in the fundamental understanding of solid lubrication phenomena.

2. The relation between rutile hardness and stoichiometry is complex; the creation of anion vacancies is accompanied initially by an increase in hardness followed by a decrease in hardness which may be due to the sequential deactivation and activation of progressively changing crystallographic slip systems.

3. Although critical experimental issues, such as stoichiometric gradients and measurement uncertainties, make direct correlation between hardness and stoichiometry difficult, the trends in the data may lend insight into the understanding of solid lubrication.

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TABLE I.—TYPICAL IMPURITY CONTENT OF U.S.-MADE XTL RUTILE BOULES GROWN BY THE VERNEUIL PROCESS (IN PARTS-PER-MILLION)

Impurity / Manufacturer	Sn	Ca	Mg	Al	Fe	Cu	Si	Ni	Mn	Cr	V	Ag
Johnson-Mathey	12	12	20	0.20	8	1	0.60	3.4	5.2	1	5	0.3
Linde	0	10	12	0.11	5	0.7	0.30	3.0	4.5	1	5	0.3

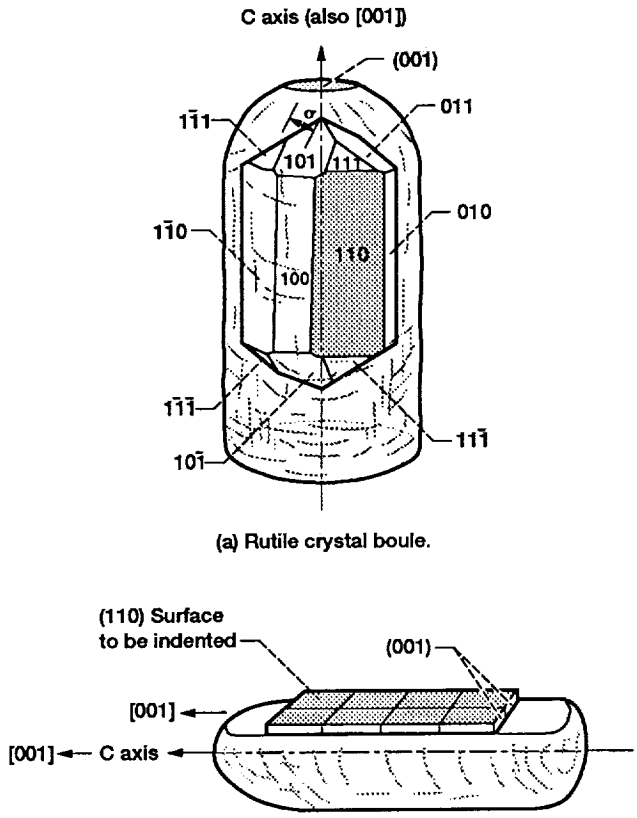

Figure 1.—Crystallographic planes and directions in an idealized rutile boule. Note: (110) surface is indentation hardness (Vickers) tested in this paper.

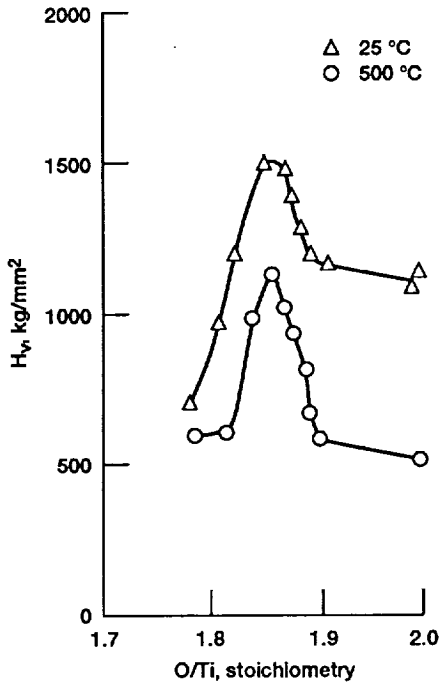

Figure 2.—Indentation microhardness (H_v in kg/mm^2) of hydrogen reduced (at 800 °C) rutile (110) surface as a function of stoichiometry (O/Ti ratio).

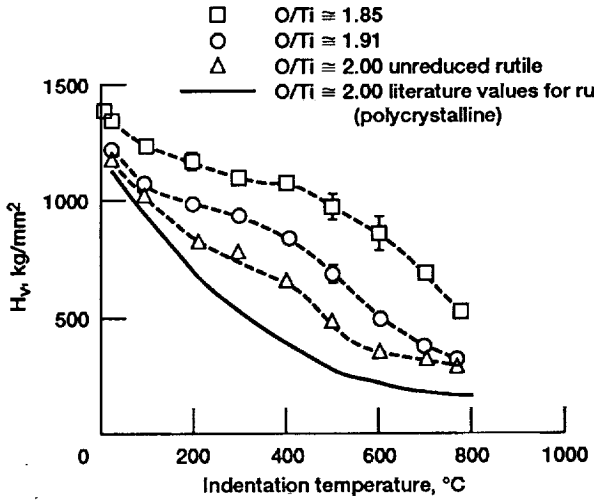

Figure 3.—Indentation microhardness for reduced (in H_2 at 800 °C) and stoichiometric rutile (110) surface as a function of indentation temperature. Error bars (where shown) represent one standard deviation of at least six indents. Where not shown, error bars are approximately equal to symbol size.

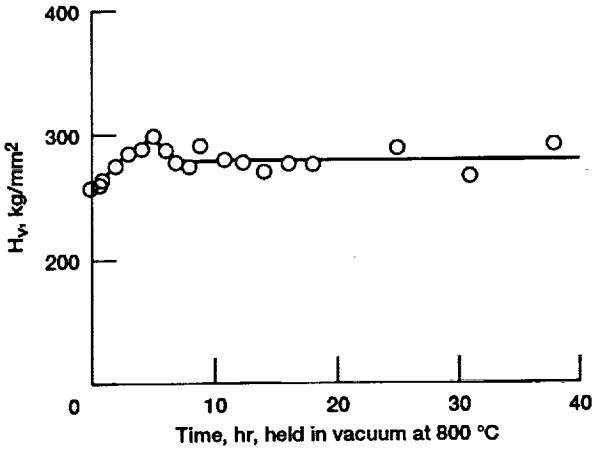

Figure 4.—Indentation microhardness of rutile (110) surface during thermal exposure to vacuum (10^{-5} torr) at 800 °C. Note that hardness increases slightly during initial exposure (reduction) then remains fairly constant over test period.

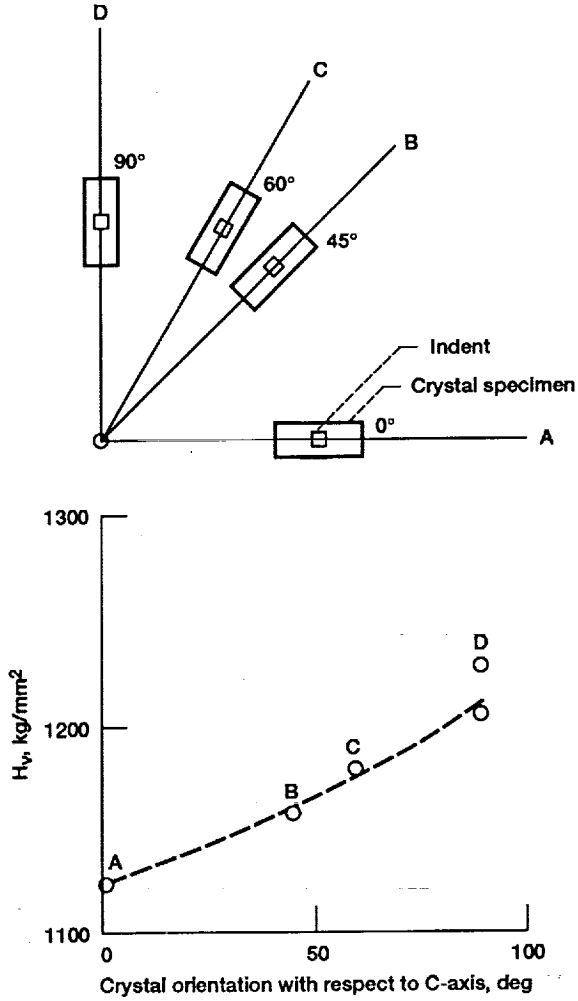

Figure 5.—Effect of indentor orientation on microhardness at room temperature. Difference in microhardness between A (0°) and D (90°) may indicate non-symmetrical indentor.

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13. ABSTRACT (*Maximum 200 words*)

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