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Deformation by moving interfaces (deformation twinning) in monoclinic zirconia (Baddeleyite)

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Abstract—Deformation in many crystalline solids can occur by the motion of glissile interfaces. Martensitic phase transformations and deformation twinning are the most important such processes, and compete with conventional dislocation motion for inducing plastic deformation. The formation and migration of such glissile interfaces is important, not least because their motion can be induced on occasion at stresses much lower than those needed for dislocation generation and motion. A description of deformation twinning in formal terms using a matrix algebraic format will be presented and applied to twinning around microhardness indents in synthetic monoclinic ZrO_2 (Baddeleyite) single crystals.

INTRODUCTION

Plastic deformation of crystalline solids at low temperatures often occurs by the formation of a new phase or by the nucleation and growth of twins, as low temperatures can render dislocation generation and motion difficult. Such deformation processes involve the formation and movement of glissile interfaces. For example, many minerals respond to applied stresses by deformation twinning, or undergo a martensitic transformation, a closely related process.

It is clearly of interest to predict and understand the incidence of deformation twinning in various stress fields; in fact, this is readily achieved using a matrix algebraic approach (Christian 1982). In this paper, we review Christian's work along these lines and apply them to twinning in monoclinic zirconia (m-ZrO_2 or Baddeleyite). We follow Christian's derivations in detail.

The approach considers the interface as a surface defect and represents it by the shape deformation tensor **E**, and its orientation by the unit vector normal **n**. In the absence of lattice dislocation movement, if two orientations remain in contact at the interface **n** and this interface migrates toward its normal, the inelastic shape change must be an invariant plane strain; it may, however, incorporate small elastic strains. Figure 1 shows that this invariant plane strain can be realized as a combination of a simple shear s**d** and a uniaxial expansion or contraction ξ**n** normal to this plane.

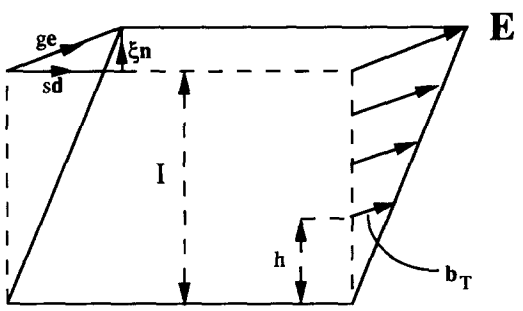
Although the overall deformation process is represented by **E**, the actual mechanism is very sensitive to the fine-scale atomic structure of the interface. Incoherent, semi-coherent and coherent interfaces may arise in these processes; for the sake of simplicity, we shall consider here only the case of the coherent interface. For this situation, the invariant plane is termed the composition plane and is more commonly referred to as K_1.

Deformation twinning involves a homogeneous simple shear of a parent lattice to produce a volume of material with a different crystallographic orientation. Type I twins require that K_1 be rational. Twins have a characteristic minimum spacing h over which stress occurs, as shown in Fig. 1. A twinning mode with a shear of magnitude s in the direction **d** (**d** is more commonly referred to as η_1 in the deformation twinning literature) would therefore lead to the following successive displacements of parallel K_1 planes:

$$\mathbf{b}_T = sh\mathbf{d}, \tag{1}$$

where $\mathbf{b}_T$ is less than an interatomic spacing.

This displacement appears as a mistake in the stacking sequence along **n** and may remain as a single-layer, metastable stacking fault. Any type I twin may thus be described as an array of successive stacking faults. The edge of any fault of finite thickness may be thought of as a glissile partial dislocation with Burgers vector, $\mathbf{b}_T$. The passage of dislocations of this type through successive K_1 layers will lead to the growth of the twin; again, this growth is in the direction of **n**, the normal to the twin plane. This partial dislocation has been termed a twinning dislocation and has been discussed elsewhere



$$\mathbf{ge} = \mathbf{sd} + \xi\mathbf{n}$$
$$\mathbf{E} = \mathbf{I} + \mathbf{gen}'$$
$$\mathbf{b}_T = \mathbf{hge}$$

Fig. 1. Schematic diagram of a general invariant plane strain deformation. The ξ term is zero for deformation twinning.

(Frank & Van der Merwe 1949). An interface containing a partial dislocation has associated with it a long-range stress field, whereas the purely coherent K_1 interface does not. The twinning dislocation will consequently lead to a step in the interface.

CHARACTERISTICS OF INVARIANT PLANE-STRAIN DEFORMATION

The invariant plane strain shown in Fig. 1 is represented by the matrix

$$\mathbf{E} = \mathbf{I} + s\mathbf{dn}' \tag{2}$$

for the case of deformation twinning (Christian 1982). Here, $\mathbf{I}$ is the unit matrix with components δ^i_j, $\mathbf{d}$, is a column matrix formed from the contravariant (direct lattice) components d^i of the unit vector $\mathbf{d}$, and $\mathbf{n}'$ is the unit normal to the variant plane. We shall adhere with Christian's (1975) notation and also use an orthonormal coordinate system and the standard matrix notation, where $\mathbf{u}'$ and $\mathbf{S}'$ represent the transposes of the 3×1 and 3×3 matrices $\mathbf{u}$ and $\mathbf{S}$, respectively, $\mathbf{S}^{-1}$ is the matrix reciprocal to $\mathbf{S}$ and the deformation tensor $\mathbf{S}$ converts a vector $\mathbf{u}$ into a new vector $\mathbf{S}\,\mathbf{u}$ and a plane normal $\mathbf{h}'$ into a new normal $\mathbf{h}'\,\mathbf{S}^{-1}$.

The inverse, or reverse, deformation process is also an invariant plane strain and is represented by

$$\mathbf{E}^{-1} = \mathbf{I} - f\mathbf{dn}', \tag{3}$$

where $f = s$. All planes that are parallel to the zone axis $\mathbf{d}$ have normals which are invariant.

The only vectors which are invariant are contained in the composition plane $\mathbf{n}$, but there is a second plane which remains undistorted during deformation twinning. Similarly, there is a second zone axis of undistorted plane normals. These are typically referred to as K_2 and η_2, respectively, but will be termed $\bar{\mathbf{n}}$ and $\bar{\mathbf{d}}$ here for consistency; they are represented as follows:

$$\bar{\mathbf{n}} = (4 + 4s\mathbf{n}'\mathbf{d} + s^2)^{-1/2}(2\mathbf{d} + s\mathbf{n}) \tag{4}$$

and

$$\bar{\mathbf{d}} = (4 - 4f\mathbf{n}'\mathbf{d} + f^2)^{-1/2}(2\mathbf{n} - f\mathbf{d}). \tag{5}$$

The vectors $\mathbf{n}$, $\bar{\mathbf{n}}$, $\mathbf{d}$ and $\bar{\mathbf{d}}$ all lie in the plane S which is termed the plane of shear, as shown in Fig. 2. A rotation

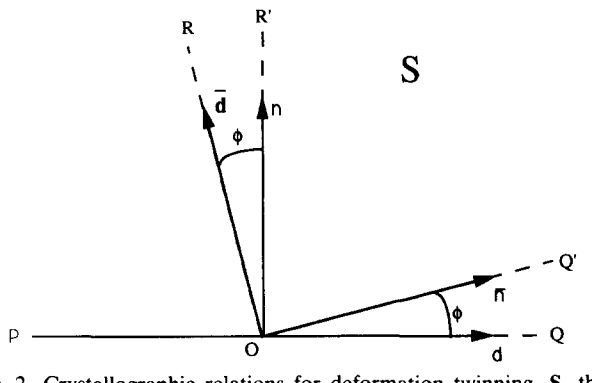


Fig. 2. Crystallographic relations for deformation twinning. S, the plane of shear, is the plane of the paper and contains $\mathbf{n}$, $\bar{\mathbf{n}}$, $\mathbf{d}$ and $\bar{\mathbf{d}}$.

$\bar{\mathbf{R}}$ about the normal to S through an angle θ will restore $\bar{\mathbf{n}}$ and $\bar{\mathbf{d}}$ to their original positions. It follows that

$$\cos\theta = \cos 2\phi = 1 - \tfrac{1}{2}s^2\cos^2\phi \tag{6}$$

which defines θ in terms of the original parameter s. The deformation $\bar{\mathbf{E}} = \bar{\mathbf{R}}\mathbf{E}$ represents the same invariant plane strain that was considered on the composition plane $\mathbf{n}$. The roles of $\bar{\mathbf{n}}$ and $\bar{\mathbf{d}}$ are now analogous to those of $\mathbf{n}$ and $\mathbf{d}$, respectively. It follows that, since deformation twinning is a simple-shear process, equation (6) may be rewritten as

$$\cos\theta = (4 - s^2)(4 + s^2)^{-1};\ \tan\phi = \tfrac{1}{2}s. \tag{7}$$

As many minerals have several twin systems which can be activated, it is often useful to be able to predict which system may be active under a given set of experimental conditions. For this, it is useful to first consider the strain produced by deformation twinning. The shape deformation tensor $\mathbf{E}$ will produce a net expansion or contraction which can be derived as follows. A general unit vector $\mathbf{x}$ is transformed into $\mathbf{x} + (s\mathbf{d})\,\mathbf{n}'\mathbf{x}$. If we define χ_o as the angle between $\mathbf{x}$ and the invariant plane, this can be rewritten as $\mathbf{x} + (s\mathbf{d})\sin\chi_o$. The square of the new length becomes $(1 + 2s\sin\chi_o\cos\lambda_o + s^2\sin^2\chi_o)$, as the square of the initial length $\mathbf{x}$ is $\mathbf{x}'\mathbf{x} = 1$; λ_o is the initial angle between $\mathbf{x}$ and $\mathbf{d}$. For a certain orientation defined by χ_o and λ_o, the ratio of the final and initial lengths along the axis of orientation is

$$\frac{l}{l_o} = \{1 + 2s\sin\chi_o\cos\lambda_o + s^2\sin^2\chi_o\}^{1/2} \tag{8}$$

and the strain ε is $\Delta l/l_o$. Equation (8) represents the fractional change in length during uniaxial tension or compression of a sample which is totally transformed into its twin. This is a generalization of the case first put forth by Schmid & Boas (1950) for a simple-shear process, which allows for both twinning and slip. The above derivation requires that the ends of the specimen remain in alignment; in practice, the specimen ends will bend to accommodate the slight change in orientation and are not considered in this treatment. Furthermore, in many experimental tension or compression setups, the ends of the sample are fixed by the experimental equipment; different expressions are needed to treat the strains involved in this situation and are not considered here.

Equation (8) indicates that a specimen will increase in length if the following criterion is met

$$\frac{\cos\lambda_o}{\sin\chi_o} > -\tfrac{1}{2}s. \tag{9}$$

Comparison with equation (4) indicates that this requires the projection of $\mathbf{x}$ onto S to lie within the region QOR in Fig. 2. If a specimen orientation defined by the vector $\mathbf{x}$ ($\mathbf{x}$ being the specimen crystallographic axis which coincides with the experimental compression or tension axis) is such that its projection lies within the region POR in Fig. 2, twinning of such samples will lead to a decrease in sample length. Some of these vectors (those within ϕ of $\mathbf{n}$) will initially decrease in length and

then increase. The overall condition for an increase in specimen length is

$$\frac{\cos\lambda_o}{\sin\chi_o} > 0. \quad (10)$$

If s^2 is small in comparison with s, equation (8) may be simplified to give ε as follows

$$\varepsilon = \frac{\Delta l}{l_o} \approx s \sin\chi_o \cos\lambda_o. \quad (11)$$

It follows that, for a certain orientation, the twin system which maximizes the change in length along the tension–compression axis should be that system for which the twinning Schmid factor (i.e. $\sin\chi_o \cos\lambda_o$) is the greatest. In other words, the maximum useful work that can be done in a given stress field will be by operation of that system which has the largest Schmid factor.

EXPERIMENTS

Single crystals of flux-grown m-ZrO_2 were used to study deformation at room temperature. Calculations of Schmid factors were performed to predict which twin system(s) might be activated during Vickers diamond indentation experiments; samples containing vicinal (100) growth planes were ground and polished to a 1 μm finish using diamond paste. A Vickers microindenter (4.9 N) was used to introduce localized deformation into the (100) sample surface.

Optical microscopy was used to observe the macroscopic deformation associated with the indents, while transmission electron microscopy (TEM) was used to analyze the microscopic deformation mechanisms in the deformed region surrounding the indent.

CRYSTALLOGRAPHY OF BADDELEYITE (m-ZrO_2)

Baddeleyite (m-ZrO_2) (Fig. 3) has the space group P $2_1/c$; its unit cell parameters are as follows: $a = 0.515$ nm, $b = 0.520$ nm, $c = 0.532$ nm and $\beta = 99.38°$.

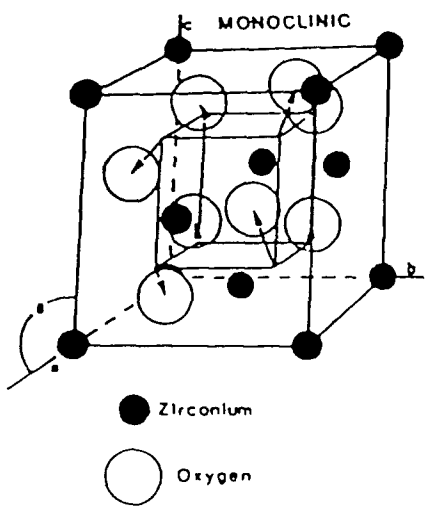


Fig. 3. Schematic diagram of the m-ZrO_2 crystal structure.

Table 1. Twinning elements for monoclinic zirconia, m-ZrO_2 (Bischoff & Rühle 1983)

K_1	η_1	K_2	η_2	s
100	001	001	100	0.328
110	$1\bar{1}8$	$1\bar{1}25$	110	0.228
$1\bar{1}0$	118	1125	$1\bar{1}0$	0.228
011	$251\bar{1}$	$81\bar{1}$	$0\bar{1}1$	0.228
$0\bar{1}1$	$25\bar{1}1$	$8\bar{1}\bar{1}$	$0\bar{1}1$	0.228
001	100	100	001	0.328

Monoclinic ZrO_2 twins according to the several sets of twinning elements listed in Table 1 (Bischoff & Rühle 1983); the most common system involves (100), while twinning on {110} was most prevalent during these indentation studies. The twinning elements listed for all the twin systems in Table 1 are plotted in the (100) stereographic projection shown in Fig. 4. The geometry of the {110} twin elements in relation to the m-ZrO_2 unit cell is depicted in Fig. 5. Here, the (100) indentation plane is in the plane of the paper.

RESULTS

The stress field associated with the diamond indenter is much more complex than the situation encountered in a simple compression or tensile experiment (Marshall & Lawn 1979, Chiang *et al.* 1982), and calculation of Schmid factors for a given twinning law is complicated. McColm (1990, p.111) has treated a simplified case and modelled the indenter geometry as a long, flat punch. While this approach gives an indication of the shear stress involved in indentation, it does not allow a ready comparison of Schmid factors for random orientations compared to specific twins around the indenter. However, a simple, more general approach can be used,

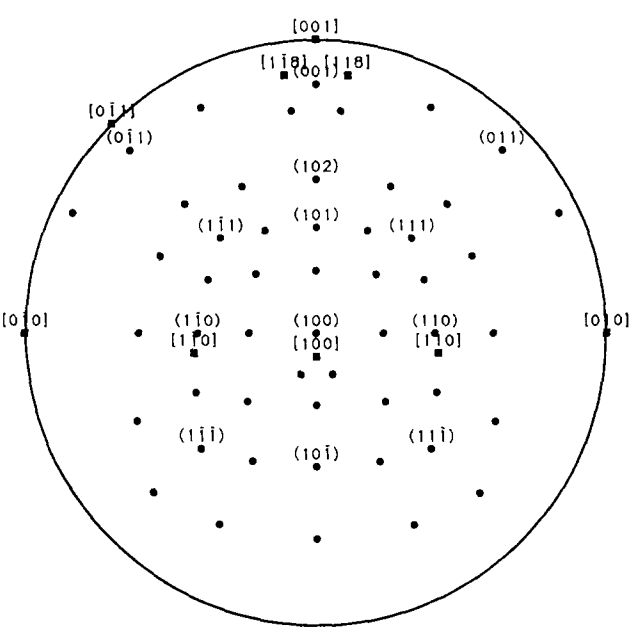


Fig. 4. (100) stereographic projection indicating the twinning elements known for m-ZrO_2.

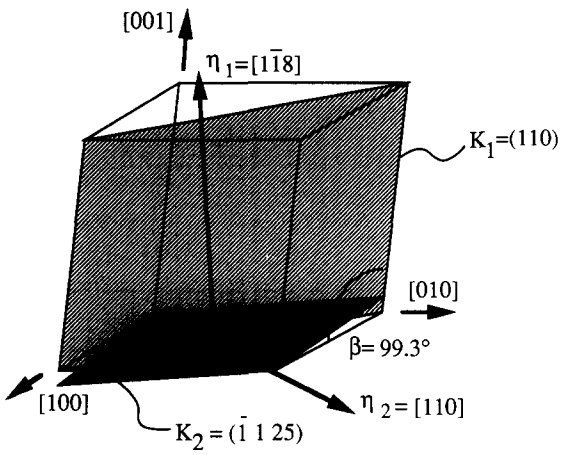


Fig. 5. Elements of twinning for the (110) twin system for m-ZrO_2.

which only assumes that there is a state of radial compression and tangential tension around the indent. Compression axes are thus assumed to emanate radially from the indent, and are further contained within the surface. Schmid factors can then be calculated for a given set of twin elements and the assumed compression axis, given that the sample surface is (100).

As indentations were made on the (100) plane, Schmid factors for the twinning elements of Table 1 have been tabulated for a number of possible compression axes contained within the (100) plane. All Schmid factors for the K_1 = (100) system are zero, as the angle between the normal to K_1 and any of the possible compression axes is 90°. For the systems with K_1 = (001), (011) and (0$\bar{1}$1), the Schmid factors are very small, the largest being <0.2 and only occurring for a few orientations.

The systems with K_1 = (110) and (1$\bar{1}$0) have the largest Schmid factors for most compression axes in the (100) plane; the calculations for the (110) system are shown in Fig. 6 (the values for the (1$\bar{1}$0) system are similar, as the two sets of twin elements are related by symmetry). The Schmid factors appear to be largest for the various [011] directions and are also large for the many ⟨021⟩ and ⟨012⟩ directions. Note that only [hkl] and [$h\bar{k}l$] are equivalent by symmetry in P $2_1/c$ monoclinic crystals. This figure also reveals very low or zero Schmid factors for the [001] and [010] compression axes.

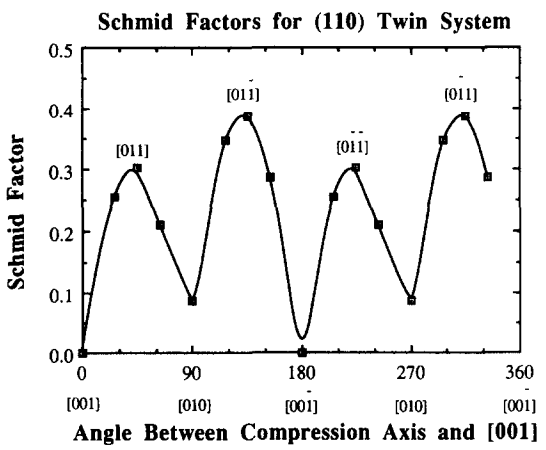


Fig. 6. Schmid factors for the (110) twin system for m-ZrO_2. Schmid factors for the (1$\bar{1}$0) twin system are equivalent, as they are related by symmetry.

Figure 7(a) shows an array of indents in a Nomarski-contrast optical micrograph (more details of these experiments can be found in First & Heuer (1992)). Profuse deformation extends into the [001] direction while virtually no deformation occurs in the opposite or perpendicular directions. TEM investigation showed the primary deformation mechanism was {110} twinning. Twinning on (001) was also found around these indents, but to a much lesser extent. It should be noted that this deformation morphology was independent of the indenter orientation.

Cracking is also associated with these indents and is shown in the normal incidence, reflected light micrograph in Fig. 7(b). A long crack follows the twinned region along [001] and several small cracks extend from the indent along [010] and [0$\bar{1}$0].

DISCUSSION

The Schmid factor calculations discussed earlier appear to be in good agreement with the observed twinning modes in our experiments. As {110} twins have large Schmid factors for many compression axes in the (100) plane, {110} twinning is the primary deformation mechanism. (001) twins are also found in the deformation region around the indent, but have much lower Schmid factors for many orientations. These twins may form because of their large magnitude of shear; (001) and (100) twin systems have s = 0.328, whereas all other systems have s = 0.228.

The asymmetry of the deformation region is directly related to the twinning elements and the direction of shear. The sense of shear is such that the direction of η_1 lies near [001], as does η_1 for the (1$\bar{1}$0) system. The Schmid factor calculations indicate a symmetrical stress state around the indentation; however, as twinning depends upon the crystallography of the material, as well as the possible partial dislocations that can be produced, the symmetry of the indenter stress field will not necessarily produce symmetrical twinning behavior. The dislocations present around these indents have not yet been analyzed; these results would help to explain this asymmetrical behavior observed here. Asymmetric behavior is seen in similar identation experiments performed on sapphire, where rhombohedral twins are generated on only one side of an indent (B. Farber personal communication, 1992). In sapphire, the reason for the asymmetry lies in the difference in anion stacking along opposite directions in the crystal.

The Schmid factor calculations may also give insight into the cracking associated with these indents. In principle, cracks may emanate from the indent radially in any direction, given the assumed radial compression and tangential tension at any point around the indent. The tensile stresses can hence act to form and propagate a crack if other deformation mechanisms are unavailable

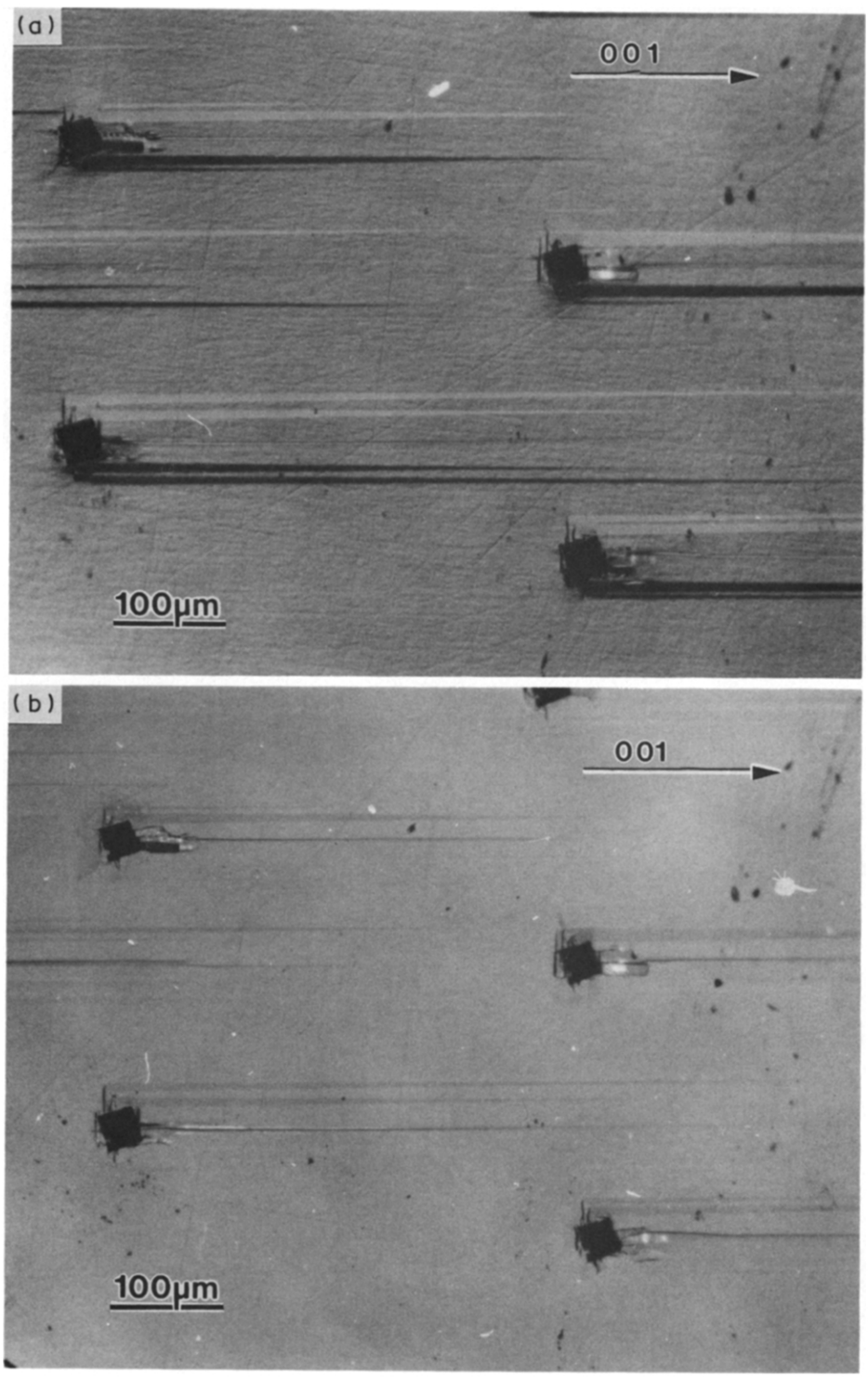


Fig. 7. Nomarski-contrast optical micrograph showing the profuse deformation twinning in m-ZrO_2 associated with room temperature 4.9 N Vickers indents on polished (100) surfaces. (b) Normal incidence, reflected light optical micrograph showing the cracking associated with the indents in (a).

to accommodate the applied stress. Typically, in polycrystalline materials, cracks will emanate from the corners of the indent due to the stress field associated with the indenter. In single crystals, preferential cracking will often occur along certain crystallographic directions. Cracks associated with these indents are evident along the [001] and [010] directions. These directions correspond to Schmid factors of 0 to 0.086 for the {110} twin system. These low Schmid factors indicate that twin formation due to compression along these axes is unfavorable, and that cracking takes place instead.

It should, again, be emphasized that, although this treatment suggests a comparison between the Schmid factor calculations and possible activated twin systems that may be present during an indentation experiment, twinning is a shear-activated deformation mechanism and takes place via the motion of twinning dislocations. Hence, possible partial dislocations for a given structure and shear stresses associated with the indenter geometry must be considered to successfully predict the twinning system that will be activated for a given set of experimental conditions.

CONCLUSIONS

A treatment of twinning using a matrix algebraic approach has been given. The twin system activated for a given compression or tension experiment can be predicted by the use of Schmid factors, just as in the case of dislocation slip. These ideas have been applied to m-ZrO_2 to successfully predict the dominance of {110} twinning behavior found in room temperature microindentation experiments.

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