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PART I

Transformation Analysis

DISPLACIVE PHASE TRANSFORMATIONS IN ZIRCONIA-BASED CERAMICS

B.C. MUDDLE
Department of Materials Engineering, Monash University, Clayton, Victoria, Australia 3168

ABSTRACT

A review is presented of experimental observations of the mechanism and crystallography of the martensitic tetragonal to monoclinic transformation occurring both in dispersed tetragonal ZrO_2 particles in partially stabilized zirconia and in polycrystalline tetragonal zirconia. Preliminary results of determination of the orientation relationship and habit plane for the stress-activated transformation in a CeO_2-stabilized TZP ceramic are reported and compared with predictions of the crystallographic theory for the transformation. This orientation relationship is such that $(100)_m//(100)_t$ and $[001]_m//[001]_t$, and for this variant of the orientation relationship the habit plane is approximately $(301)_t$. These results are in good agreement with theoretical predictions. Progress in the application of the formal theory of martensitic transformations to the transformations in both types of system is examined critically and implications for theories of transformation toughening are discussed.

Attention is also given to tetragonal $\rightleftharpoons$ orthorhombic and orthorhombic $\rightleftharpoons$ monoclinic transformations occurring in ZrO_2 particles in thin foil specimens of partially stabilized zirconia. Formation of a metastable orthorhombic phase appears a possible, but not essential, intermediate stage in the tetragonal to monoclinic transition. However, present evidence strongly suggests that the orthorhombic structure only occurs in those particles experiencing the relaxed matrix constraints typical of thin foil specimens.

1. INTRODUCTION

Transformation-toughened ceramics constitute a new and important class of materials combining high strength and useful toughness [1,2]. Theories of transformation toughening [3] and transformation-induced plasticity [4] in zirconia-based ceramics involve consideration of the interaction between the stress field of a propagating crack and the strains accompanying the martensitic tetragonal (t) to monoclinic (m) transformation occurring within tetragonal zirconia (t-ZrO_2) in the vicinity of the crack tip. To assess the toughening that may be achieved these theories require a reliable determination of these strains and, since the transformation is displacive, this in turn requires a detailed understanding of the crystallography of the transition. For this reason the transformation has received considerable attention in pure bulk zirconia [5-11], in t-ZrO_2 particles dispersed in a ceramic matrix [11-17] and, more recently, in zirconia-based systems with a microstructure comprising polycrystalline tetragonal phase [11,18]. It is the purpose of the present paper to review briefly experimental observations relating to the t → m transformation both in dispersed t-ZrO_2 particles and in tetragonal zirconia polycrystals (TZP), and to assess progress in the application of the formal theory of martensitic transformations.

Attention will also be given to the occurrence of tetragonal $\rightleftharpoons$ orthorhombic and orthorhombic $\rightleftharpoons$ monoclinic transformations in small ZrO_2 particles which are either in unconstrained form or dispersed in the cubic

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matrix phase in thin foils of partially stabilized zirconia (PSZ). Identification of a novel orthorhombic (o) phase in MgO-PSZ [19-21] has led to considerable speculation regarding not only its contribution to determining mechanical properties [20,22], but also its possible role in the important t → m transition. It has been suggested [19,20], for example, that the orthorhombic phase is an essential intermediate reaction product in the t → m transformation and it is thus important that the role of the orthorhombic phase be clearly established.

2. CRYSTALLOGRAPHIC THEORY

The structural change that accompanies a martensitic transformation is characterized by the maintenance of a unique lattice correspondence between unit cells of the parent and product lattices. The existence of this correspondence implies that the change in structure may be accomplished by atomic displacements equivalent to a homogeneous deformation of the parent lattice. When combined with a rigid body rotation, R, the homogeneous lattice strain, B, implied by the correspondence defines the total lattice strain, S_t, that will generate the product lattice in its observed orientation relationship with the parent lattice [23]; i.e.

$$S_t = RB. \qquad (1)$$

The total strain provides, however, an incomplete description of the transformation for it is, in most cases, incompatible with the homogeneous shape deformation that accompanies formation of the transformed volume. The shape strain, P, approximates to an invariant plane strain in which the interface plane (i.e. the habit plane) remains invariant and it is rare that the total lattice strain generates a matching plane between parent and product lattices. This apparent incompatibility may be reconciled if it is assumed that the total strain is only locally homogeneous and occurs inhomogeneously on a macroscopic scale in order that the habit plane remain an invariant plane of the shape strain. The shape strain may thus be considered the product of the total lattice strain and an additional strain which periodically relieves the accumulating misfit across the transformation interface and maintains a macroscopically undistorted plane of

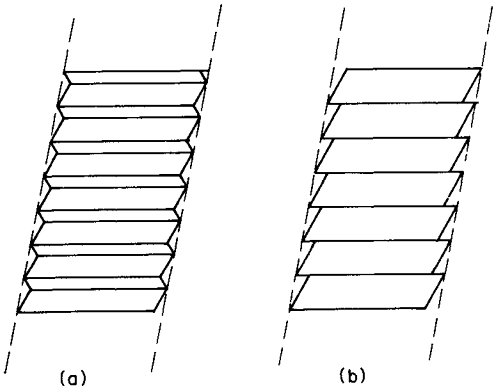

Figure 1 Schematic representation of martensite plates in which the lattice invariant strain involves (a) twinning, and (b) slip.

contact; i.e.

$$P = S_t L = RBL. \tag{2}$$

The strain L is lattice invariant and must constitute either a slip or twinning shear of the product lattice. This description of the transformation represents the basis of the formal crystallographic theory [23,24]. It implies transformation products such as those depicted schematically in Fig. 1.

In its simplest form, the theory assumes the lattice invariant strain (LIS) be a simple shear and the total lattice strain is thus the resultant of consecutive invariant plane strains,

$$S_t = PL^{-1}. \tag{3}$$

Such a strain is an invariant line strain, characterized by the existence of an invariant line, **x**, defined by the intersection of the two invariant planes, and a plane with invariant normal, **n'**, containing the two displacement directions. The strain B extends all vectors to their final lengths, leaving unrotated a set of principal axes, and is thus specified by the measured lattice parameters of the initial and final lattices and the assumed correspondence between them. The direction **x** and normal **n'** are not

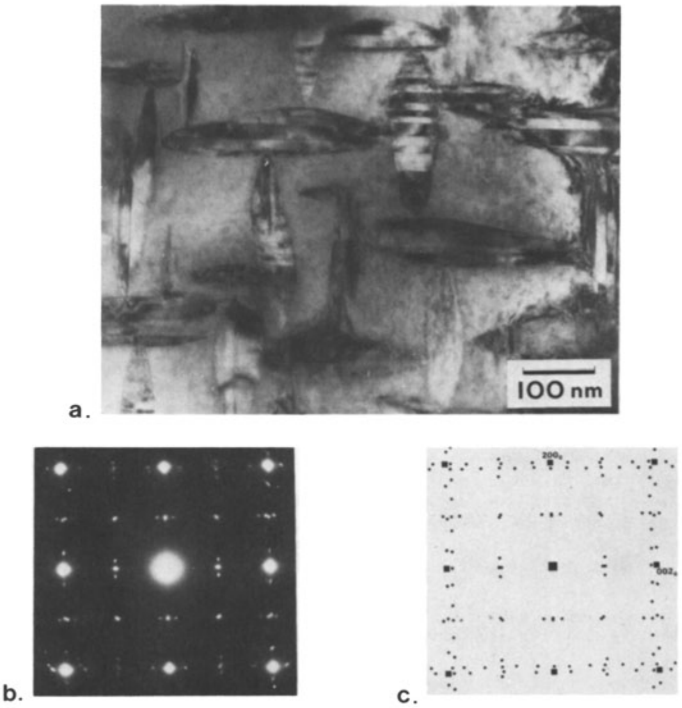

Figure 2 (a) TEM micrograph showing disposed m-ZrO_2 particles in MgO-PSZ, (b) corresponding $\langle 100 \rangle_c$ SAED pattern, and (c) schematic pattern expected of 24 permitted monoclinic orientations [17].

rotated by S_t, so that R is the unique rotation which reverses the rotations of **x** and **n'** due to B. If the strain S_t is specified in this manner and the plane, $\mathbf{p}_2'$ and direction, $\mathbf{d}_2$, of the LIS are assumed, then the invariant line strain may be factored uniquely into its component invariant plane strains and explicit predictions obtained for the elements of the shape strain and the orientation relationship. These predictions for the t → m transformation in metastable $t\text{-}ZrO_2$ are examined in Section 3.2

It is to be noted that for solutions to exist with a particular lattice correspondence and LIS system, the LIS plane must intersect what is termed the initial Bain cone [23], defined by those directions in the initial lattice left unchanged in length by the lattice deformation B. The vectors defined by the points of intersection remain unchanged in length as a result of both the LIS and the strain B and, depending on the rotation R, at least one of them will define an invariant line in the habit plane. The habit plane normal will thus lie in one of the planes whose poles are the intersections of the LIS plane with the Bain cone. The location of the habit plane normal within a given plane is determined by the direction of the LIS [16].

3. THE TETRAGONAL-MONOCLINIC TRANSFORMATION IN PSZ

3.1 Experimental Observations [17]

Dispersed, coherent particles of metastable $t\text{-}ZrO_2$ in MgO-PSZ take the form of lenticular plates parallel to $\{100\}_c$ planes of the cubic (fluorite) matrix phase. The orientation relationship between cubic and tetragonal lattices is such that the principal axes of the tetragonal and fluorite unit cells are parallel and, for each of three variants observed in a given matrix orientation, the c_t axis is perpendicular to the habit plane of the plate [25]. In both particles transformed athermally and those transformed under stress, the product of the t → m transition comprises parallel domains of the monoclinic phase extending either parallel or perpendicular to the original particle habit plane. The typical microstructure is shown in Fig. 2, along with the associated selected area electron diffraction (SAED) pattern.

Figure 3 shows an example of a large particle in which the monoclinic domains extend parallel to the particle habit plane and the corresponding electron microdiffraction pattern from adjacent monoclinic domains. In the schematic solution provided, the direction of the incident beam is defined parallel to $[010]_c$ and is in turn parallel to $[010]_m$ and $[0\bar{1}0]_m$ zone axes of the monoclinic domains. The trace of the domain boundaries is parallel to the trace of $(001)_m$ and the patterns for adjacent domains are related by reflection in this plane. Within experimental accuracy, adjacent domains are thus twin related, the apparent twinning plane being $(001)_m$. If an identity relationship is assumed between the principal axes of the cubic and tetragonal unit cells, then the orientation relationship between the monoclinic and tetragonal cells is such that $(001)_m//(001)_t$ and $[100]_m//[100]_t$.

For the monoclinic particle containing transverse domains in Fig. 4, the incident beam is defined parallel to $[0\bar{1}0]_c$ and is in turn parallel to $[0\bar{1}0]_m$ and $[010]_m$ zone axes of adjacent monoclinic domains. In this case, however, the trace of the domain boundary is parallel to the trace of $(100)_m$ and the domains appear twin-related about $(100)_m$. The orientation relationship implied between tetragonal and monoclinic lattices is in this case such that $(100)_m//(100)_t$ and $[001]_m//[001]_t$. This relationship differs from that observed for $(001)_m$ twin-related domains by a rotation of ~9° about the [010] axis common to the tetragonal and monoclinic lattices

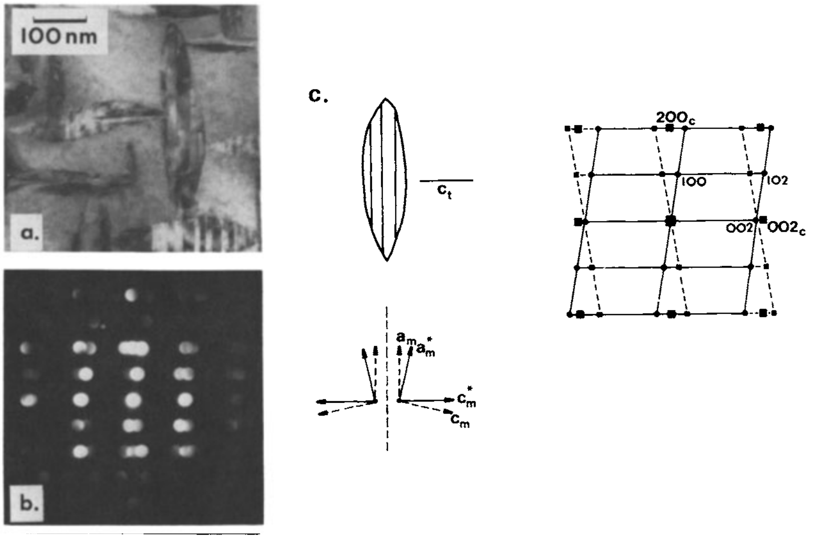

Figure 3 (a) m-ZrO_2 particle comprising domains parallel to $(001)_m$, (b) corresponding electron microdiffraction pattern, and (c) schematic solution to (b).

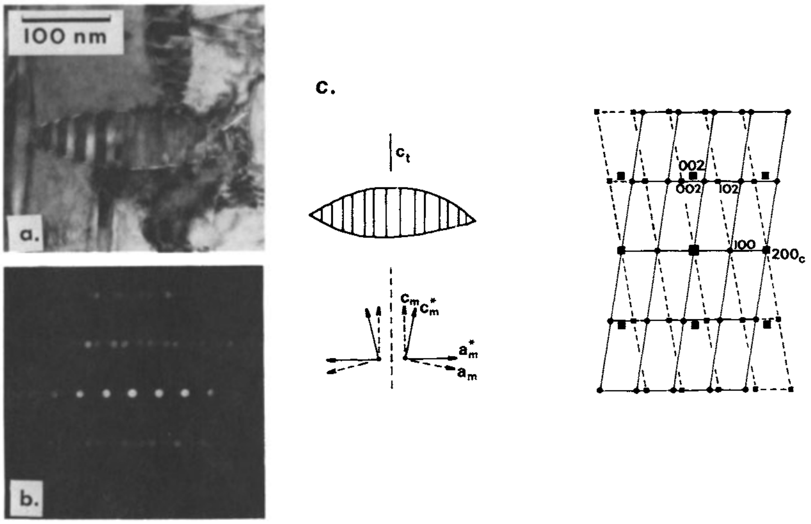

Figure 4 (a) m-ZrO_2 particle comprising transverse monoclinic domains parallel to $(100)_m$, (b) corresponding microdiffraction pattern, and (c) schematic solution to (b).

[17]. However, the lattice correspondence implied by both orientation relationships is such that the c_m axis is parallel to c_t.

Since there is 4-fold symmetry about the c_t axis, there are four crystallographically equivalent variants of each of the above orientation relationships and for each relationship these variants occur in two twin-related pairs. Given that there are three variants of the tetragonal lattice, two possible orientation relationships between tetragonal and monoclinic lattices, and four possible variants of each relationship, a total of twenty four different monoclinic orientations (occurring in twin-related pairs) is possible within particles observed in a given orientation of the matrix phase. The schematic $\langle 100 \rangle_c$ diffraction pattern formed by superimposing single crystal patterns expected for all 24 monoclinic orientations is shown in Fig. 2(c). It is noted that it is in excellent agreement with that observed experimentally, Fig. 2(b).

3.2 Application of the Crystallographic Theory

In the absence of clear experimental evidence, it has been common to identify three possible lattice correspondences that may arise between t and m lattices, depending on which monoclinic axis a_m, b_m or c_m is parallel to the tetragonal c_t axis. These are commonly referred to as lattice correspondences A, B and C respectively. For application of the theory to the transformation in dispersed t-ZrO_2 particles, it is clear that the appropriate choice is correspondence C for both particle forms observed [17]. The immediate problem involves the choice of the LIS system and, bearing in mind the anticipated substructure of a martensitic product (Fig. 1), it is initially tempting to identify the twinning within transformed particles as evidence of the LIS. However, it has recently been shown [16] that neither of the twinning planes $(100)_m$ or $(001)_m$ intersect the Bain cone, defined by initial lattice directions left unchanged in length by the lattice deformation B. As indicated in Section 2, this means that neither plane, as the plane of LIS, will give rise to real solutions in theoretical calculations. Furthermore, neither of these planes is itself a potential habit plane with any choice of simple shear as the LIS [16]. If the theory is to be applicable, an alternative choice of LIS is necessary and each individual monoclinic domain within a transformed particle is to be regarded as a discrete variant of the transformation product. The junction plane between adjacent monoclinic variants is not to be confused with the habit plane for the tetragonal-monoclinic transformation.

In the most comprehensive calculations yet undertaken, Kelly and Ball [16] have recently reported predictions of the crystallographic theory assuming the LIS to be a simple shear. They have identified a number of possible shear planes giving rise to plausible real solutions and permitted all possible slip directions within each of these planes. They have eliminated those solutions involving unrealistically large values for the magnitudes m_1 and m_2 of the shape strain and LIS respectively and identified as most plausible those solutions involving the smallest values of these strains in combination. More importantly, they have recognised that for the chosen correspondence C there are four crystallographically equivalent variants of the correspondence associated with the 4-fold symmetry about the c_t axis. For certain LIS and certain variants of the correspondence taken in pairs, it is possible to generate equivalent solutions to the theory, which are at least approximately twin-related and for which the potential contact plane between twin-related variants is either $(100)_m$ or $(001)_m$. Two of four such solutions examined in detail by Kelly and Ball are reproduced in Table I; the notation 6A and 14B is that adopted in the original paper [16].

For system 6A, the solution shown has been calculated assuming that the lattice correspondence is of the form:

$$ {}_{m}C_{t} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad (4) $$

If alternatively, an equivalent correspondence related by a rotation of 180° about $[001]_t$ is assumed, an equivalent solution is achieved in which the monoclinic variants are approximately twin related. As shown in Table I, the junction plane (or contact plane) anticipated between these two variants is exactly parallel to $(100)_t$ and only ~ 0.1° from $(100)_m$. The predicted morphology for a ZrO_2 particle transforming to a combination of such variants is shown in Fig. 5(a) and is in good agreement with the observed morphology, Fig. 4, for particles comprising transverse domains of the monoclinic structure twin-related about $(100)_m$. For system 14B, twin-related variants may be generated in a similar fashion, with a junction plane parallel to $(001)_t$ and just 0.1° from $(001)_m$. In this case the predicted morphology accounts well, Fig. 5(b), for those particles observed to comprise monoclinic variants twin-related about $(001)_m$. Figure 5 contains schematic representations of partially transformed particles to emphasize that the transformed particle comprises discrete variants of the monoclinic phase and that a distinction is to be made between the habit plane between tetragonal and monoclinic phases and the junction plane between monoclinic variants. In a fully transformed particle, no trace of

Table I Selected Predictions of the Crystallographic Theory for the Tetragonal-Monoclinic Transformation in MgO-PSZ [16]

Solution	6A	14B
Lattice Invariant Shear	$(011)[0\bar{1}1]$	$(110)[1\bar{1}0]$
m_2	0.0377	0.0377
m_1	0.1627	0.1592
Displacement Direction (d_1)	$\begin{bmatrix} -0.0324 \\ 0.0188 \\ 0.9993 \end{bmatrix}$	$\begin{bmatrix} 0.9979 \\ 0.0195 \\ 0.0615 \end{bmatrix}$
Habit Plane (p_1)	$\begin{bmatrix} 0.9674 \\ 0.0054 \\ 0.2532 \end{bmatrix}$	$\begin{bmatrix} 0.1665 \\ -0.0014 \\ 0.9860 \end{bmatrix}$
Junction Plane (j)	(100)	(001)
Angle p_1,j	14.7°	9.6°
Orientation Relationship		
$(100)_m$^$(100)_t$	0.07°	8.89°
$(010)_m$^$(010)_t$	1.08°	1.10°
$(001)_m$^$(001)_t$	9.04°	0.09°

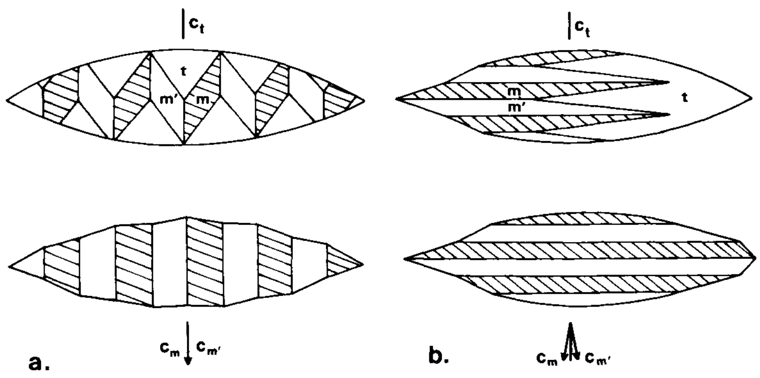

Figure 5 Schematic representation of predicted morphology [16] for m-ZrO_2 particles comprising (a) $(100)_m$ twin-related variants, and (b) $(001)_m$ twin-related variants. Upper figures illustrate partially transformed particles.

the habit plane is preserved. It is to be noted that the angle between the habit plane and the junction plane has been exaggerated in Fig. 5 for clarity; the true angles for the two examples discussed are given in Table 1.

3.3 Implications for Transformation Toughening

The strain around particles such as those represented schematically in Fig. 5 will be the resultant of the accumulated shape strains for twin-related monoclinic variants. For both forms of particle observed, it has been established [16] that the strain component normal to the junction plane is equal for variants across that plane, while the shear components of the strain in the junction plane are directly opposed in twin-related variants. Thus in a transformed particle comprising equal volume fractions of twin-related variants, the shear components parallel to the junction plane will exactly cancel. Adjacent twin-related variants are in large part self-accommodating and the transformation to approximately equal fractions of twin-related variants minimizes the strain accumulating around a given particle. The axial strains accumulated parallel to the base vectors of the tetragonal unit cell are shown in Table II, for the four solutions considered in detail by Kelly and Ball [16]. In all cases the strain parallel to $[010]_t$ (i.e. $[010]_m$) is negligible and the accumulated misfit strain approximates closely to a plane strain. This model of the transformed product is to be contrasted with that in which the particle is regarded as an internally twinned plate of the monoclinic phase (Fig. 1). In the latter case, the shape change would be macroscopically homogeneous over the particle as a whole and the misfit strain would contain large shear and dilatational components.

A further implication of a transformed particle comprising approximately twin-related variants of the monoclinic phase, is that significant local strains will be generated at the intersections of the junction plane with the original interface between tetragonal and cubic phases. For a