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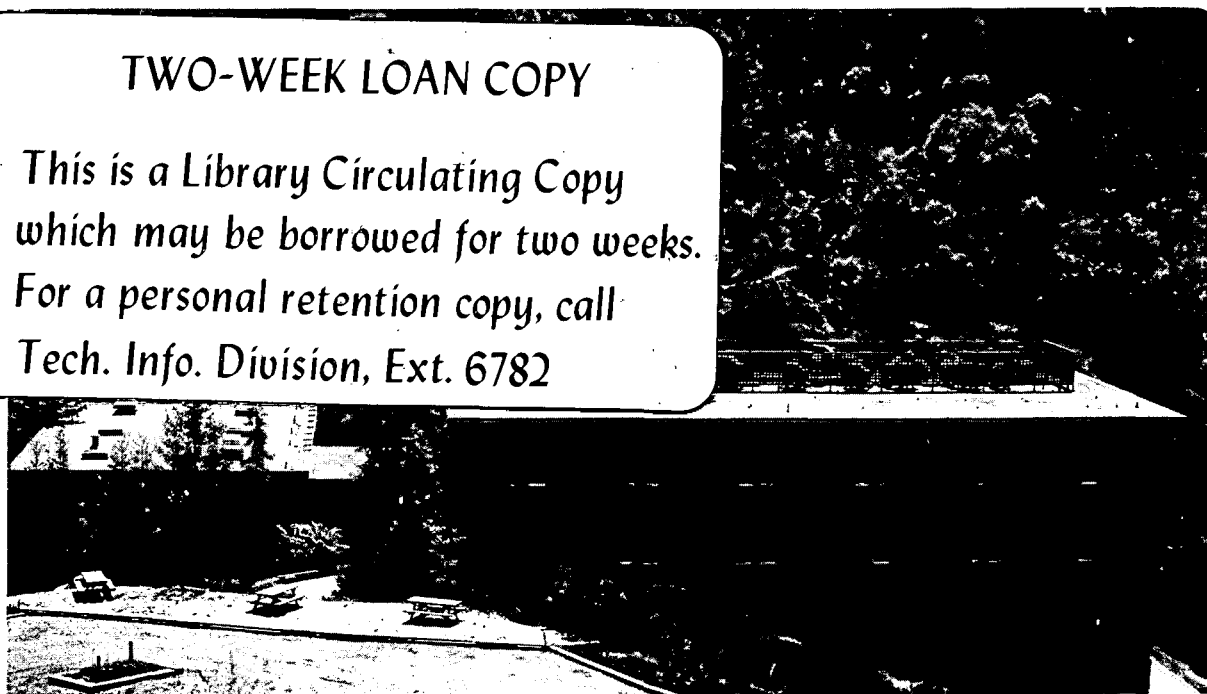
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TRANSFORMATIONS IN CRACK TIP STRESS FIELDS

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ABSTRACT

The toughness of ceramics can be substantially enhanced by inducing a martensitic transformation in the stress field of the dominant crack. The specific characteristics of martensitic transformations pertinent to this toughening process are examined in this paper. Then, a generalized model of the toughening is developed, which indicates the specific roles of the transformation parameters on the expected magnitude of the toughening. Finally, the implications of the analysis for the development of high toughness ceramics are briefly discussed.

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I. Introduction

The occurrence of martensitic transformation in the stress fields of propagating cracks leads to dramatic increases in the toughness of two-phase ceramics. This has been demonstrated for zirconia ceramics containing precipitates of tetragonal ZrO_2 ⁽¹⁻³⁾, which martensitically transform to monoclinic symmetry. The same phenomenon occurs in Al_2O_3 and Si_3N_4 ceramics, in which the same tetragonal ZrO_2 particles exist as a dispersed phase. Furthermore, a fine-grained single-phase tetragonal ZrO_2 can be produced⁽⁴⁾, which undergoes the martensitic transformation to monoclinic symmetry during fracture. Optimization of the toughening that can be achieved by such transformations is clearly a research goal of major importance. However, while the importance of martensitic transformations in controlling the properties of ferrous alloys has long been recognized by metallurgists, this type of transformation has not received much attention from ceramists. Accordingly, the first portion of this paper reviews the general physical characteristics of martensitic trans-

formations. The mechanism of transformation appears to be the same in particles contained in a matrix as in bulk material. The following review of martensitic transformations thus makes no specific distinction between these two cases. However, the presence of a matrix can perturb the transformation in several subtle ways; these are given specific attention.

The final part of the paper is devoted to a generalized analysis of transformation toughening in brittle materials. Explicit results are obtained for spherical particles; these provide the necessary insights into the physical phenomena and suggest the conditions necessary for optimum toughening.

2. Martensitic Transformations

Martensite is the hard metastable product phase which develops when Fe-C alloys are strengthened by quenching. The particular type of solid state transition which leads to the formation of martensite is known as a martensitic reaction, and has been widely studied⁽⁵⁾. Although martensite in Fe-C alloys is a metastable phase and martensitic reactions are usually associated with rapid cooling, equilibrium phases are known to form martensitically in both metallic and non-metallic systems (the transformation in tetragonal ZrO_2 is to an equilibrium structure). In this section of the present review, we summarize the characteristic features of martensitic reactions.

Martensitic transformations are usually diffusionless, occur athermally, and involve a shape deformation. The last characteristic is usually cited as the characteristic feature of martensitic reactions and is of special importance; among other things, it contributes to the transformation-

toughening in ceramics.

2.1.1 Shape Deformation

The observation of a change of shape in the transforming region is the most convenient experimental criterion for recognizing the occurrence of martensitic reactions (Fig. 1). The transition is accomplished by the shearing of discrete volumes of material, resulting in a shape change. This, in turn, implies (as will be seen below) that the product regions remain essentially coherent with the parent phase (i.e., for a given composition, there is a definite and constant orientation relationship between the parent and the product crystals* and there exists a definite habit plane (the planar interface common to parent and product phases along which the plates of martensite lie)).

In all martensitic reactions, an originally flat and polished surface remains planar in the transformed region, but is tilted about its lines of intersection with the habit plane (Figure 1a). As can be seen from this figure, the straight lines ST, TT', and T'S' inscribed on the surface remain straight in the transformed regions, but their directions are changed. Thus, planes and straight lines in the parent phase are transformed into planes and straight lines in the product, respectively. The surface region of the martensite ABCD remains plane, but is tilted about AB and DC (with respect to the rest of the surface). In order to accommodate this distortion between AB and DC, there must be elastic or plastic

*The reader is reminded that when discussing martensitic reactions in precipitate particles, the language "parent" and "product" refer to partial transformation within the particle.

deformation in the surrounding matrix. Within the accuracy of experimental observation in several metallic systems, the line AB is unrotated by the transformation and since this applies to all arbitrary free surfaces, no line in the habit plane ABML can be rotated by more than a few minutes of arc.

Moreover, since the originally straight reference line STT'S' remains continuous, lines in the habit plane must be unchanged in length to within a few percent. Thus, the habit plane is assumed to be an undistorted and unrotated plane. The position or magnitudes of vectors lying in the habit plane remain unchanged due to the transformation. The macroscopic shape deformation involved in the formation of a martensite plate is believed to be a shear parallel to the habit plane plus a simple (uniaxial) tensile or compressive strain perpendicular to the habit plane.

2.2 Athermal Nature of the Transformation

Martensitic reactions are usually (but not always) athermal, i.e., they only occur when the temperature is changing. This behavior obtains because the shape and volume changes associated with the change in crystal structure set up large strains which, due to the diffusionless nature of the reaction (see below), are not relieved by atomic migration. The resultant increase in strain energy opposes the progress of the transition, causing it to stop while still incomplete -- hence, only a few nuclei are active at a particular temperature. A greater driving force, which comes from larger undercooling, is required to induce further reaction. The additional strain energy of transformation explains both the occurrence of the transition over a temperature range (instead of at a single characteristic temperature) as well as the existence of a hysteresis in

in the forward (cooling) and reverse (heating) reactions.

On cooling, transformation invariably begins at a characteristic "martensite start" temperature, M_s , and is complete when the temperature falls to M_f . If reversibility obtains, i.e., no intervening reactions occur, the reverse transformation begins at A_s and is complete at A_f . The hypothetical stress-free transformation temperature, T_0 , is $\frac{M_s + A_s}{2}$. In the presence of an applied elastic or plastic deformation, transformation can begin at M_d , which must satisfy the condition that $M_s < M_d < T_0$. (Note that M_s is a strong function of composition in alloy systems.)

2.3 Diffusionless Nature of the Transformation

The transformation is diffusionless in that no thermally activated diffusion is required. Many martensitic reactions occur at quite low temperatures, even close to absolute zero. Because of the rapid rate of formation of martensite at these temperatures, it is clear that diffusion is not required, and that the activation energy for martensite growth is essentially zero. Furthermore, M_s is a function of pressure, and such transformations can be induced by a change in pressure. Although some transitions in non-metallic solids, e.g., that in bulk ZrO_2 , occur at high temperatures, they are also believed to be diffusionless. In the absence of diffusion, the atomic movement must be coordinated and orderly, in agreement with the observation that most atoms have the same neighbors (differentially arranged) in the product and parent phases. Thus, the reactions must also be composition invariant, i.e., the product and parent phases must have the same composition.

3. Crystallographic Theories of Martensitic Reactions

Two distinct but fundamentally equivalent theories -- due to Bowles and Mackenzie (B-M)⁽⁶⁾ and Wechsler, Lieberman and Read (W-L-R)⁽⁷⁾ -- exist to deal with the crystallography of martensitic reactions. These crystallographic theories are phenomenological in nature, i.e., they provide a means of describing consistently what has happened, rather than how it actually happened. (It is important to note that the theories do not present any detailed picture of the actual process by which atoms move during the transformation.)

The theories conceive of martensitic reactions as consisting of three basic steps -- a Bain (or lattice) deformation, a lattice-invariant deformation, and a rigid body rotation.

3.1 Bain Deformation

In 1924, Bain⁽⁸⁾ first pointed out that since a fcc lattice could also be represented as a body-centered tetragonal lattice, the fcc bcc transition can be visualized as an "upsetting" of the fcc lattice, i.e., it occurs by a compression parallel to the c axis and an expansion along the two a axes of the tetragonal cell (Fig. 2). Any simple homogeneous pure deformation of this nature, which converts one lattice into the other by a simple expansion or contraction along the crystallographic axes, is known as a Bain deformation.

While the product lattice can be formed from the parent lattice by a Bain deformation, there is no undistorted plane that can be associated with the habit plane of the reaction. This can conveniently be seen by considering a martensitic transformation from a tetragonal

cubic to unit cell by a contraction along the c axis and an expansion along the other two axes, as shown in Fig. 3⁽⁹⁾. The shape change involved in such a martensitic transformation can be represented by a sphere in the untransformed material becoming an ellipsoid after deformation. Such a shape change involves a combination of a rigid body rotation and a deformation involving only principal strains $\epsilon_1, \epsilon_2, \epsilon_3$, i.e., the deformation changes the lengths of three mutually perpendicular axes to $1 + \epsilon_1, 1 + \epsilon_2$, and $1 + \epsilon_3$. If $\epsilon_1 = 0$ and ϵ_2 and ϵ_3 are of opposite sign, then part of the ellipsoid lies within the sphere and the ellipsoid and sphere intersect along two curves, which are the traces of two undistorted planes.

In order for one part of the crystal to undergo a homogeneous deformation and remain in contact with the undeformed part along a habit plane, it is necessary to have a planar interface and since the undeformed part is not only undistorted, but also unrotated, the interface must also be unrotated. As the sphere deforms into the ellipsoid, however, the traces of the undistorted planes rotate in opposite directions from their initial positions, and a rotation must be added to the deformation to obtain an undistorted and unrotated plane. A strain of this kind which permits the undeformed and deformed regions to meet along a habit plane is called an invariant plane strain.

Let lines ab and cd in Fig. 3 represent those directions on the front surface whose lengths do not change during transformation, i.e., these lengths are preserved both in the cubic and tetragonal phases. All other directions on this surface, such as ef and gh , have their lengths either increased or shortened by the deformation. An invariant plane must contain one of the two lines whose lengths do not change. Let that line be ab and

let the other trace of the plane, whose dimension is also unchanged by the reaction, be bm . Thus, the plane defined by abm possesses the characteristic that the magnitudes of ab and bm are preserved during the deformation. However, the angle α between these two directions is obviously changed. For plane abm to act as a habit plane, it should not only preserve the magnitudes of ab and bm , but should also preserve the angular separation between the two. Thus, the Bain deformation alone cannot give an undistorted plane.

3.2 Lattice-Invariant Deformation

This deformation maintains the lattice symmetry, i.e., it does not change the crystal structure, but in combination with the Bain deformation produces an undistorted plane. It can occur by either slip or twinning and the substructure of the habit plane will be different in the two cases, as shown in Fig. 4. In both cases, the misfits at the parent/product interface are periodically alleviated by the twinned or slipped lamellae. Local regions of the interface are thus alternately extended and contracted, but on a macroscopic scale the interface is (on the average) undistorted.

3.3 Rotation of the Transformed Lattice

The undistorted plane derived from the combination of the Bain deformation and the lattice invariant shear has different orientation in the parent and product phases and for this reason, does not yet satisfy the requirements of a habit plane. A rotation of the structure of the product phase must now be added to insure coincidence.

With respect to martensitic reactions, therefore, when a body under-

goes a Bain deformation, there must always be at least one set of mutually orthogonal directions, the principal axes, which are transformed into a set of orthogonal directions by the distortion. The three principal Bain strains must possess different signs if an undistorted plane exists. The Bain deformation in general does not yield a zero value for one of the principal strains and an arbitrary amount of lattice invariant shear must be imposed. The amount of shear is adjusted so that the shape ellipsoid touches the unit sphere along one of its principal axes. Thus, in combination with the Bain deformation, the shear makes one of the principal strains (ϵ_1) of the resultant deformation zero and the other two (ϵ_2 and ϵ_3) opposite in sign. The final rotation yields the habit plane. The crystallographic theories perform these operations using matrix algebra (6,7) and application of the W-L-R theory to the ZrO_2 transformation can be found in ref. 10.

4. General Transformation Relationships

The key to transformation toughening in ceramics containing tetragonal ZrO_2 particles is that the transformation to monoclinic symmetry, which usually occurs at about $\sim 1,000^\circ C$ in bulk forms of ZrO_2 (10), is suppressed, except in the stress field of propagating cracks (Fig. 5). While the tetragonal particles present in bulk materials have been described (2) as metastable with respect to monoclinic symmetry, it should be recognized that they are in fact stable except near crack tips, implying that their M_s temperature must be below room temperature. M_s appears to be a function of particle size in tetragonal ZrO_2 , as larger particles in all three matrices so far studied (cubic ZrO_2 , Al_2O_3 , and Si_3N_4) undergo spontaneous transformation on cooling from elevated temperatures. This

is not yet fully understood and may involve a variation of particle composition, and hence M_s , with particle size, the difficulty of nucleating the martensitic transformation, or both*; whatever the reason, it is of interest to consider the general energetics governing martensitic transformations within constrained particles and then how the transformation can be used to increase fracture toughness. A well-known approach due to Eshelby⁽¹⁴⁾ involving ellipsoidal particles is ideally suited to this problem and is the basis of our analysis. We therefore first derive the stresses and strain energies that develop after transformation using Eshelby's theory, and then deduce the transformation condition from the change in Helmholtz free energy. Subsequently, specific relations for the transformation stress and the transformation zone size around a crack tip, i.e., the region in the matrix where second phase particles will transform, are derived for the case of a spherical particle. Finally, the transformation toughening that results from the zone of transformed material is evaluated and is followed by a discussion of the implications for optimum toughness.

4. GENERAL RELATIONS

4.1 Transformation Stresses

The stresses p_{ij}^I , that develop within a particle contained in an infinite matrix when the particle undergoes a transformation characterized by an unconstrained strain e_{ij}^T are^{14,15};

$$p^I = 3\kappa_p(e^C - e^T) = 3\kappa_m(e^C - e^{T*}) \quad (1)$$

$$'p_{ij}^I = 2\mu_p('e_{ij}^C - 'e_{ij}^T) = 2\mu_m('e_{ij}^C - e_{ij}^{T*})$$

where μ and κ are the shear and bulk moduli respectively, the quantities p^I , e are the hydrostatic components of stress and strain, while $'p_{ij}^I$, $'e_{ij}^C$ are the deviatoric components, e^C is the constrained strain in the particle and the subscripts p and m refer to particle and matrix respectively; e^{T*} is the transformation strain of the 'equivalent' particle, a concept introduced by Eshelby to incorporate the elastic modulus mismatch between the particle and the matrix. The constrained strain is related to the equivalent transformation strain by the Eshelby tensor, S_{ijkl} ;¹⁴

$$e_{ij}^C = S_{ijkl} e_k^{T*} \quad (2)$$

where S_{ijkl} depends only on the particle shape. Combining Eqns. (1) and (2) enables the stress to be expressed in terms of known quantities -- the transformation strain, the particle shape and the elastic constants.

4.2 The Strain Energy

The increase in strain energy, ΔU_T , of the system (particle and matrix) caused by the transformation is related directly to the stress within the particle and the unconstrained transformation strain of the particle¹⁴; it is written as

$$\Delta U_T = V_p p_{ij}^I e_{ij}^T / 2 \quad (3)$$

where V_p is the particle volume. When the transformation occurs in the presence of an applied stress, p_{ij}^A , the strain energy change is modified. The modification can be expressed as an interaction energy, ΔU_I ¹⁴. The interaction energy between the applied displacement field and the displacement field of a particle has two components. The first, due solely to the

elastic modulus mismatch, does not involve an actual transformation¹⁴ and is given by

$$\Delta U_I = -V_p p_{ij}^A e_{ij}^\tau / 2 \quad (4)$$

where e_{ij}^τ is a function of the applied strain. This component of the interaction energy is generally similar before and after transformation (because transformations do not generally produce an appreciable change in particle moduli) and will therefore be neglected. The second component reflects the relative influence of the applied stress field before and after transformation, and is given (for a uniform stress) by¹⁴;

$$\Delta U_I^\tau = -V_p p_{ij}^A e_{ij}^\tau \quad (5)$$

This component must always be taken into account, and the resultant strain energy change accompanying transformation is;

$$\Delta U = U_T + \Delta U_I^\tau = -V_p e_{ij}^\tau [p_{ij}^A + (1/2)p_{ij}^I] \quad (6)$$

4.3 Transformation Conditions

The transformation of a particle is governed by the Helmholtz free energy of the entire system, particle plus matrix¹⁴. The change in Helmholtz free energy of a system containing a single particle, due to transformation, is given by;

$$\begin{aligned} \Delta F &= -V_p \Delta F_o + \Delta U \\ &\equiv -V_p \Delta F_o - V_p e_{ij}^\tau [p_{ij}^A + (1/2)p_{ij}^I] \end{aligned} \quad (7)$$

where ΔF_0 is the difference in chemical free energy per mole between the transformed and untransformed phases. It should be noted that Eqn. (7) includes the work done by the applied stress¹⁴. The applied stress level required for the transformation to be thermodynamically favorable is thus;

$$p_{ij}^A \geq -p_{ij}^I/2 - \Delta F_0/e_{ij}^T \quad (8)$$

In principle, a surface energy term, ΔS , should be added to the free energy term,

$$\Delta S = A(S_s - S_m) \quad (9)$$

where A is the surface area of the particle, S is the surface energy per unit area, and the subscripts m and s refer to the particle/matrix interfaces before and after transformation. This term is ignored in the present analysis, but can be readily introduced, as required.

For the transformation of particles in the vicinity of a crack tip under a Mode I stress state, the stresses p_{ij}^A can be obtained from the plane strain linear elastic field equations¹⁶;

$$\left. \begin{matrix} p_{yy}^A \\ p_{xx}^A \\ p_{xy}^A \end{matrix} \right\} = \frac{K_I \cos(\theta/2)}{\sqrt{2\pi r}} \left\{ \begin{matrix} 1 - \sin(\theta/2)\sin(3\theta/2) \\ 1 + \sin(\theta/2)\sin(3\theta/2) \\ \sin(\theta/2)\cos(3\theta/2) \end{matrix} \right\} \quad (10)$$

$$p_{zz}^A = \nu(p_{xx}^A + p_{yy}^A) \quad (r \ll a)$$

where K_I is the stress intensity factor, a the crack length, r the distance from the crack tip, and θ the angular coordinate referred to the crack plane. The conditions required to induce transformation of a single particle located in the vicinity of a crack tip can be approximately obtained by simply inserting the p_{ij}^A from Eqn. (10) into Eqn. (18). The approximation is most appropriate when the particle is small and remote from the tip (although still retaining the condition $r < a$), so that a relatively uniform stress is established over a zone of length $\sim 2\ell$ (ℓ is the particle size): this zone contains most ($\sim 90\%$) of the transformation strain energy. Remoteness of the particle from the crack tip also minimizes the influence on transformation of stress relaxation effects that occur over the crack surface.

The maximum distance from the crack tip at which a single particle will transform, $r_c(\theta)$, can be regarded as a first order estimate of the transformation zone size, r_T . Clearly, however, the presence of other transformed particles closer to the crack tip, especially in materials containing appreciable concentrations of untransformed particles, will modify the transformation distance. We will assume that the zone size is proportional to $r_c(\theta)$.

$$r_T = \eta(V_f) r_c(\hat{\theta}), \quad (11)$$

such that the proportionally constant η is some function of the volume fraction V_f of untransformed particles; $\hat{\theta}$ is the orientation with respect to the crack tip that establishes the zone width (see Fig. 1 below).

5. TRANSFORMATION CHARACTERISTICS

Explicit consequences of crack-tip martensitic transformations resulting from the present analysis can be conveniently deduced by examining the energy changes that accompany the transformation of a spherical particle. The equivalent results for ellipsoidal particles can be obtained numerically.

5.1 Strain Energy Changes

The changes in strain energy involved in a martensitic transformation can be evaluated by following the sequence of calculations outlined in the preceding section.

The constrained strains are firstly obtained by noting that they are related to the transformation strain of the equivalent particle, through the Eshelby tensor, by¹⁴;

$$e^c = \frac{e^{T^*}}{3} \begin{pmatrix} 1+\nu_m \\ 1-\nu_m \end{pmatrix}, \quad 'e_{ij}^c = \frac{2'e_{ij}^{T^*}}{15} \begin{pmatrix} 4-5\nu_m \\ 1-\nu_m \end{pmatrix} \quad (12)$$

where ν_m is the Poisson ratio of the matrix. (The hydrostatic strain can, in general, contain a component due to thermal expansion mismatch as well as the component due to the actual transformation.) Then, eliminating the unknown e^{T^*} by substituting into Eqn. (1), we obtain;

$$e^c = \frac{e^T \kappa_p}{\kappa_p + 2\kappa_m(1-2\nu_m)/(1+\nu_m)} \quad (13)$$

$$'e_{ij}^c = \frac{'e_{ij}^T \mu_p}{\mu_p + \mu_m(7-5\nu_m)/2(4-5\nu_m)}$$

Similarly, the transformation strain of the 'equivalent' particle can be related to the actual transformation strain by eliminating e_{ij}^c from Eqns. (12) and (13).

The hydrostatic and deviatoric stresses within the particle can be obtained from Eqns. (13) and (1) and from the relations for Young's modulus ($E = 3\kappa(1-2\nu) = 2\mu(1+\nu)$) as;

$$p^I = - \frac{e^T}{(1+\nu_m)/2E_m + (1-2\nu_p)/E_p} \quad (14)$$

$$'p_{ij}^I = - \frac{'e_{ij}^T}{(1+\nu_p)/E_p + 2(1+\nu_m)(4-5\nu_m)/E_m(7-5\nu_m)}$$

These particle stresses can be coupled with the applied stresses and the transformation strain of the equivalent particle to obtain the strain energy change that accompanies transformation (Eqn. 6); alternatively, the applied stresses required to induce transformation can be obtained, if the chemical free energy change accompanying transformation is known (Eqn. 7). For this purpose, it is particularly appropriate to separately obtain the strain energy contributions that derive from the deviatoric and hydrostatic components. These can be combined to yield the total strain energy; thus from Eqn. (6);

$$\frac{\Delta U}{V_p} = - \left[\Delta V(p^A + p^I/2) + \sum 'e_{ij}^T ('p_{ij}^A + p_{ij}^I/2) \right] \quad (15)$$

where the first term is the contribution ΔU_h due to the hydrostatic strain, ΔV being the volume change that accompanies transformation, and the second term is the shear contribution, ΔU_s .

The influence of the volume change (i.e., the hydrostatic component) on the strain energy of transformation can be obtained directly from Eqns. (6), (12), (13) and (14) as;

$$\frac{\Delta U_h}{E_p V_p \Delta V^2} = \frac{(E_m/3)}{E_p(1+\nu_m)+2E_m(1-2\nu_p)} = \frac{p^A}{\Delta V E_p} \quad (16)$$

while the influence of each component of the shape change (the deviatoric component) is

$$\frac{\Delta U_s}{E_p V_p ('e_{ij}^T)^2} = \frac{(7-5\nu_m)E_m}{2E_p(1+\nu_m)(4-5\nu_m)+E_m(1+\nu_p)(7-5\nu_m)} = \frac{p_{ij}^A}{e_{ij}^T E_p} \quad (17)$$

The relative contribution to the total strain energy of the hydrostatic and deviatoric components, in the absence of an applied stress, is thus;

$$\frac{\Delta U_h}{\Delta U_s} = \frac{1}{3(7-5\nu_m)} \left[\frac{2E_p(1+\nu_m)(4-5\nu_m)+E_m(1+\nu_p)(7-5\nu_m)}{E_p(1+\nu_m)+2E_m(1-2\nu_p)} \right] \frac{\Delta V^2}{\sum ('e_{ij}^T)^2} \quad (18)$$

For equivalent values of the transformation strains ($e^T \approx 'e_{ij}^T$), and for typical values of Poisson's ratio, $\nu_m \approx \nu_p \approx 0.2$, the shear contribution and the hydrostatic contribution are comparable, emphasizing the significance of shear in martensitic transformations. Note, however, that the shear contribution can be appreciably diminished when the particles are thin plates¹⁴.

5.2 The Transformation Conditions

The application of an external stress modifies the strain energy change accompanying transformation, but does not influence the chemical free energy change. The nature of the stress required to induce transformation can thus be deduced by examining the relation between the strain energy and the applied stress (Eqns. 16, 17); applied stresses that diminish the transformation strain energy obviously encourage transformation. Transformations involving an increase in volume, i.e., a positive e^T , require an applied hydrostatic tension to reduce the strain energy. Conversely, transformations that involve a volume decrease will be encouraged by a hydrostatic compression. Furthermore, even a transformation involving no volume change, but only a shape change, can cause toughening. Combinations of positive/positive or negative/negative shear stresses and shear strains are required to suppress the deviatoric component of the strain energy. Such combinations are, in fact, a prerequisite for martensitic transformations.

The magnitudes of the stresses required to induce transformation, obtained from Eqns. (7) (16) and (17), are thus;

$$p_c^A v + \sum \left| (p_{ij}^A)_c e_{ij}^T \right| \quad (19)$$

$$= -\Delta F_0 + E_p \beta \left[\frac{(1/3)\Delta V^2}{(1+v_m)+2\beta(1-2v_p)} + \frac{\sum (e_{ij}^T)^2(7-5v_m)}{2(1+v_m)(4-5v_m)+\beta(1+v_p)(7-5v_m)} \right]$$

where $\beta = E_m/E_p$ and the subscript c refers to the critical condition. Inspection of Eqn. (19) indicates that, as generally anticipated, the transformation stresses increase as the chemical free energy difference decreases

and as the transformation strains increase. To ascertain the role of the elastic moduli, it is convenient to reduce Eqn. (19) to a form pertinent to a pure dilational transformation (with $\nu_p = \nu_m = 0.2$);

$$\frac{p_c^A}{E_p \Delta V} = 0.28 \frac{\beta}{(1+\beta)} - \mathcal{F} \quad (20)$$

where $\mathcal{F} = \Delta F_0 / \Delta V^2 E_p$. It is then evident that the transformation stress increases continuously as the relative matrix modulus β increases.

5.3 Crack Tip Transformation Zones

The Mode I crack tip stress field (Eqn. 10) contains both deviatoric and hydrostatic components of comparable magnitude (except at $\theta \approx 0$ and $\pi/3$). For simplicity, we will assume that the principle transformation shear strains are of the type $'e_{xy}^T$, and $'e_{yx}^T$, and occur with equal facility in both the positive and negative directions, so that the transformation can initiate at all θ . Then, the maximum transformation distance r_c , obtained from Eqn. (10) and (19), is expressed by the relation;

$$\begin{aligned} & \frac{K_I}{\sqrt{2\pi r_c}} \cos(\theta/2) \left[(2/3)(1+\bar{\nu})\Delta V + |\sin(\theta/2)\cos(3\theta/2)'e_{xy}^T| \right] \\ & = - \Delta F_0 + \beta E_p \left[\frac{(1/3)\Delta V^2}{(1+\nu_m)+2\beta(1-2\nu_p)} + \frac{|('e_{xy}^T)^2(7-5\nu_m)|}{2(1+\nu_m)(4-5\nu_m)+\beta(1+\nu_p)(7-5\nu_m)} \right] \end{aligned} \quad (21)$$

where $\bar{\nu}$ is the average value of Poisson's ratio for the composite material. The expression for $r_c(\theta)$ can be presented in a simpler form if we adopt

the reasonable assumption that $\bar{v} \approx v_m \approx v_p \approx 0.2$. Then, Eqn. (21) simplifies to

$$r_c \left(\frac{\Delta V E_p}{K_I} \right)^2 = \frac{4.1}{\pi} \left[\frac{\cos(\theta/2) [\pm 1 + 1.25\xi |\sin(\theta/2) \cos(3\theta/2)|] (1+\beta)}{\beta [1 + 3\xi^2] - 3.6(1+\beta)} \right]^2 \quad (22)$$

where $\xi = 'e_{xy}^T / \Delta V$: the positive sign refers to a positive hydrostatic component of transformation strain and vice versa. Contours of the dimensionless transformation radius, $R_c [\equiv r_c (\Delta V E_p / K_I)^2 \text{ or } r_c ('e_{xy}^T E_p / K_I)^2]$ are plotted in Fig. 1 for several ξ , normalized such that the maximum zone radius is the same for each ξ . The strong dependence of the zone shape on the relative dilational and deviatoric components of the transformation strain is clearly evident from the contours.

The transformation zone width r_T can be estimated from the transformation distances r_c as described in Section 2. For example, for $\xi = \infty$, the maximum width occurs at $\theta \approx 0.6\pi$ (Fig. 7). Hence, r_T is obtained by inserting r_c from Eqn. (22), with $\theta \approx 0.6\pi$, into Eqn. (11).

6. THE TRANSFORMATION TOUGHENING

The extra toughness available from the martensitic transformation can be estimated from the release of strain energy needed to compensate for the change in Helmholtz free energy of the transformed particles, through the relation

$$\Gamma_T = (\Delta U_0 - V_p \Delta F_0) r_T f,$$

where Γ_T is the increase in toughness due to transformation, ΔU is the

strain energy of transformation in the absence of an applied stress and f is the number of particles in unit volume. Values of Γ_T can be obtained by substituting for ΔU_0 from Eqns. (16) and (17) and for r_T from Eqns. (22) and (10): noting that K_I in the latter should be equated to the critical value, $K_{Ic} = \sqrt{2\bar{E}(\Gamma_T + \Gamma_0)}$. The final expression for Γ_T (when $\nu_p = \nu_m = 0.2$) is;

$$\frac{\Gamma_T}{\Gamma_0} = \frac{0.73\eta f V_p (\bar{E}/E_p) \{\cos(\hat{\theta}/2) [\pm 1 + 1.25\xi \sin(\hat{\theta}/2) \cos(3\hat{\theta}/2)]\}^2 (1+\beta)}{\beta(1+\xi^2) - 3.6(1+\beta) \mathcal{F} - 0.73\eta f V_p (\bar{E}/E_p) \{\cos(\hat{\theta}/2) [\pm 1 + 1.25\xi \sin(\hat{\theta}/2) \cos(3\hat{\theta}/2)]\}^2 (1+\beta)} \quad (23)$$

where $\hat{\theta}$ is the orientation with respect to the crack tip that yields the maximum zone width r_T . A simplified form of Eqn. (23) suitable for predicting the trends in toughness can be obtained by allowing $\hat{\theta}$ to be $\sim \pi/2$, noting that fV_p is the volume fraction V_f of particles, and by letting $\bar{E} \approx \nu_m E_m (1 - V_f) + E_p V_f$. Then, for $\eta \approx 1$, we obtain;

$$\frac{\Gamma_T}{\Gamma_0} \approx \frac{0.73V_f [\beta(1 - V_f) + V_f] [0.34\xi \pm 1]^2 (1+\beta)}{\beta(1+3\xi^2) - 3.6(1+\beta) \mathcal{F} - 0.73V_f [\beta(1 - V_f) - V_f] [0.34\xi - 1]^2 (1+\beta)} \quad (24)$$

Note that the result depends only on the volume fraction of particles and not on the particle size; and that V_f appears in both the numerator and denominator by virtue of the dependence of K_{Ic} on the sum, $\Gamma_T + \Gamma_0$. Inspection of Eqn. (24) indicates that the toughness tends to a maximum as the denominator approaches zero. This is merely a manifestation of the intuitively obvious result that the closer the particles are to the transformation condition in the absence of an external stress, the larger will be the transformation zone size in the crack tip stress field and hence, the

larger the toughness. This result is directly analagous to the toughening of metals due to crack tip plasticity; wherein, the more imminent the plasticity (i.e., the lower the yield strength), the larger the toughness. Further inspection indicates that generally, the last term in the denominator of Eqn. (24) will be appreciably smaller than the first term (because particulate composites with $V_f \gtrsim 0.3$ cannot normally be fabricated with small particle sizes). A further simplification thus takes the form;

$$\frac{\Gamma_T}{\Gamma_0} \approx \frac{V_f[\beta(1-V_f)+V_f][0.34\xi^{-1}]^2(1+\beta)}{[\beta(1+3\xi^2)-3.6(1+\beta)\mathcal{F}]} \quad (25)$$

demonstrating the direct dependence of the toughening on the volume fraction V_f of particles. Setting the denominator of Eqn. (21) to zero for the maximum, we obtain

$$\frac{(1+3\xi^2)}{\mathcal{F}} = \frac{3.6(1+\beta)}{\beta} \quad (26a)$$

or reverting to the basic quantities;

$$\left[\Delta V^2 + 3(e_{xy}^T)^2 \right] = 3.6(1/E_p + 1/E_m) \Delta F_0 \quad (26b)$$

The interrelations between e^T , e_{xy}^T , ΔF_0 , E_p , and E_m specified by Eqn. (26b) can be used to select particles and matrices that optimize the toughness*.

*The reader is reminded that the numerical quantity 3 preceding the shear strain in Eqn. (26) has been obtained for a spherical particle that does not undergo twinning during transformation. For plate-like particles or for a twinned martensite, the numerical coefficient can be appreciably reduced. This factor is the most uncertain aspect of the predictive capability implied by Eqn. (26).

For example, given the transformation properties of the particle (e_{xy}^T , e^T , and ΔF_0), the matrix modulus can be selected that most closely satisfies the equality of Eqn. (26b); alternatively, recognizing that E_m/E_p will typically be in the range $0.1 < E_m/E_p < 10$ for ceramic systems, particles with the ΔF_0 and $e_{ij}^T/\Delta V$ properties specified by Eqn. (26b) can be selected from the available possibilities. Finally, it should be noted that the toughening is predicted to be proportional to the fundamental toughness of the material Γ_0 (Eqn. 25). This proportionality arises because, the larger the fundamental toughness, the greater the transformation zone size that can be developed prior to crack extension.

7. IMPLICATIONS

The relations for the martensitic toughening developed in the preceding section (Eqns. 25 and 26) suggest clear guidelines for achieving optimum toughness. It is appropriate, however, to examine the constraints that impose potential limits upon the attainment of high toughness. The chemical free energy, ΔF , has a strong temperature dependence, increasing as the undercooling below the equilibrium stress-free transformation temperature T_0 increases. It is clearly of great importance, therefore, to choose a system in which ΔF_0 is maintained at the temperature range of interest, consistent with substantial crack tip transformation.

The relative roles of the dilational and deviatoric transformation strains are also of interest. The influence of the dilational component is invariant with particle shape, while the deviatoric component depends on both the particle shape and the propensity for twinning. For approximately spherical particles, the deviatoric strain makes the larger contri-

bution to the transformation strain energy. However, the extent to which the strain can be alleviated by twinning is likely to be unpredictable and not amenable to close control. This uncertainty suggests that transformations with a dominant shear strain contribution may not be as desirable as those with a significant contribution from the more predictable dilational component.

The trend toward increased toughness as the volume fraction of particles increases is perhaps self evident; but the predicted absence of a particle size effect at constant volume fraction requires some qualification. The absence of a size effect obtains only if the shear component of the strain energy and the chemical composition are independent of size. This requires that the particle shape, the twinning intensity in the transformed particle, and chemical composition gradients be size-independent. It is not known a priori whether these conditions will be satisfied. Size effects on toughness might well emerge from toughening studies; the interpretation of such effects should reside in the trends with size of particle shape, chemical composition and twinning. For example, there is cursory evidence that the twinning intensity increases with particle size; such a trend would cause the toughness to increase with particle size.

APPENDIX

STRAIN ENERGY DISTRIBUTION

The strain energy U of a tensile body of unit width containing a crack of length $2a$ subjected to a stress (neglecting a transformation zone) is¹⁶;

$$U = \frac{\pi\sigma^2 a^2}{E} (1-\nu^2) + U^* \quad (A1)$$

where U^* is the strain energy in the absence of a crack. The decrease in strain energy accompanying a crack increment Δa under fixed grip conditions is thus;

$$\frac{\Delta U}{\Delta a} = - \frac{2\pi\sigma^2 a}{E} (1-\nu^2) \quad (A2)$$

By comparison, the strain energy U_r contained in a zone, r_0 , around the crack tip, obtained from Eqn. (10), is

$$U_r = \frac{K_I^2(1+\nu)}{\pi E} \int_0^{r_0} \int_{-\pi}^{\pi} \cos^2(\theta/2) [2(1-2\nu)(1+\nu) + \sin^2(\theta/2)\cos^2(3\theta/2)] dr d\theta \quad (A3)$$

$$= \frac{K_I^2 r_0 (1+\nu)}{E} \left[\frac{16(1+\nu)(1-2\nu) + 39}{8} \right]$$

Noting that K_I for a tensile sample is;

$$K_I = \sigma \sqrt{\pi a} \quad (A4)$$

the change in strain energy in the zone r_0 during a fixed grip crack tip increment becomes;

$$\frac{\Delta U_r}{\Delta a} = - \frac{\sigma^2 \pi r_0}{E} (1+\nu) \left[\frac{16 (1+\nu) (1-2\nu) + 39}{8} \right] \quad (A5)$$

Comparison with Eqn. (A2) indicates that the proportion of the change in strain energy that resides in the crack tip zone is $\sim 3r_0/a$. The proportion thus becomes negligibly small in zones $r_0 \ll a$. Also, note that the strain energy change in the zone r_0 is independent of the current crack length and therefore, represents a constant small contribution to the strain energy release rate.

The presence of a transformation zone will modify the strain energy changes. The crack surfaces are largely subjected to a modest level of stress (i.e., of the order of the applied stress). A large proportion of the transformation zone is thus contained in essentially stress free material; only a small proportion is contained in the highly stressed crack tip region, r_0 (Fig. 10). The strain energy U_R associated with a transformation zone of width r_T can thus be approximately expressed as;

$$U_R \approx 4(\Delta U_0 - V_p \Delta F_0) r_T f a + U_T^*(\sigma, a, r_T f, \Delta U_0 - V_p \Delta F_0) \quad (A6)$$

U_T^* is that proportion of the strain energy associated with the transformation zone at the crack tip. The equivalent strain energy change is;

$$\Delta U_R / \Delta a \approx 4(\Delta U_0 - V_p \Delta F_0) r_T f + \partial U_T^* / \partial a \quad (A7)$$

The change in effective surface energy is

$$\Delta S / \Delta a = 4\Gamma_0 \quad (A8)$$

where Γ_0 is the fracture energy in the absence of transformation. Combining Eqns. (A2), (A7) and (A8) to obtain the total energy change and equating to zero for the instability condition gives;

$$\pi\sigma^2 a(1-\nu^2) - 2E[\Gamma_0 + r_T f(\Delta U_0 - V_p \Delta F_0)] + (E/2)(\partial U^*/\partial a) = 0 \quad (A9)$$

Since, as noted above, the strain energy change in the crack tip zone is a small fraction of the total strain energy change, the last term should be very much smaller than the first. The critical crack extension stress thus reduces to;

$$\pi\sigma^2 a(1-\nu^2) \approx 2E[\Gamma_0 + r_T f(\Delta U_0 - V_p \Delta F_0)] \quad (A10)$$

and the effective fracture energy $\Gamma_T (= \pi\sigma^2 a(1-\nu^2)/2E)$ becomes;

$$\Gamma_T = \Gamma_0 + r_T f(\Delta U_0 - V_p \Delta F_0) \quad (A11)$$

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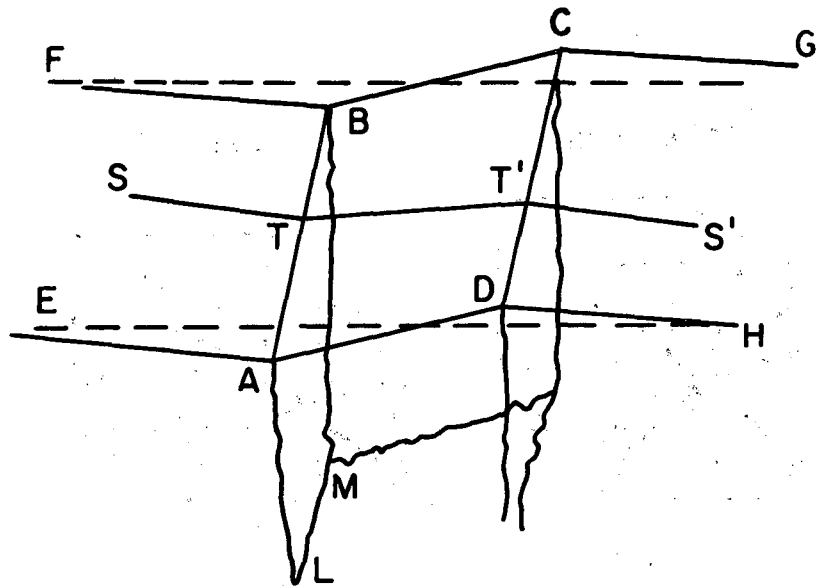
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FIGURE CAPTIONS

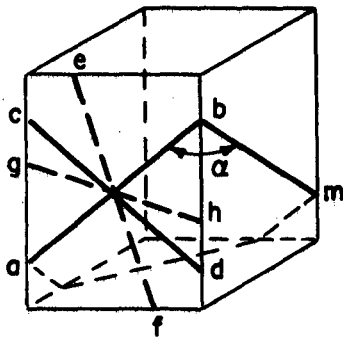
- Fig. 1. The shape deformation produced in a flat surface by the formation of a martensite plate is indicated by the new path of an initially straight scratch, STT'S.
- Fig. 2. (a) shows a body-centered tetragonal (bct) unit cell delineated in a face centered cubic (fcc) lattice. The Bain deformation, involving a change from bct to bcc symmetry ((b)→(c)), is thus equivalent to a change from an fcc to a bcc lattice.
- Fig. 3. Tetragonal to cubic transformation. See text for further details.
- Fig. 4. Schematic drawing showing internally-twinned and dislocated martensite.
- Fig. 5. Coherent tetragonal precipitate particle in 8 mole % MG-PSZ. (a) shows the precipitate distribution, while (b) shows that particles adjacent to a macro-crack (arrowed) originating from a 500-g Vickers microhardness indenter have transformed. Note that some untransformed tetragonal particles (T) are still present, and that none of the particles were cleaved during crack propagation. Bright-field transmission electron micrographs, 125 kV, reference 2.
- Fig. 6. A schematic indicating the orientation of the zero in-plane shear stress trajectory at a crack tip, and the assumed direction of the transformation strain ϵ_{xy}^T for spherical particles on each side of this trajectory.
- Fig. 7. Contours of the normalized transformation distance R_c , plotted for the different types of transformation strain.
- Fig. 8. A schematic indicating that crack growth results in an increase in the volume of transformed material located near the crack center, where the stresses are relatively low.

Figure 1

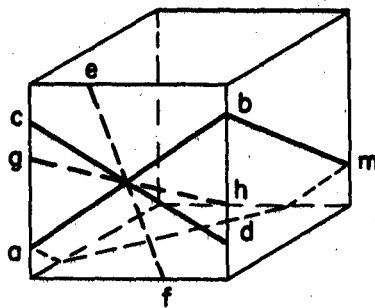


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tetragonal

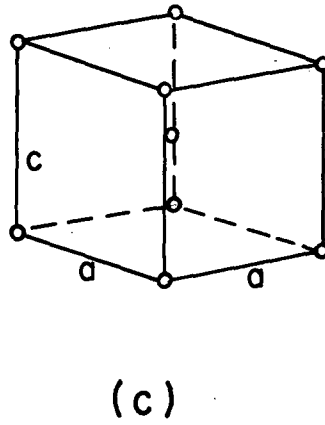
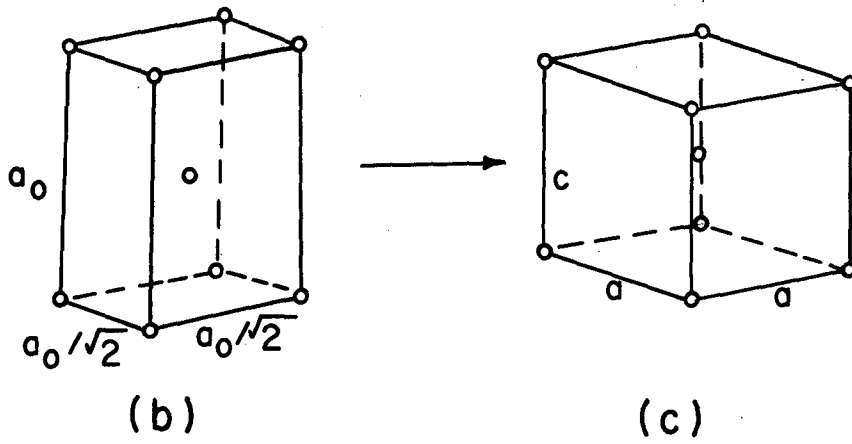
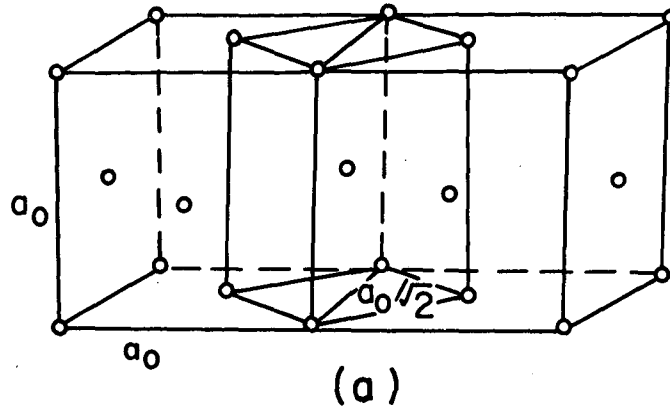


cubic



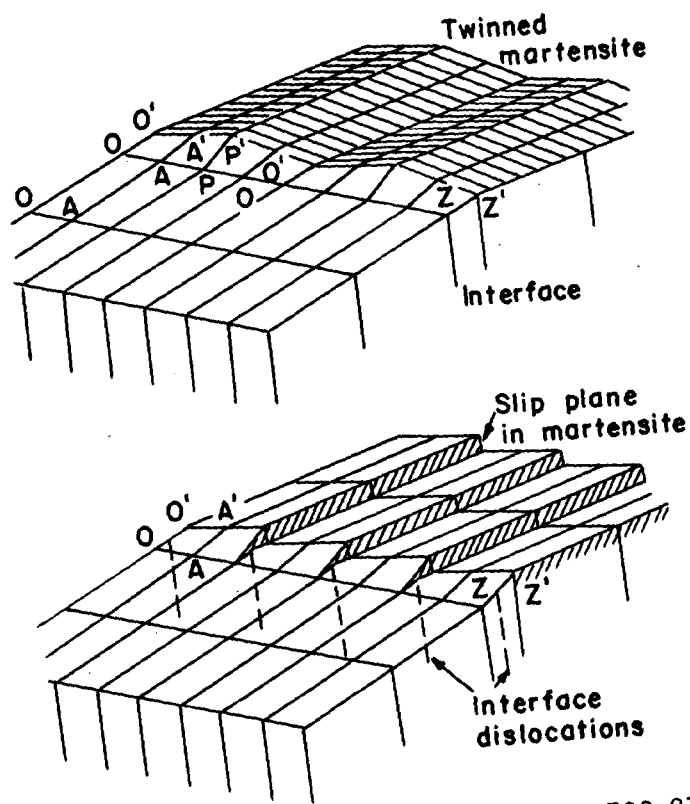
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Figure 3

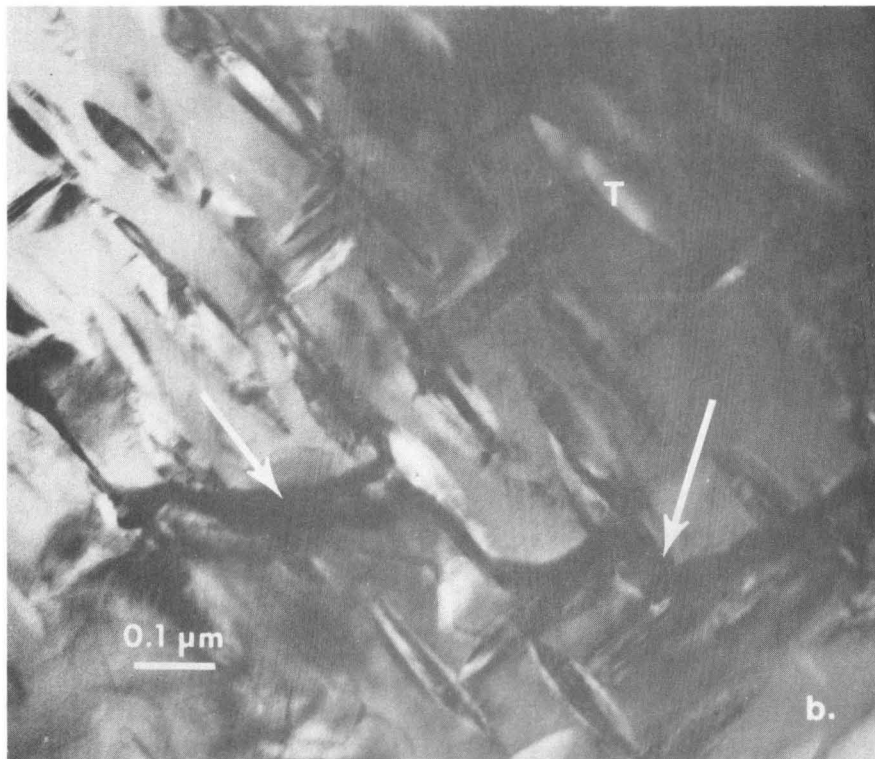
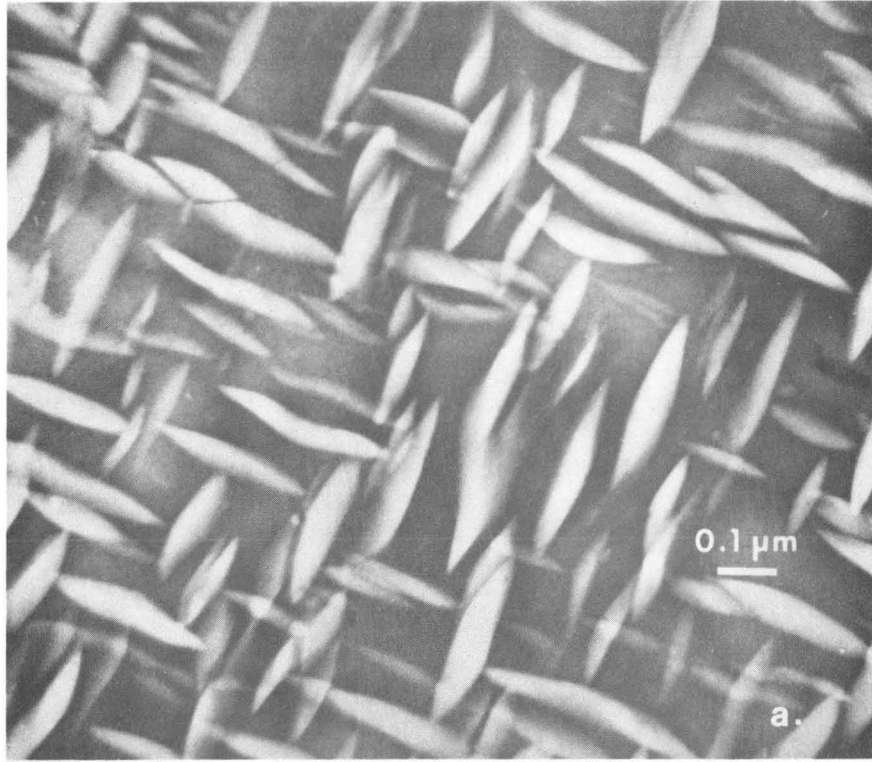


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Figure 4

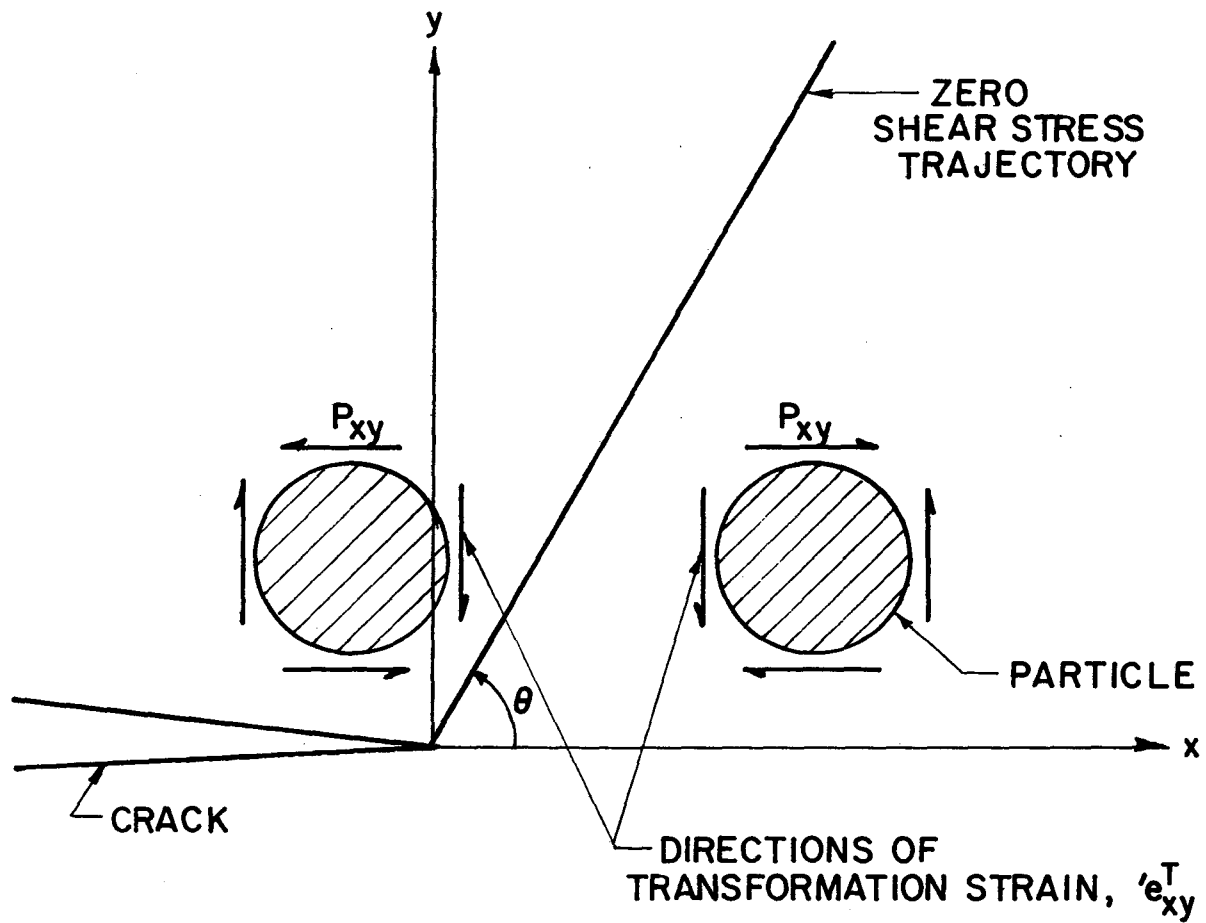


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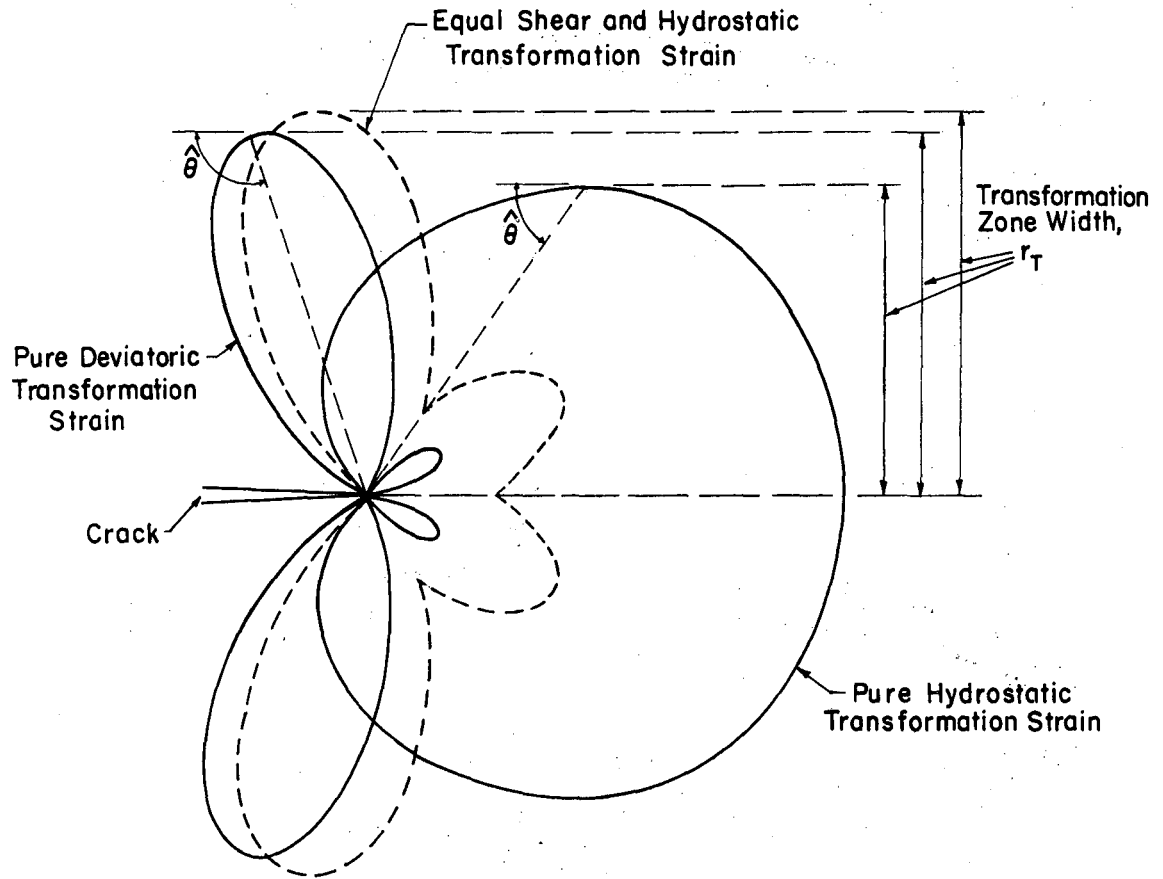
Figure 5



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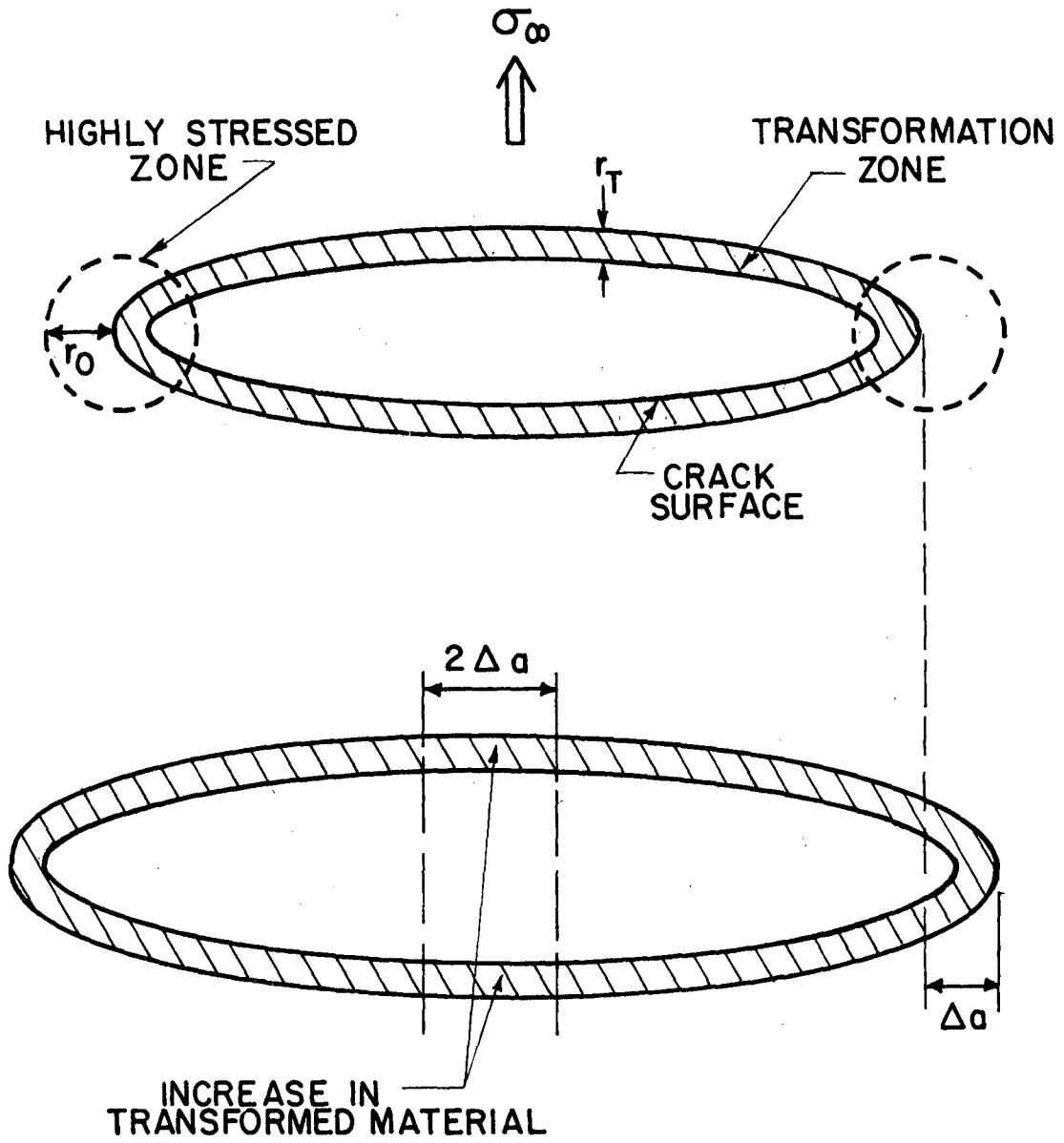
Figure 6

Figure 7



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Figure 8



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