

AD-A076 532 ROCKWELL INTERNATIONAL THOUSAND OAKS CA SCIENCE CENTER F/6 11/2
MICROSTRUCTURALLY DEVELOPED TOUGHENING MECHANISMS IN CERAMICS. --ETC(U)
OCT 79 F F LANGE N00014-77-C-0441
UNCLASSIFIED SC5117.6TR NL

| OF |
AD
A076532



END
DATE
FILMED
12-79
DDC

12 LEVEL #

SC5117.6TR

SC5117.6TR

8076 439

Copy No. 13

MICROSTRUCTURALLY DEVELOPED TOUGHENING MECHANISMS IN CERAMICS

TECHNICAL REPORT NO. 6

AD A076532

STRESS-INDUCED PHASE TRANSFORMATIONS:
THEORY OF PHASE RETENTION AND FRACTURE TOUGHNESS

GENERAL ORDER NO. 5117
CONTRACT NO. N00014-77-C-0441

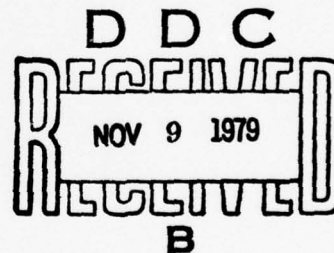
DOCUMENT NO. SC5117.6TR

Prepared for

Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217

F. F. Lange
Principal Investigator

OCTOBER 1979



DDC FILE COPY

Approved for public release; distribution unlimited

Reproduction in whole or in part is permitted
for any purpose of the United States Government



Rockwell International
Science Center

79 11 08 072

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) MICROSTRUCTURALLY DEVELOPED TOUGHENING MECHANISMS IN CERAMICS - Stress-Induced Phase Transformations: Theory of Phase Retention and Fracture Toughness		5. TYPE OF REPORT & PERIOD COVERED Technical Report June 1, 1978 - May 31, 1979
6. AUTHOR(s) F.F. Lange		7. PERFORMING ORG. REPORT NUMBER SC5117.6TR
9. PERFORMING ORGANIZATION NAME AND ADDRESS Rockwell International Science Center, 1049 Camino Dos Rios P.O. Box 1085, Thousand Oaks, CA 91360		8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0441
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy Street Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 032-574 (471)
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Dr. R.C. Pohanka Office of Naval Research 800 N. Quincy Street Arlington, VA 22217		12. REPORT DATE 11 October 1979
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release, Distribution unlimited 9 Technical Rept. no. 69		13. NUMBER OF PAGES 24
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) 1 Jun 78 - 31 May 79		15. SECURITY CLASS. (of this report) Unclassified
18. SUPPLEMENTARY NOTES		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Microstructure, Fracture Toughness, Martensitic Transformation, ZrO_2		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The thermodynamics of a constrained transformation has been examined with regard to the conditions for phase retention during fabrication and the effect of a stress-induced transformation on the fracture toughness. Constraint of the shape change associated with the transformation by an elastic matrix will lower the transformation temperature. Retention also requires that a critical grain size (or particle size) cannot be exceeded during fabrication. Two bonding solutions for the critical stress intensity factor (K_{IC}) were obtained: one for the		

DD FORM 1473 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

389949

y/B

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. Abstract (cont.)

case where the transformation suffers no stress hysteresis effect and the other for a large stress hysteresis effect. Both indicate that K_c will depend on the transformation's shape change, the elastic properties of the constraining matrix, the volume fraction of the retained, metastable phase and temperature. K_c is predicted to decrease with increasing temperature.

ACCESSION for	
NTIS	White Section ☒
DDC	Buff Section ☐
UNANNOUNCED	☐
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
Dist. Avail. and/or SPECIAL	
A	

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)



Rockwell International
Science Center

SC5117.6TR

STRESS-INDUCED PHASE TRANSFORMATIONS:
THEORY OF PHASE RETENTION AND FRACTURE TOUGHNESS

F. F. Lange
Structural Ceramics
Rockwell International Science Center
Thousand Oaks, CA 91360

Abstract

The thermodynamics of a constrained transformation has been examined with regard to the conditions for phase retention during fabrication and the effect of a stress-induced transformation on the fracture toughness. Constraint of the shape change associated with the transformation by an elastic matrix will lower the transformation temperature. Retention also requires that a critical grain size (or particle size) cannot be exceeded during fabrication. Two bonding solutions for the critical stress intensity factor (K_{IC}) were obtained: one for the case where the transformation suffers no stress hysteresis effect and the other for a large stress hysteresis effect. Both indicate that K_{IC} will depend on the transformation's shape change, the elastic properties of the constraining matrix, the volume fraction of the retained, metastable phase and temperature. K_{IC} is predicted to decrease with increasing temperature.



1.0 INTRODUCTION

It has been shown that a stress-induced, martensitic transformation can be used to increase the fracture toughness of brittle materials based on ZrO_2 .⁽¹⁻⁵⁾ Metastable, tetragonal ZrO_2 is the toughening agent. Transformation to its stable, monoclinic structure in the vicinity of the crack front is believed to be responsible for the increased fracture toughness.

Two questions arise from these observations: 1) How can the tetragonal structure be retained upon cooling from its fabrication temperature when it usually undergoes a transformation? 2) How does the stress-induced transformation contribute to fracture toughness? Theoretical results concerning an inquiry into these two questions will be presented herein.

2.0 RETENTION OF THE TETRAGONAL PHASE

2.1 The Tetragonal+Monoclinic Transformation

The ZrO_2 tetragonal+monoclinic transformation is athermal, diffusionless and involves a shape change, i.e., both a shear strain and a volume change. Based on analogous transformations observed in metallic systems, it is termed a martensitic transformation. The reader is referred to reviews by Subbarao et al⁶ and Heuer and Nord⁷ for details. Although some differences of opinion exists, Bailey,⁸ Bansal and Heuer,⁹ and more recently, Buljan et al¹⁰ have shown that the orientation relation between the monoclinic and tetragonal (fcc) unit cells is given by $(110_m) \parallel 100_t$ and $[001_m] \parallel [001_t]$, which can be represented by the strain tensor



$$\tilde{\epsilon}^t = \begin{pmatrix} \frac{a_m \cos(\frac{90-\beta}{2}) - a_t}{a_t} & 0 & \tan(\frac{90-\beta}{2}) \\ 0 & \frac{b_m - a_t}{a_t} & 0 \\ \tan(\frac{90-\beta}{2}) & 0 & \frac{c_m \cos(\frac{90-\beta}{2}) - c_t}{c_t} \end{pmatrix} \quad (1)$$

where a , b , c are the cell dimensions of the respective tetragonal (t) and monoclinic (m) structures, and β ($<90^\circ$) is the monoclinic angle. Substituting the appropriate crystallographic data into Eq. (1), it can be shown that the transformation involves a large shear strain ($\sim 8\%$) and a substantial volume increase (3-5%).*

During cooling, the tetragonal $\rightarrow$ monoclinic transformation of pure ZrO_2 begins at $\sim 1200^\circ C$ and proceeds over a temperature range (e.g., 1200° to $\sim 600^\circ C$) until the transformation is complete,⁶ typical of other martensitic transformations. Both composition and pressure affect the transformation temperature. Metal oxides (e.g., Y_2O_3 , CeO_2 , etc.) lower the transformation temperature. In this regard, the ZrO_2 - Y_2O_3 system has been best studied. Srivastava et al¹² have shown that additions of Y_2O_3 to ZrO_2 lowers the transformation temperature to $565^\circ C$ where a eutectoid exists at ~ 3.5 m/o Y_2O_3 . Scott¹³ and Stubican et al¹⁴ appear to be in agreement.

*The crystallographic data of Pratil and Subbarao⁽¹¹⁾ can be extrapolated to room temperature to show that the volume increase changes from 3% at $1150^\circ C$ to 4.5% at room temperature; β is relatively insensitive to temperature.



2.2 Thermodynamics of The Constrained Transformation

Retention of the tetragonal structure is the key factor for fabricating a tougher material based on the transformation-toughening concept. As will be shown shortly, retention of the tetragonal structure depends on the magnitude of the strain energy arising from the elastic constraint imposed by surrounding material on the transformation shape change. Constraint can arise from several sources. First, if the polycrystalline body were single phase, neighboring grains, each with a different crystallographic orientation, will constrain the anisotropic shape change of one another. Second, for two phase materials, any matrix surrounding the particle will constrain the particle's shape change. The strain energy arising due to these constraints can be reduced by microcracking and/or plastic deformation (e.g., twinning). Namely, both microcracking and twinning can accommodate some of the shape change associated with the transformation and thus reduce the constraint imposed by the surrounding material. Thus, as will be shown, retention of the tetragonal phase not only depends on the elastic properties of constraining material, but also on the possible occurrence of microcracking and/or twinning during transformation.

To examine the thermodynamics of the constrained $ZrO(t)_2 + ZrO_2(m)$ reaction, consider a stress-free, spherical particle of the tetragonal phase embedded within a matrix material. Upon transforming to its monoclinic



SC5117.6TR

phase,* a state of stress arises within both the transformed particle and the surrounding matrix due to the shape change. Eshelby⁽¹⁵⁾ has shown that the difference in free energy ($\Delta G_{t \rightarrow m}^C$) between these two states is given by

$$\Delta G_{t \rightarrow m}^C = \Delta G_{t \rightarrow m}^{\text{chem}} + U_{se}^0 + U_s \quad (2)$$

where $\Delta G_{t \rightarrow m}^{\text{chem}}$ is the chemical free energy change which is a function of temperature and composition, U_{se} is the strain energy associated with the transformed particle and surrounding matrix, and U_s is the change in energy associated with the particle's surface. All terms in Eq. (2) have the dimensions of energy per unit volume of the transformed material. Since both the surface area change and the surface energy difference between the two phases are small, U_s is usually neglected in Eq. (2).

The condition for the transformation requires that $\Delta G_{t \rightarrow m}^C > 0$, or from Eq. (2) (neglecting U_s),

$$-\Delta G_{t \rightarrow m}^{\text{chem}} > U_{se}^0 \quad (3)$$

Since U_{se} is always positive and ΔG^{chem} is negative below the unconstrained transformation temperature, it can be seen that the effect of the constraint (or U_{se}) is to lower the transformation temperature.

*It is assumed through this paper that the whole particle transforms in a spontaneous and uniform manner. Although this assumption neglects the conditions for the nucleation and growth of martensitic plates usually associated with these transformations, it does allow us to examine the limiting condition concerning the thermodynamic stability of the constrained particle.



Eshelby⁽¹⁵⁾ has shown that

$$U_{se}^0 = \frac{1}{2} \sigma_{ij}^I \epsilon_{ij}^t \quad (4)$$

where σ^I defines the state of stress within the transformed particle; ϵ^t is defined by Eq. (1) for ZrO_2 . The effect of the constraining matrix on the transformation temperature can be examined with several simplifying assumptions. Assume that the transformation only involves an isotropic volume expansion ($\Delta V/V$), viz $\epsilon_{ij}^t = 1/3 \Delta V/V \delta_{ij}$. With this assumption it can be shown that $\sigma_{ij} = k/3 \Delta V/V \delta_{ij}$, where

$$k = \frac{2E_1E_2}{(1+\nu_1)E_2 + 2(1-2\nu_2)E_1} \quad (5)$$

$E_{1,2}$ and $\nu_{1,2}$ are Young's modulus and Poisson's ratio of the matrix (1) and transformed particle (2). Thus, $U_{se}^0 = k/6 (\Delta V/V)^2$ and Eq. (3) reduces to

$$-\Delta G_{t \rightarrow m}^{chem} > \frac{k}{6} \left(\frac{\Delta V}{V}\right)^2 \quad (6)$$

illustrating that the transformation temperature will depend on the elastic properties of the two materials, expressed here as the constraining modulus, k , and the magnitude of the shape change, expressed here as the volume change, $\Delta V/V$. Alloying additions that lower the unconstrained transformation temperature (i.e., that increase $\Delta G_{t \rightarrow m}^{chem}$) will also lower the constrained transformation temperature. Also, the transformation temperature will be inversely proportioned to the rigidity of the constraint, i.e., the



constraining matrix should have a high elastic modulus to achieve a low transformation temperature. Thus retention of a high temperature phase below its usual transformation temperature can be predicted with the thermodynamics of constrained transformations.

2.3 Transformation and Microcracking

Microcracks are commonly produced during the $ZrO_2(t) \rightarrow ZrO_2(m)$ transformation.⁽⁶⁾ Microcracks relieve some constraint and thus alter the thermodynamics of the constrained transformation from that discussed above. Conditions that produce microcracks must be avoided to maintain constraint and to retain the high temperature phase.

Current observations show that in polycrystalline ZrO_2 , microcracking can be avoided and retention of the tetragonal phase can be achieved by fabricating material with a grain size below a critical value.⁽⁵⁾ As will be shown, this experimental observation can be predicted by examining the thermodynamics of constrained transformation which includes the strain energy release through microcracking.

Assume that during transformation, a small flaw at the particle/matrix interface extends and becomes a microcrack of length c as shown in Fig. 1a. A radial crack would be a likely type of crack due to the volume expansion associated with the transformed ZrO_2 particle. For scaling purposes, a normalized crack length $\mu = c/D$ can be defined, where D is the size of the transformed particle which is assumed to closely resemble a sphere. The presence of the crack will change the energetics of the trans-



formed particle in two respects. First, the crack will relieve a fraction ($f_c(\mu)$) of the strain energy, U_{se} , associated with the uncracked, transformed system. Second, the crack introduces new surface.

The change in free energy of this microcracked system can be written as follows:

$$\Delta G_{t+m}^C = \Delta G_{t+m}^{chem} + U_{se}^0 f_c(\mu) + \frac{A_c \gamma_c}{V} \quad (7)$$

The last term in Eq. (7) is the energy per unit volume of transformed material associated with the crack surface; A_c is the area of the crack surfaces, γ_c is the fracture energy per unit area, and V is the volume of the particle. By defining the area of the crack with respect to the particle's surface ($A_c = \pi D^2 g_c(\mu)$) and using $V = \pi/6 D^3$, Eq. (7) can be rewritten as

$$\Delta G_{t+m}^C = \Delta G_{t+m}^{chem} + U_{se}^0 f_c(\mu) + \frac{6\gamma_c}{D} g_c(\mu) \quad (8)$$

Both $f_c(\mu)$ and $g_c(\mu)$ are dimensionless functions of the normalized crack size, μ ; by definition, $0 < f_c(\mu) \leq 1$ and $g_c(\mu) \geq 0$. When $\mu = 0$, $f_c(\mu) = 1$ and $g_c(\mu) = 0$, and Eq. (8) reverts to Eq. (2).

Eq. (8) shows that the size of the transformed particle (D) is brought into the thermodynamics of the transformation. The transformation will only proceed ($\Delta G_{t+m}^C \leq 0$) for a given crack length, μ_f , when the particle size is greater than a critical value



$$D_{crit}^C > - \frac{6\gamma_c g_c(\mu_f)}{\Delta G_{t \rightarrow m}^{chem} + U_{se}^0 f_c(\mu_f)} \quad (9)$$

Thus, it can be seen that if microcracking were spontaneous with the transformation, a critical particle size exist below which neither transformation nor microcracking could occur. Above this critical size, a possibility exists for transformation and microcracking. As previously shown,* the possibility of microcracking depends on the size of the preexisting flaw, the explicit functions $f(\mu)$ and $g(\mu)$, and the fracture energy γ_c . Inspection of Eq. (9)** shows that for a given μ_f , the critical particle size decreases as $\Delta G_{t \rightarrow m}^{chem}$ becomes more negative. Thus, if the material contains a distribution of particle sizes, the largest particles would be the first to transform and microcrack, proceeded by succeeding smaller particles as the temperature is decreased after fabrication.

2.4 Transformation and Twinning

Extensive twinning occurs during the $ZrO_2(t) \rightarrow ZrO_2(m)$ transformation.⁽⁶⁻¹⁰⁾ Twinning will accommodate a fraction of the shear deformation, and thus reduce the strain energy associated with the transformation. In a manner similar to that discussed for microcracking, (see Fig. 1b), the energetics of the constrained transformation in which the transformed particle twins can be written as

*Extension of the preexisting flaw μ_0 to a size μ_f requires that $\delta \Delta G^C / \delta \mu < 0$. In order to quantitatively use Eq. (9), relations need to be established between μ_0 and μ_f .⁽¹⁶⁾

**Eq. (9) only has physical meaning when $\Delta G_{t \rightarrow m}^{chem} > U_{se}^0 f_c(\mu_f)$.



$$\Delta G_{t \rightarrow m}^C = \Delta G_{t \rightarrow m}^{\text{chem}} + U_{se}^0 f_t(\mu) + \frac{6\gamma_t}{D} g_t(\mu) \quad . \quad (10)$$

The last term is the energy of the twin surfaces per unit volume of transformed material. Here, the total area of the twin boundaries (A_t) is normalized by the particle's surface area ($\mu = A_t/\pi D^2$). The functions $f_t(\mu)$ and $g_t(\mu)$ are dimensionless, $0 < f_t(\mu) \leq 1$, $g_t(\mu) \geq 0$; γ_t is the twin boundary energy per unit area.

Similar in all respects to the microcracking phenomena, a critical particle size exist above which transformation and twinning is possible for a given μ_f :

$$D_{crit}^t > - \frac{6\gamma_t g_t(\mu_f)}{\Delta G_{t \rightarrow m}^{\text{chem}} + U_{se}^0 f_t(\mu_f)} \quad . \quad (11)$$

Below this critical particle size, transformation is not possible. Nucleation and growth of the twins must satisfy the condition $\delta \Delta G^C / \delta \mu < 0$ similar to the treatment of microcracking. The possibility of twinning will depend on the size of the twin nucleus, the explicit functions $f_t(\mu)$ and $g_t(\mu)$, and the twin boundary energy γ_t .

2.5 Conclusion Concerning Retention

Eshelby's treatment of the constrained transformation shows that the elastic constraint of the shape change accompanying a transformation will change the transformation temperature. For the case of ZrO_2 , the transforma-



tion temperature will be lowered. Alloy additions that lower the unconstrained transformation temperature will also lower the constrained transformation temperature. The higher the elastic modulus of the constraining matrix, the lower the transformation temperature.

An extension of Eshelby's treatment has shown that the possibility of microcracking and/or twinning, both of which relieve some of the transformation strain energy, must be avoided by developing a microstructure in which the size of the particle is kept below a critical value. Thus retention of the high temperature phase at lower temperatures is possible if the material is fabricated with the proper microstructure.



3.0 FRACTURE TOUGHNESS

Investigations of the fracture of ceramics containing metastable tetragonal ZrO_2 have shown that transformation to the monoclinic structure occurs in the volume of material adjacent to the fracture surface.⁽³⁻⁵⁾ The depth of the transformed layer is uncertain; Porter and Heuer's TEM studies indicates a depth of $<2\mu m$.⁽³⁾ The transformation is presumed to occur during crack propagation, and to be induced by the stress field of the crack.

In view of the foregoing arguments that the prevention of the $ZrO_2(t)/ZrO_2(m)$ reaction is due to constraint, it is consistent to argue that the stress field of the crack front can release this constraint and allow the reaction to proceed. As will be shown, energy is consumed to release this constraint which contributes to the fracture toughness of the material.

3.1 Contribution to Fracture Toughness

Let us first examine the energetics of crack extension within a material containing a dispersion of retained tetragonal ZrO_2 (volume fraction, V_d). Ignoring for the moment the mechanics and energetics of the stress-induced transformation, it can be stated that a process zone exists at the crack front in which energy is consumed by the transformation. The process zone is shown by the hatched volume surrounding a penny-shaped crack in Fig. 2. The radius (R) of the process zone is assumed to remain constant during crack extension. The energy consumed in forming the process zone is $U_p = U_0 V_d V_p$, where U_0 is the energy consumed per unit volume of transformed



material, and V_p is the volume of the process zone surrounding the crack,
 $V_p = \pi/2(c + 2R)^2 R \approx \pi/2 c^2 R$ when $R \ll c$; c is the crack length. Thus

$$U_p = \frac{\pi}{2} U_o V_d c^2 R \quad (12)$$

As shown by Sack,⁽¹⁷⁾ the net change in energy of a cracked body during the application of an applied stress σ is

$$U_a = - \frac{(1-\nu_c)^2 \sigma^2 c^3}{3E_c} \quad (13)$$

where ν_c and E_c are the elastic properties of the composite. The increase in energy due to the formation of the new fracture surfaces is

$$U_s = \frac{\pi}{4} c^2 G_o \quad (14)$$

where G_o is the critical strain energy release rate associated with forming the new surface. Adding these energy terms together (Eqs. (12), (13), (14)) and invoking Griffith's fracture criteria, i.e., that the change in the system's energy with respect to crack extension must be ≤ 0 , it can be shown that the critical strain energy release rate for the composite is expressed as

$$G_c = G_o + 2 U_o V_d R \quad (15)$$

or expressed as the critical stress intensity factor,



$$K_c = \left[K_0^2 + \frac{2U_0 E_c V_d R}{(1 - \nu_c^2)} \right]^{1/2} \quad (16)$$

Thus, the contribution of the stress-induced transformation to the toughness as expressed by the second term in Eqs. (15) and (16), depends on the energy absorbed per unit volume of transformed material (U_0), the volume fraction of this transformation phase (V_d), the size of the process zone (R), and the elastic properties (E_c , ν_c) of the composite material.

3.2 Determination of U_0

Let us consider the energetics of a isolated particle within the process zone of the stressed crack. As shown by Eshelby,⁽¹⁵⁾ the change in free energy of such a particle within an applied stress field (σ_{ij}^a) is

$$\Delta G_{t \rightarrow m}^c = \Delta G_{t \rightarrow m}^{\text{chem}} + \frac{1}{2} \sigma_{ij}^l \epsilon_{ij}^t - \sigma_{ij}^a \epsilon_{ij}^t \quad (17)$$

For the case considered here, σ_{ij}^a is the stress field in front of a crack. The last term in Eq. (17) is the work performed by the applied stress per unit volume of transformed material. Any stress field which causes the last term in Eq. (17) to have a negative sign will aid the transformation. Because the crack's stress field has the opposite sense to the stress tensor σ^l , negative sign has been placed in front of the last term in Eq. (17). For example, the σ_{ij}^a components are tensile and thus, aid in unconstraining the transformation.



The sum of the last two terms in Eq. (17), as defined by Eshelby,⁽¹⁵⁾ is the increase in the free energy of the system due to the applied stress. If, for some reason, the transformation did not reverse itself once the applied stress was removed, e.g., due to the loss of constraint when the crack propagates through the transformed particle, then the increased energy due to the applied stress is consumed in the fracture process, thus

$$U_0 \equiv \frac{1}{2} \sigma_{ij}^I \epsilon_{ij}^t - \sigma_{ij}^a \epsilon_{ij}^t \quad (18)$$

The condition for the stress-induced transformation is $\Delta G_{t \rightarrow m}^C < 0$, thus from Eq. (17) and (18)

$$U_0 = \frac{1}{2} \epsilon_{ij}^t (\sigma_{ij}^I - 2\sigma_{ij}^a) = -\Delta G_{t \rightarrow m}^{\text{chem}} \quad (19)$$

which allows us to rewrite K_C (Eq. (16)) as either

$$K_C^2 = \left[K_0 + \frac{\epsilon_{ij}^t (\sigma_{ij}^I - 2\sigma_{ij}^a) E_C V_d R}{(1 - \nu_C^2)} \right]^{1/2} \quad (20)$$

or in terms of $\Delta G_{t \rightarrow m}^{\text{chem}}$,

$$K_C = \left[K_0^2 - \frac{2\Delta G_{t \rightarrow m}^{\text{chem}} E_C V_d R}{(1 - \nu_C^2)} \right]^{1/2} \quad (21)$$

If it is assumed for the moment that K_0 , E_C , ν_C and R are unaffected by temperature, Eq. (21) directly shows the temperature dependence of K_C .



Namely, for temperatures where $\Delta G_{t \rightarrow m}^{\text{chem}} > 0$, the transformation will not proceed and $K_c = K_0$. For temperatures where $\Delta G_{t \rightarrow m}^{\text{chem}} < 0$, the contribution of the stress induced transformation will depend on the magnitude of $-\Delta G_{t \rightarrow m}^{\text{chem}}$ until the temperature is reached where the constrained transformation is spontaneous without an applied stress. Below this temperature K_c will again be equal to K_0 . As shown by Eq. (20), the maximum contribution occurs when $\sigma_{ij}^d \approx 0$, i.e., at an applied stress that just pushes the transformation in the forward direction. This condition occurs at a temperature where $-\Delta G^{\text{chem}} \approx 1/2 \sigma_{ij}^I \epsilon_{ij}^t$, or where the constrained transformation is almost spontaneous without an applied stress. Thus, the maximum K_c is given by

$$K_c^{\text{max}} = \left[K_0^2 + \frac{\sigma_{ij}^I \epsilon_{ij}^t E_c V_d R}{(1-\nu_c^2)} \right]^{1/2}. \quad (22)$$

It should be noted here that the upper temperature where the stress-induced transformation will contribute to the fracture toughness will also depend on the alloying composition that affects the condition where $\Delta G_{t \rightarrow m}^{\text{chem}} = 0$. Thus, for pure ZrO_2 where $\Delta G_{t \rightarrow m}^{\text{chem}} = 0$ at $\sim 1200^\circ\text{C}$, toughening should increase as the temperature is cooled from $\sim 1200^\circ\text{C}$; where as for $\text{ZrO}_2 + 3 \text{ m/o } \text{Y}_2\text{O}_3$, where $\Delta G_{t \rightarrow m}^{\text{chem}} = 0$ at $\sim 565^\circ\text{C}$, toughening should not occur until temperatures $< 565^\circ\text{C}$.



3.3 Size of The Process Zone

The preceding section did not discuss the thermodynamics of the transformation that may effect the size of the process zone, R . Two views can be taken on this subject. First, if it is assumed that the transformation is completely reversible with respect to the stress state, it can be shown that the size of the process zone should be constant with respect to temperature. Second, if it is assumed that the stress induced transformation is irreversible, it can then be shown that the size of the process zone strongly depends on temperature. Both views can be developed by examining the size of the zone which would be affected by the stress field of the crack.

The stress distribution close to the crack front has the form

$$\sigma_{ij}^a = \frac{K_c f_{ij}(\theta)}{(2\pi r)^{1/2}} \quad , \quad (23)$$

where $f_{ij}(\theta)$ is an angular function and r is the radial distance from the crack front. Ignoring the angular dependence and assuming that the stress can be approximated by a hydrostatic tension ($\sigma_{ii}^a = \sigma^a$; $\sigma_{ij}^a = 0, i \neq j$), then the radius of a process zone can be defined in which the stress state for $r < R$ is σ^a :

$$R = \frac{K_c^2}{2\pi(\sigma^a)^2} \quad (24)$$



By assuming that the transformation only involves an isotropic volume increase ($\epsilon_{ij}^t = \Delta V/3V$; $\epsilon_{ij}^t = 0$, $i \neq j$) then Eq. (19) can be used to define the magnitude of σ^a required to cause the transformation:

$$\sigma_a = \frac{\Delta G_{t \rightarrow m}^{\text{chem}} + \frac{k}{6} \left(\frac{\Delta V}{V} \right)^2}{\Delta V/V} \quad (25)$$

Substituting Eq. (21) and (25) into Eq. (24) results in

$$R = \frac{K_o^2}{2\pi \left[\frac{\Delta G_{t \rightarrow m}^{\text{chem}}}{\Delta V/V} \right]^2 + \Delta G_{t \rightarrow m}^{\text{chem}} \left[\frac{2\pi}{3} k + \frac{2EV_d}{(1-\nu_c)^2} \right] + \frac{\pi k^2}{18} \left(\frac{\Delta V}{V} \right)^2} \quad (26)$$

Examination of Eq. (26) shows that when $\Delta G_{t \rightarrow n}^{\text{chem}} < 0$, R increases as the temperature is decreased due to the temperature dependence of $\Delta G_{t \rightarrow m}^{\text{chem}}$. Eq. (26) also predicts that a temperature exists where the denominator approaches zero and $R \rightarrow \infty$. This condition is not within the scope of the assumption that $R \ll c$, on which Eq. (23) is based, and it should be neglected.

The discussion to this point has been concerned with the amount of material that could transform within the stress field of a crack. The question that now arises is what proportion will remain in the transformed state once the crack extends and the stress within transformed zone is reduced to zero. Only the material that remains in its transformed state will contribute to the fracture toughness.



The first view is to consider the case where the transformation is stress reversible without a significant hysteresis. In this view, only that proportion of the transformed zone that can not be reconstrained by the matrix, i.e., material adjacent to the new crack surface, will stay in its transformed state and contribute to fracture toughness. That is, the size of the process zone contributing to fracture toughness will only depend on the conditions for loss of constraint due to the fracture surface, e.g., the distance of the transformed particle from the fracture surface. In this case the size of the process zone (R) will be relatively insensitive to temperature and the fracture toughness will be given by Eq. (22).

If on the other hand, the transformation involves a large stress hysteresis, such that the transformation is essentially non-reversible, then the size of the process zone contributing to toughness can be approximated (within the range $R \ll c$) by Eq. (26), which when substituted into Eq. (21) gives

$$K_C = K_0 \left[1 + \frac{2\Delta G_{t \rightarrow m}^{\text{chem}} E_C V_d \left(\frac{\Delta V}{V}\right)^2}{\left[2\pi(1 - \nu_C^2) \Delta G_{t \rightarrow m}^{\text{chem}} + \frac{k}{6} \left(\frac{\Delta V}{V}\right)^2 \right]^2} \right]^{-1/2} \quad (27)$$

Regardless of which view is taken, both Eq. (21) and Eq. (27) illustrate that K_C will increase with decreasing temperature. Eq. (27) predicts a much larger increase in K_C relative to Eq. (21); thus, Eq. (21) and Eq. (27) are lower and upper bound solution for K_C , respectively.



3.4 Conclusions Concerning Fracture Toughness

An energetics approach has been taken to examine the possible contribution of a stress-induced transformation to the fracture toughness of a material containing a metastable phase. The crack's stress field can promote the transformation. The energy consumed by the stress induced transformation per unit volume of permanently transformed material is equal to the change in chemical free energy and thus has the same temperature dependence. Other factors of importance are the volume fraction of the transformed phase and the elastic properties of the composite. The higher the elastic modulus of the composite, the greater the contribution of the stress-induced transformation to toughness. If it is assumed that the transformation suffers no hysteresis with respect to stress, then the size of the process zone should be relatively unaffected by temperature, and K_{IC} is given by Eq. (21). On-the-other-hand, if the transformation suffers a large stress hysteresis, the size of the process zone is significantly affected by temperature, and K_{IC} can be approximated by Eq. (27). In either case, K_{IC} will increase with decreasing temperature.



Rockwell International
Science Center

SC5117.6TR

ACKNOWLEDGEMENT

The author would like to acknowledge the valuable discussions with A.G. Evans and D. R. Clarke. This work was supported by the Office of Naval Research, Contract Number N00014-77-C-0441.



REFERENCES

1. R. C. Garvie, R. H. Hennick and R. T. Pascoe, *Nature* 258, 703 (1975).
2. R. C. Garvie and R. T. Pascoe, *Processing of Crystalline Ceramics*, ed. by H. Palmour III, R. F. Davis and T. M. Hare, p. 263, Plenum Press (1978).
3. D. L. Porter and A. H. Heuer, *J. Am. Ceram. Soc.* 60, 183 (1977); *ibid.* 280 (1977).
4. T. K. Gupta, J. H. Bechtold, R. C. Kuznichi, L. H. Cadoff and B. R. Rossing, *J. Mat. Sci.* 12, 2421 (1977).
5. T. K. Gupta, F. F. Lange and J. H. Bechtold, *J. Mat. Sci.* 13, 1464 (1978).
6. E. C. Subbarao, H. S. Maiti and K. K. Srivastava, *Phys. Stat. Sol.* 21, 9 (1974).
7. A. Heuer and G. L. Nord, Jr., *Electron Microscopy in Mineralogy*, ed. by H. R. Weuk, p. 274, Springer-Verlag (1976).
8. J. E. Bailey, *Proc. Roy. Soc.* 279A, 395 (1964).
9. G. K. Bansal and A. H. Heuer, *Acta Met.* 22, 409 (1974).
10. S. T. Buljan, H. A. McKinstry and V. S. Stubican, *J. Am. Ceram. Soc.* 59, 351 (1976).
11. R. N. Patil and E. C. Subbarao, *J. Appl. Cryst.* 2, 281 (1969).
12. K. K. Srivastava, R. N. Patil, C. B. Chandary, K. V. G. K. Gokhale and E. C. Subbarao, *Trans. Brit. Ceram. Soc.* 73, 85 (1974).
13. H. G. Scott, *J. Mat. Sci.* 10, 1527 (1975).
14. V. S. Stubican, R. C. Hink and S. P. Ray, *J. Am. Ceram. Soc.* 61, 17 (1978).
15. J. D. Eshelby, *Progress in Solid Mechanics*, Vol. 2, ed. by I. N. Sneddon and R. Hill, p. 89, North-Holland (1961).
16. F. F. Lange, *Fracture Mech. of Ceramics*, Vol. 4, ed. by R. C. Bradt, D. P. H. Hasselman and F. F. Lange, p. 799, Plenum Press (1978).
17. R. A. Sack, *Proc. Phys. Soc. (London)* 58, 729 (1946).



FIGURE CAPTIONS

- Fig. 1 a) Schematic of the untransformed (t) and transformed, microcracked (m) states; μ_f is the final, normalized microcracked size.
b) Schematic of the untransformed (t) and transformed, twinned (m) states; μ_f is the total area of the twin boundaries normalized to the particle's area.
- Fig. 2 Crack of length c with a process zone of radius R.



SC5117.6TR

SC79-5844

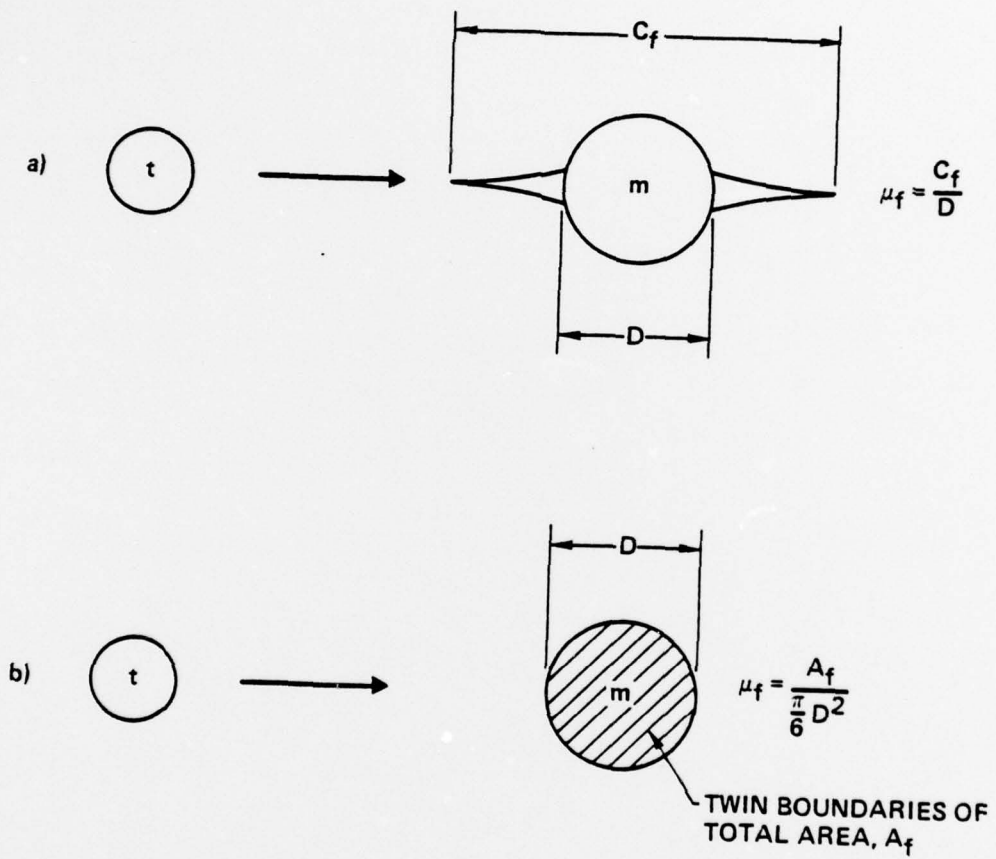
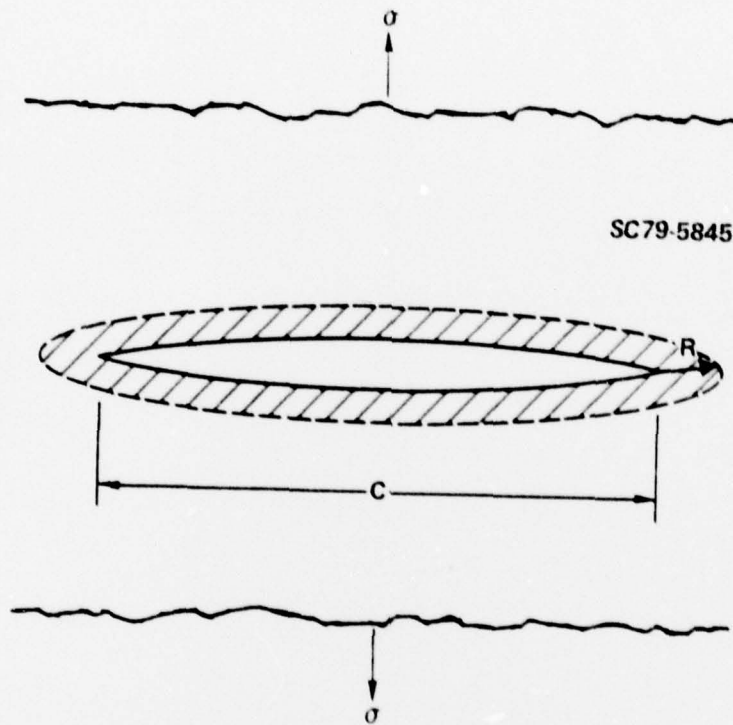


Fig. 1



SC5117.6TR



SC79-5845

Fig. 2