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Nucleation in Stress-Induced Tetragonal-Monoclinic Transformation of Constrained Zirconia*

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**NUCLEATION IN STRESS-INDUCED TETRAGONAL-MONOCLINIC
TRANSFORMATION OF CONSTRAINED ZIRCONIA**

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Abstract

A theory for stress-induced tetragonal→monoclinic transformation of constrained zirconia is presented based on the assumption that when forcibly strained to a regime of absolute instability where the free energy density of the tetragonal phase has a negative curvature, the constrained tetragonal zirconia becomes unstable with respect to the development of a modulated strain pattern that will evolve into a band of twin monoclinic domains. The temperature range for such an instability, the critical size of the inclusion, the corresponding critical strain, and the periodicity of the modulation are derived in terms of parameters that can be related to the elastic stiffness coefficients of various orders of the inclusion and the shear modulus of the host matrix. An entirely different mechanism is suggested for the reverse monoclinic→tetragonal transformation because the monoclinic phase is metastable when the extrinsic stress is removed. Estimates for the parameters are inferred from a variety of experimental data for pure zirconia and the numerical values for the predicted physical quantities are obtained.

I. Introduction

The stress-induced tetragonal (t) \rightarrow monoclinic (m) transformation of constrained zirconia has been of intense interest since the heyday of the discovery of the phenomenon of transformation toughening.¹ Various theories have been attempted based on different nucleation perspectives^{2,3} and on end-point thermodynamics.⁴ Although a generally satisfactory quantitative description of the transformation is still an elusive goal, these attempts explored the consequences of useful ideas, leading to information for later research to draw on. Recently some experimental and theoretical work have been carried out for unconstrained zirconia to obtain a basic science perspective of the lattice properties,^{5,6,7} vibrational modes,^{8,9} the interplay between symmetry and collective atomic movements,¹⁰ nonclassical nucleation from partially soft lattice modes,^{11,12} and stability limits for the t and m phases.¹³ Based on the understanding obtained in these efforts for the unconstrained situation, some ideas will be explored and results presented in this paper for stress-induced t \rightarrow m transformation of constrained zirconia. The objectives of this exposition are (1) the factors that determine the critical strain, (2) the temperature ranges for the t \rightarrow m transformation and for the switching of t domains, (3) the critical size of a transformable inclusion, and (4) the difference between the plausible mechanisms of the t \rightarrow m and the reverse m \rightarrow t transformations.

II. Thermodynamic Instabilities and Modes of Transformation

A thermodynamic state of a system is stable if its corresponding free energy F is at a minimum $\delta^2 F > 0$, i.e., second order variation with respect to appropriate parameter is positive definite. When the minimum is a global one, i.e., it has the

lowest F compared to all other minima, the state is absolutely stable against all manners of probing by perturbation. However, when the minimum is a local one, the state is only metastable in the sense that the system is stable against perturbations of small amplitudes but unstable against perturbations of larger amplitudes that can take the system from the local minimum over the intervening barrier into the global minimum. When a state ceases to correspond to a minimum in free energy because of changing parameters and becomes associated with an inflexion or a saddle point, i.e., $\delta^2F = 0$ for variation in at least one degree of freedom, the system is absolutely unstable against even small amplitude perturbations. Based on this difference in response to large and small amplitude perturbations, Gibbs^{14,15} introduced a classification scheme that divides phase transformations into two types (I) those that start with a perturbation that is large in the degree of transformation but small in spatial extent and (II) those that start with a perturbation that is small in the degree of transformation but large in spatial extent. The former type corresponds to first order transformations that begin with the nucleation of critical nuclei (or embryos) of the new phase and are followed by their subsequent growth (Fig. 1, upper). The latter type corresponds to all homogeneous transformations including spinodal decomposition and other modes involving long wavelength modulations (Fig. 1, lower) that proceed by the amplification of the initially small amplitudes. The term nucleation was originally used exclusively for type I transformations only. However, in recent times, it is used frequently in a more generalized sense to cover the beginning of any transformation, including type II ones that involve no critical nuclei at all. The intention of this paper is to examine the onset of modulated strain instability (type

II) when a constrained inclusion of t zirconia is forcibly taken from a stable thermodynamic state ($\delta^2F > 0$) into an unstable regime ($\delta^2F \leq 0$) by an extrinsic stress field and the possible reversal when the stress is removed. The term nucleation should be understood here in the generalized sense.

III. Lattice Modes and Driving Parameter for the t→m Transformation

In general, displacive and martensitic transformations involve minute but cooperative movements of atoms from their original equilibrium positions and are describable in terms of the symmetry-allowed lattice vibrational modes of the parent structure. For the t→m transformation of zirconia, the m structure is related to the parent t structure by a small number of collective motions. Three of these quantify the macroscopic size and shape changes in terms of nonlinear Lagrange strains^{10,11}

$$\eta_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} + \sum_k \frac{\partial u_k}{\partial r_i} \frac{\partial u_k}{\partial r_j} \right), \quad (1)$$

where r_i ($i = 1,2,3$) are the Cartesian coordinates attached to the axes of the unit cell of the t structure and u_i ($i = 1,2,3$) are components of a displacement vector. They are

- (1) uniform change of the basal square, $\eta_{xx} + \eta_{yy}$,
- (2) uniform change of the 4-fold axis, η_{zz} , and
- (3) homogeneous shears of the xz and yz planes, the doublet (η_{xz}, η_{yz}) .

The energies associated with these motions are embodied in the elastic constants of the t phase $c_{11} + c_{12}$, c_{33} , and c_{44} , respectively.^{10,11} They are associated with long wavelength acoustic phonons (in-phase vibrations) at the center of the Brillouin

zone of the reciprocal lattice of the t structure. There are five other motions that together quantify the sublattice movements (shuffles) within the unit cell of the t structure and produce the correct periodicity of the m structure.⁸ They are optical phonons (out-of-phase vibrations) M_1, M_2, \dots, M_5 at the M point (110) of the Brillouin zone boundary. These are associated with five different frequencies.

In principle, the free energy density f_0 relevant to the $t \rightarrow m$ transformation is a function of all these lattice modes

$$f_0 = f_0 [\eta_{xx} + \eta_{yy}; \eta_{zz}; (\eta_{xz}, \eta_{yz}); M_1, \dots, M_5]. \quad (2)$$

However, these normal mode motions are not independent of one another but are connected via anharmonic (i.e., higher than second order) coupling coefficients. As such, not all of them are needed explicitly to formulate a quantitative theory. It has been suggested⁸ that since the five optical phonon modes are triggered off simultaneously at the $t \rightarrow m$ transformation, they are passive motions dragged along by the driving shear motion (η_{xz}, η_{yz}) . Furthermore, the changes in the size represented by $\eta_{xx} + \eta_{yy}$ and η_{zz} can also be absorbed as implicit parameter¹² in the coefficients of the Taylor expansion of f_0 in terms of η_{xz} and η_{yz} . The free energy density can therefore be expressed in terms of the explicit parameters of the shears η_{xz}, η_{yz} as, up to the sixth order,

$$f_0 = f_0(\eta_{xz}, \eta_{yz}) = A\eta^2 + B_1\eta^4 + B_2\eta^4 \cos 4\phi + C_1\eta^6 + C_2\eta^6 \cos 4\phi \quad (3)$$

where $\eta^2 = \eta_{xz}^2 + \eta_{yz}^2$, $\eta_{yz} = \eta \cos \phi$, and $\eta_{xz} = \eta \sin \phi$.

The coefficients A , B 's, and C 's involve, respectively, elastic constants of the second, fourth, and sixth orders, the explicit forms of which may be found in Ref. 11.

Depending on how these coefficients are related to one another as the external parameters (such as temperature, hydrostatic pressure, composition, etc.) are varied, Eq. (3) can depict (Fig. 2) four degenerate minima at $\eta \neq 0$ representing the four variants of the m phase that are strained differently with respect to the t phase at $\eta = 0$. The behavior can best be visualized by focusing on one representative planar section $\phi = 0$ (Fig. 3) of the three-dimensional plot. We have,¹¹ in this plane,

$$f_0 = A\eta^2 - B\eta^4 + C\eta^6, \quad (4)$$

where $B = -(B_1 + B_2)$ and $C = C_1 + C_2$. Above an upper critical temperature T^* , the t phase is absolutely stable and the minima corresponding to the m phase have yet to develop from the inflexion points of the free energy for T^* . Just below T^* , four minima with $\eta \neq 0$ (two being in the plane $\phi = 0$) representing the m phase start to evolve until at T_0 when they are at the same free energy as the minimum at $\eta = 0$ for the t phase. This temperature T_0 is the coexistence temperature between the t and m phases. Below T_0 the m phase becomes more stable than the t phase. Finally, at the lower critical temperature T_c , the original minimum at $\eta = 0$ becomes an inflexion point. The temperatures T^* and T_c represent, respectively, the upper stability limit of the m phase and the lower stability limit of the t phase.^{11,13}

IV. The Onset of Stress-Induced Transformation in a Constrained Inclusion

Suppose an inclusion is homogeneously sheared and held at a strain η_0 , the interface with the similarly strained surrounding material being coherent. We want to determine the criterion under which the inclusion together with its immediate

environment would become unstable with respect to the development of modulation of the shear strain. For simplicity, we assume that the original inclusion is spherical. After being sheared, a modulation of amplitude a and wavelength λ along the direction of the original polar axis z is allowed to develop (Fig. 4):

$$\eta(z) = \eta_0 + a \cdot \sin(2\pi z/\lambda). \quad (5)$$

The local free energy density inside the inclusion depends on both the local strain η and its spatial gradient $\nabla\eta$.^{11,12} We have, to second order,

$$f_0 = f_0(\eta, \nabla\eta) = f_0(\eta_0) + f'_0(\eta_0)(\eta - \eta_0) + \frac{1}{2} f''_0(\eta_0)(\eta - \eta_0)^2 + \kappa(d\eta/dz)^2, \quad (6)$$

where $f'_0 = df_0/d\eta$ and $f''_0 = d^2f_0/d\eta^2$ are the first and second derivatives, respectively, of the homogeneous part of the free energy density $f_0(\eta_0)$, given by Eq. (3), and κ is a coefficient that can be related to interfacial free energy. The change in the total free energy of the inclusion becomes, to second order in the amplitude a ,

$$\Delta F_I = \int dV \left[\frac{1}{2} f''_0(\eta_0)(\eta - \eta_0)^2 + \kappa(d\eta/dz)^2 \right]. \quad (7)$$

The first order term involving $(\eta - \eta_0)$ drops out of the integral because η_0 is the average strain of the inclusion. Substituting Eq. (5) into Eq. (7), we have

$$\Delta F_I = \int dV \left[\frac{1}{2} a^2 f''_0(\eta_0) \sin^2(2\pi z/\lambda) + \kappa(2\pi a/\lambda)^2 \cos^2(2\pi z/\lambda) \right]. \quad (8)$$

Since the volume integration averages over many wavelengths of the modulation, each sinusoidal square term contributes to the same factor $\frac{1}{2}$ and we have

$$\Delta F_I = \frac{1}{3} \pi R^3 a^2 \left[f''_0(\eta_0) + 8\pi^2 \kappa/\lambda^2 \right]. \quad (9)$$

There will be a concomitant layer of modulated strain developed in the host matrix around the inclusion. This modulated strain field will decay away from the surface of the inclusion because of destructive interference from the ups and downs of the modulation, in accordance with the St. Venant principle in elasticity, and vanish over a distance $\sim\lambda$.^{16,17} Within this layer, the host matrix will have the additional strain $a.\sin(2\pi z/\lambda)$ leading to an additional average strain energy density $\frac{1}{4}\mu a^2$, where μ is the shear modulus of the host matrix which is assumed to be an isotropic material. The total change in the strain energy stored in the layer is therefore

$$\Delta F_M = \pi R^2 \mu a^2 \lambda . \quad (10)$$

Adding this to Eq. (9), the total change in free energy as a result of the modulation is, to second order in the amplitude a ,

$$\Delta F = \Delta F_I + \Delta F_M = \frac{1}{3} \pi R^3 a^2 \left[f_0''(\eta_0) + 8\pi^2 \kappa / \lambda^2 + 3\mu \lambda / R \right] . \quad (11)$$

For any amplitude a , the most energetically favorable wavelength λ corresponds to $\partial\Delta F/\partial\lambda = 0$, i.e.,

$$\lambda_m^3 = \frac{16\pi^2 \kappa}{3\mu} R . \quad (12)$$

For this particular wavelength, the total change in free energy is

$$\Delta F = \frac{1}{3} \pi R^3 a^2 \left[f_0''(\eta_0) + \beta / R^{\frac{2}{3}} \right] , \quad (13)$$

where $\beta = \left(486\pi^2 \mu^2 \kappa\right)^{\frac{1}{3}}$. Provided that the curvature f_0'' at η_0 is sufficiently negative, the criterion for instability with respect to strain modulation is

$$R > R_c = \sqrt{486\kappa} \pi\mu / (-f_0'')^{\frac{3}{2}}. \quad (14)$$

The precise geometry of the free energy surface represented by Eq. (3) and depicted in Fig. 4 changes with external parameters (e.g., temperature and hydrostatic pressure) in a rather complex manner. To make the task of obtaining numerical estimates simple, we shall assume that reasonable parametric dependence of the curvature f_0'' can be obtained from consideration of the planar section $\phi = 0$ (Fig. 3) alone. Then from Eq. (4), we have

$$-f_0'' = \frac{8B^2}{3C} (\sqrt{x} - x), \quad (15)$$

where

$$x = 1 - 3AC/B^2. \quad (15a)$$

If we assume that only the second order coefficient A in Eqs. (3) and (4) carry sensitive temperature dependence which can be linearized about the lower critical temperature T_c as

$$A(T) = A'(T - T_c), \quad (16a)$$

where

$$A' = \left(\frac{dA}{dT} \right)_{T_c}$$

then by differentiation of Eq. (4), we find at the upper critical temperature T^* ,

$$A(T^*) = \frac{B^2}{3C} \quad (16b)$$

and at the coexistence temperature T_0 ,

$$A(T_0) = \frac{B^2}{4C}. \quad (16c)$$

Substituting Eqs. (16a), (16b), and (16c) into Eq. (15), we find that the negative curvature $-f_0''$ is zero at T^* and, with decreasing T , rises sharply first and then much more gradually reaching a maximum value of $\frac{2B^2}{3C}$ at T_0 .

The above treatment addresses only the onset of modulated instability superposed on a homogeneously strained inclusion. To predict the final form of the product, one would have to carry out a numerical computation of the kinetics of evolution based on irreversible statistical thermodynamics. However, even without such an investigation, one can draw the following conclusions from the incipient instability:

- (1) Since T^* is the temperature above which the curvature f_0'' ceases to be negative, for a given t inclusion, however large, no macroscopic strain η_0 can induce it to transform into a modulated pattern of m domains. Above T^* , the extrinsic stress can only switch some of the original t domains in the inclusion into one favored by the biasing stress.
- (2) Somewhat below T^* , when the curvature f_0'' becomes sufficiently negative at η_0 , inclusions exceeding the critical size of radius R_c will transform into a modulated pattern while those below will not.
- (3) Since the curvature f_0'' is temperature dependent, being zero at T^* and attaining the largest negative value at T_0 , the critical radius R_c varies with temperature, being infinite at T^* and, with decreasing T , drops sharply first and then much more gradually reaching the smallest value at T_0 .
- (4) If the incipient instability leads finally to a twin band of the m phase inside the transformed inclusion, then the periodicity λ_m of the band varies with the radius R of the inclusion as $\lambda_m \sim R^{\frac{1}{3}}$.

V. The Reverse $m \rightarrow t$ Transformation After Stress is Released

In the temperature regime for which the t phase is stable, an inclusion with a twin band of m domains previously formed under the influence of an extrinsic stress is thermodynamically metastable after the stress is released. Each m domain, the free energy density of which is only a local minimum, will eventually transform back to the t phase, the free energy density of which is a global minimum. However, these m domains are stable against small amplitude perturbation of large spatial extent (i.e., type II of Gibbs) but unstable only against much larger amplitude perturbation of small spatial extent (i.e., type I of Gibbs). Since the precursors to the former perturbation, the harmonic lattice waves, are always present while those for the latter, the anharmonic solitary waves, are rare except in the vicinity of extended defects where the harmonic lattice waves can pile up to form solitary waves, the reverse $m \rightarrow t$ transformation which proceeds via the growth of critical nuclei may have a rather long incubation time. The reverse process is possible provided that the host matrix surrounding the inclusion has not undergone any irreversible change that can retain some residual stress when the inclusion originally transformed from the t phase into the m with the accompanying volume expansion.

VI. Discussions

It is appropriate to discuss how the theoretical results may be related to an actual material under hypothetical service condition. The free energy functional Eq. (4) with the gradient term in Eq. (6) is isomorphic to the Landau-Ginzburg-Devonshire generic type¹⁸ of even power free energy expansion with a negative fourth order coefficient which can lead to a first order transformation. For such a

functional, it is straightforward to derive the following measurable quantities in terms of the parameters A' , B , C , and κ :

- (1) latent heat at $T_0 = A' BT_0/(2C)$,
- (2) surface energy at $T_0 = \frac{1}{8} B^2 \sqrt{\kappa/C^3}$,
- (3) discontinuous jump of self-strain $\Delta\eta = 2B/(3C)$, and
- (4) temperature gradient of the square of the self-strain $d\eta^2/dT = A'/(2B)$.

Data on these quantities for stabilized zirconias are not available. We shall instead illustrate the results with parameters for pure zirconia. The latent heat ($1420 \text{ cal mole}^{-1}$) and the surface energy (360 erg cm^{-2}) can be obtained from Ref. 19. The temperature dependence of the self-strain η can be deduced from the x-ray data of Ref. 20 leading to $A'/(2B) \cong 5 \times 10^{-6}/^\circ\text{C}$ and $2B/(3C) \cong 2.25 \times 10^{-2}$. From these we obtain the estimates $\kappa = 1.5 \times 10^{-2} \text{ erg cm}^{-1}$, $B = 10^{13} \text{ erg cm}^{-3}$, and $C = 2.5 \times 10^{14} \text{ erg cm}^{-3}$. Assuming that spherical inclusions of pure zirconia are dispersed in a hypothetical matrix with a shear modulus of $10^{12} \text{ erg cm}^{-3}$, we have for the critical radius of a transformable inclusion $R_c \cong 0.6 \mu\text{m}$ at the largest negative curvature $-f_0'' = 2B^2/(3C)$ with a corresponding stress induced strain $\eta_0 = \sqrt{B/(6C)} \cong 0.08$. The wavelength of the modulation is $\lambda_m = 0.05 \mu\text{m}$ for an inclusion of radius $R = 1 \mu\text{m}$. These numerical results for constrained pure zirconia in a hypothetical matrix are rather reasonable compared to experimental measurements for stabilized zirconia in Al_2O_3 matrix.²¹ A more stringent test would require measurements of the higher order elastic stiffness coefficients for the stabilized zirconias.

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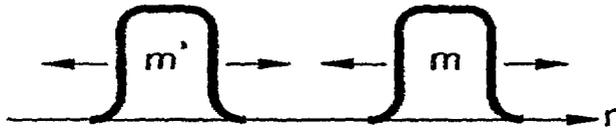
Figure Captions

- Fig. 1.** Schematic illustration of Gibbs' classification. Upper (type I): Transformation proceeds by nucleation via localized fluctuation of large amplitude followed by growth of nuclei. Lower (type II): Transformation proceeds by the development of long wavelength modulations of infinitesimal amplitude followed by increase of these amplitudes.
- Fig. 2.** Two sections of the surface of the free energy density f_0 for a homogeneous material of tetragonal symmetry. The two pairs of homogeneous strains $\pm\eta_{yz}$, $\pm\eta_{xz}$ can lead to four variants I, II, III, and IV of monoclinic symmetry. The four degenerate local minima can become competitive with the minimum at $\eta = 0$ corresponding to the tetragonal symmetry.
- Fig. 3.** One particular section of the surface of the free energy density f_0 showing the relative changes of the three extrema as the temperature varies. T^* is the upper critical temperature above which the monoclinic phase becomes absolutely unstable. T_0 is the coexistence temperature at which the tetragonal and monoclinic phases can coexist in equilibrium. T_c is the lower critical temperature below which the tetragonal phase becomes absolutely unstable. The dotted curves indicate how the inflexion points evolve into minima and maxima as the temperature varies between T^* and T_c .
- Fig. 4.** Schematic illustration of the surface of the free energy density f_0 in one quadrant. If an extrinsic stress brings about a homogeneous strain η_0 of the material that corresponds to a negative curvature f_0'' of the surface such

as on or between the dotted curves, a modulated strain pattern will develop which eventually leads to a band of alternating m_I and m_{II} domains.

Fig. 5. Schematic illustration of a spherical inclusion (inside) with a sinusoidal strain pattern superposed on a stress induced homogeneous strain η_0 . The modulation leads to destructive interference of the strain field outside the inclusion which decays completely beyond the shell (outside the inclusions) of thickness of a wavelength of the modulation.

TYPE I



TYPE II

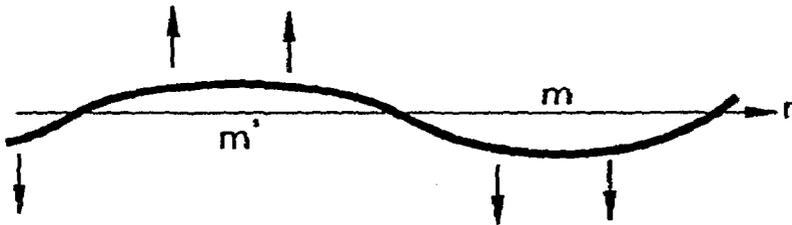


Fig. 1
(Chan)

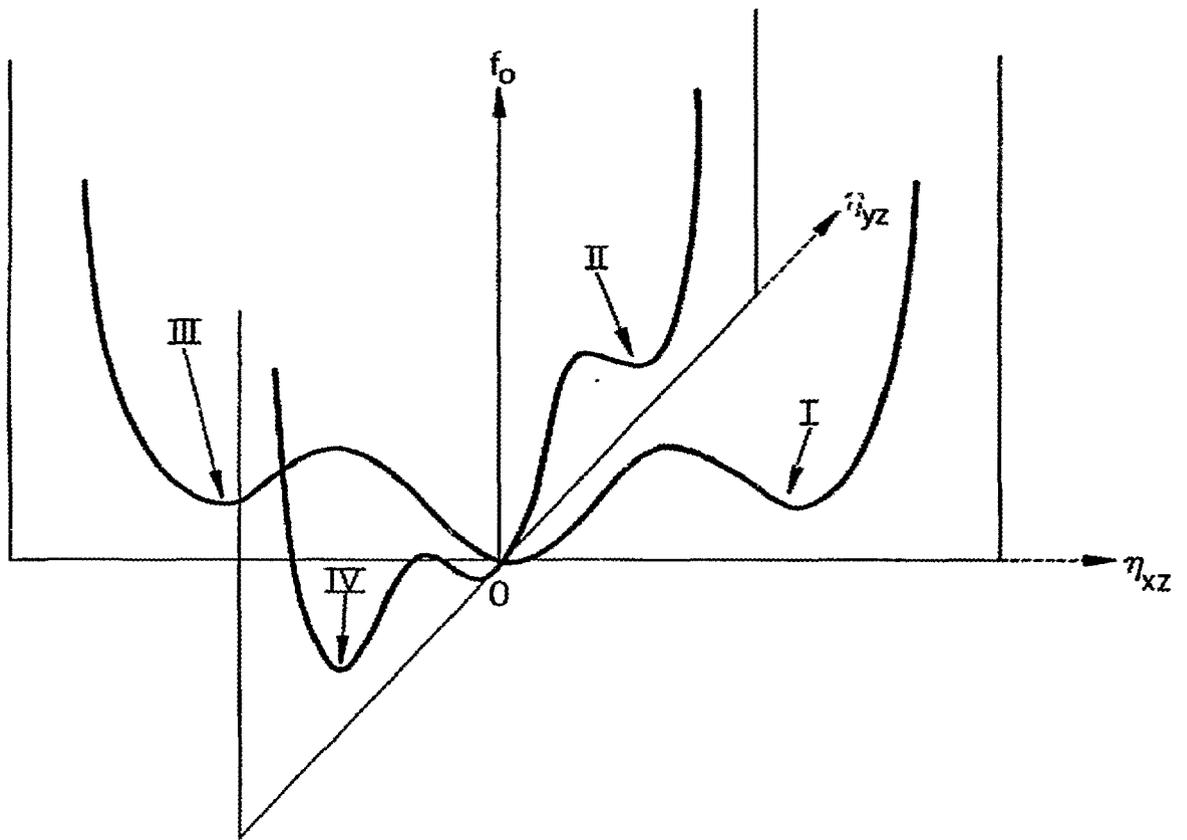


Fig. 2
(Chan)

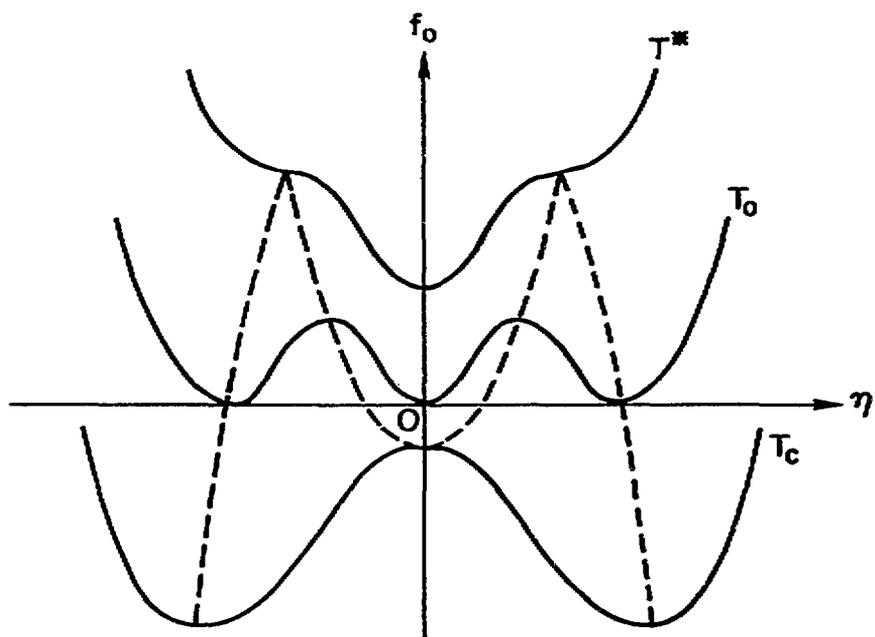


Fig. 3
(Chem)

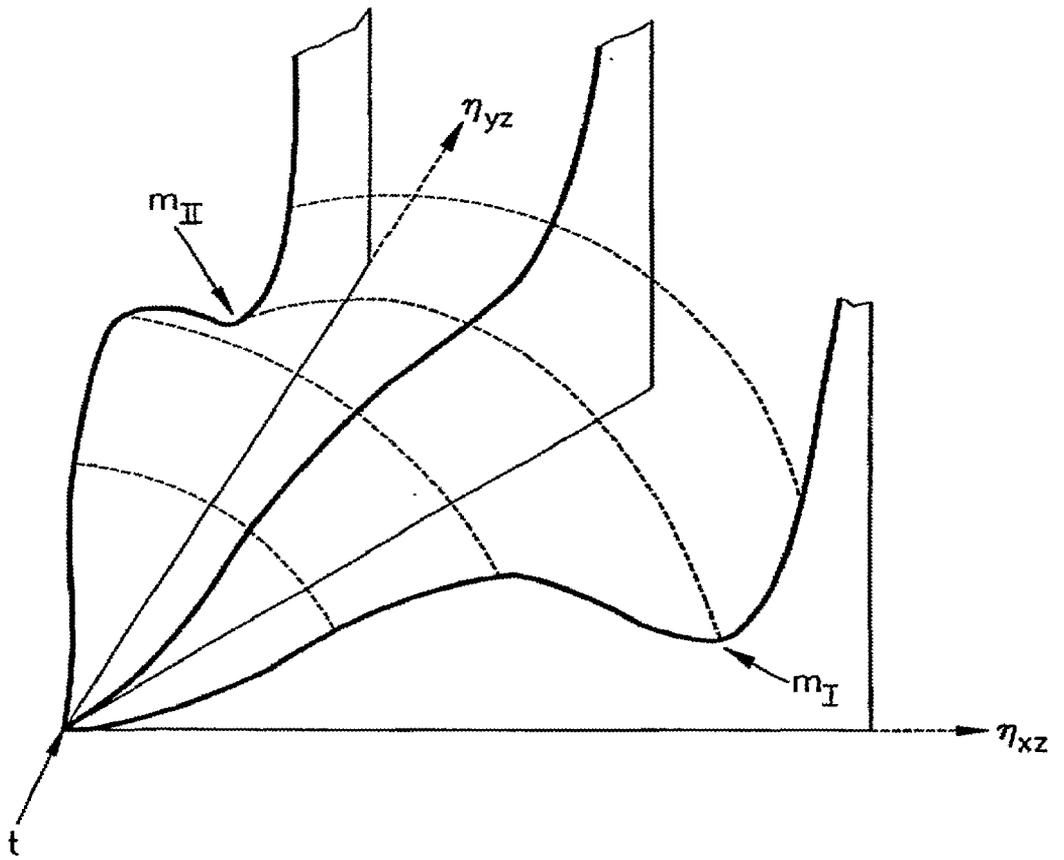


Fig 4
(Chan)

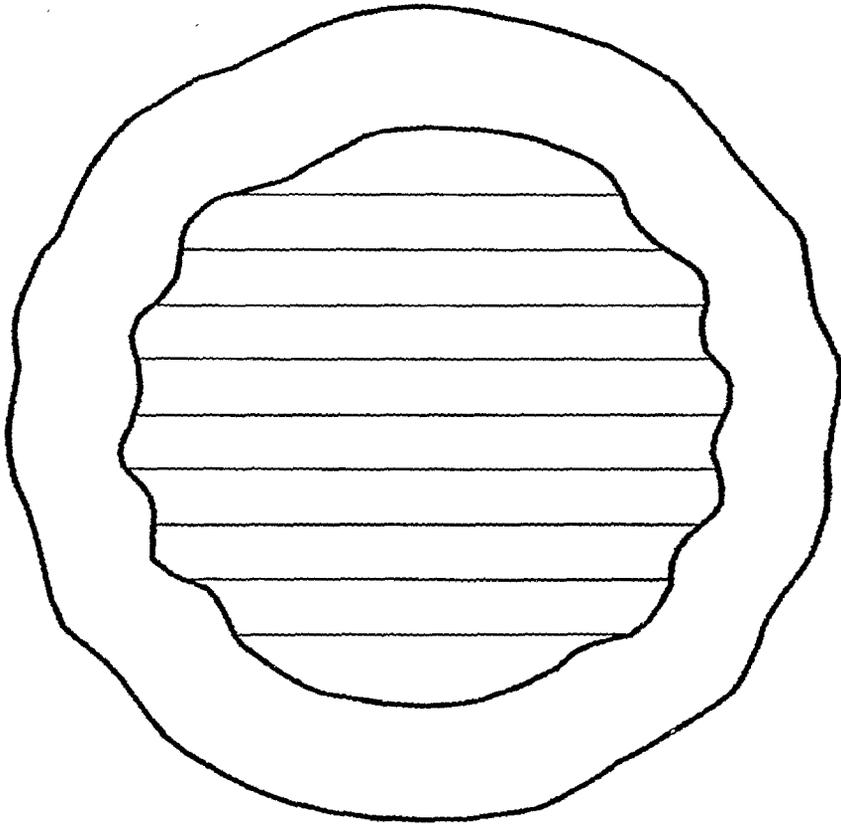


Fig 5
(Chan)

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