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A STATISTICAL MECHANICS MODEL OF PHASE TRANSFORMATION OF ZIRCONIA PARTICLES IN CERAMICS

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Abstract—In this investigation, a statistical mechanics model was developed to predict the relation between the volume fraction of zirconia particles, temperature and external load. By establishing the corresponding relation between our model and the generalized Ising model in statistical physics, the critical condition of transformation has been obtained, and when the system is near its critical state, some universal relations between the volume fraction, temperature and load have been derived.

1. INTRODUCTION

THE DISCOVERY and utilization of the transformation-toughening effects of zirconia particles in brittle matrix have resulted in improved mechanical properties of ceramics. Transformation toughening occurs as the result of a dilation and shear strain which occurs in zirconia particles during tetragonal-to-monoclinic phase transformation. To understand this important phenomenon, many experimental and theoretical researches have been carried out [1–5]. At the present stage, it is well-known that both the toughening effect and the constitutive relation of zirconia-containing ceramics are related directly to the volume fraction of transformed tetragonal particles, and the volume fraction of transformed zirconia depends on the external load and temperature. Except having developed some macroscopic conditions for the transformation, very little work seems to have been done to predict the relation between the volume fraction of transformed particles, temperature and external load through microstructural analysis. This research attempts to derive such a relation.

If we could observe a tetragonal particle in a matrix which is subjected to an external load and temperature, it would be obvious that whether it has transformed from tetragonal to monoclinic phase or not is a random event. This means that even at the same external condition, different specimens will give different results. Since we are only interested in obtaining the relation between some average or overall properties of material such as the volume fraction of transformed particles and its external conditions, this simplifies our problem a great deal. In this paper, we develop a statistical mechanics model to predict a relation between the volume fraction, temperature and external load. By establishing the corresponding relation between our model and the generalized Ising model in statistical physics, we have derived some specific characteristics of the volume fraction of transformed particles as a function of temperature and external load. For example, we have obtained the critical condition of transformation which corresponds to the yield condition in constitutive relation. When the system approaches its critical temperature, we have found some universal relation between the volume fraction, temperature and external load, etc.

2. THE STATISTICAL MODEL BASED ON THE GENERAL MAXIMUM-ENTROPY FORMALISM

Guided by various experimental observations, we attempt to build a statistical mechanics model to predict the characteristics of the phase transformation of ZrO_2 particles in ceramics which

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are subjected to an external load and temperature. Without loss of generalization, we consider the PSZ multiphase material (Fig. 1), where the particles of the second phase (tetragonal) make up the transformable materials. If the ceramics is in the environment temperature T and subjected to an external stress field σ^0_{ij}, some tetragonal particles may transform to monoclinic ZrO_2. During the tetragonal-to-monoclinic phase transformation, a stress-free strain should occur in the particles. Under the action of external field (σ^0,T), it is a random event whether a particle transforms from tetragonal to monoclinic phase or not. Therefore, even at the same external condition, we will find different configurations of transformed particles for the same material. So we introduce the following statistical mechanics model.

First, we assume that the particles of the second phase (here we refer to tetragonal ZrO_2) form some fixed lattice, and under the action of external field (σ^0,T), some particles in the lattice may transform to monoclinic phase. If we denote $\varphi(\mathbf{r}_i)$ as

$$\varphi(\mathbf{r}_i) = \begin{cases} 1 & \text{if the particle at } \mathbf{r}_i \text{ transformed from T to M} \\ 0 & \text{no transformation.} \end{cases} \tag{1}$$

For a given configuration of transformed particles $\Phi = \{\varphi(\mathbf{r}_1), \varphi(\mathbf{r}_2), \ldots, \varphi(\mathbf{r}_i), \ldots\}$, the total energy of the whole system can be written as

$$H = H_0 - h(\sigma^0,T)\sum_i \varphi(\mathbf{r}_i) - \sum_{(i,j)} J(\mathbf{r}_i - \mathbf{r}_j)\varphi(\mathbf{r}_i)\varphi(\mathbf{r}_j) - \ \ldots, \tag{2}$$

where H_0 is the total energy of the system without any transformed particles under a given temperature, and it is a sum of the strain energy and potential energy of the external force. $h(\sigma_0,T)$ is the change of the total energy of a particle when it transforms from tetragonal to monoclinic phase. It is the sum of the elastic interaction energy E^e of the stress-free strain accompanying the T-to-M transformation, the chemical energy E^c and the surface energy which is neglected in this paper. Thus,

$$h(\sigma_0,T) = -(E^e + E^c), \tag{3}$$

$J(\mathbf{r}_i - \mathbf{r}_j)$ is the elastic interaction energy of two transformed particles at $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively. To simplify the calculation, in what follows, we only consider the interaction between the nearest neighbors, so $\mathbf{r}_i$ and $\mathbf{r}_j$ can be considered as the neighboring sites in the lattice. In the following part, we will give the explicit expressions of $h(\sigma_0,T)$ and $J(\mathbf{r}_i - \mathbf{r}_j)$ for the tetragonal-to-monoclinic transformation of ZrO_2 particles.

According to the maximum-entropy formalism in statistical mechanics [6], the occurrence probability of the configuration $\Phi = \{\varphi(\mathbf{r}_1), \varphi(\mathbf{r}_2), \ldots, \varphi(\mathbf{r}_i), \ldots\}$ of transformed particles is related to the system energy of this configuration as follows

$$P(\Phi) = \frac{1}{Z}e^{-H/BT}, \tag{4}$$

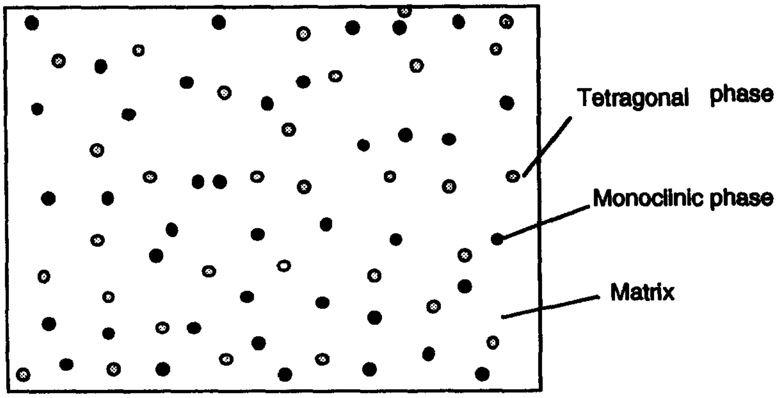

Fig. 1. Schematic of PSZ material.

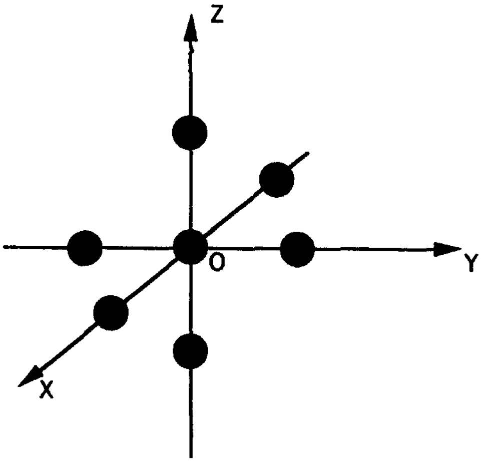

Fig. 2. Schematic of a cell in a cubic lattice.

where B is a material constant rather than Boltzmann's constant, T is absolute temperature and

$$Z = \sum_{\{\varphi\}} e^{-H/BT} \tag{5}$$

is called the partition function, $\Sigma_{\{\varphi\}}$ means a sum over all possible configurations of the transformed particles.

Since we assume that the parent ZrO_2 particles form a fixed lattice, for example, a cubic lattice, each site of which has six nearest neighbors which are along x, y, z directions (Fig. 2). For this case, eq. (2) becomes

$$H = H_0 - h(\sigma^0,T)\sum_i \varphi(\mathbf{r}_i) - J_x\sum_{(i,j)}^{x} \varphi(\mathbf{r}_i)\varphi(\mathbf{r}_j) - J_y\sum_{(i,j)}^{y} \varphi(\mathbf{r}_i)\varphi(\mathbf{r}_j) - J_z\sum_{(i,j)}^{z} \varphi(\mathbf{r}_i)\varphi(\mathbf{r}_j), \tag{6}$$

where J_x, J_y, J_z are the interaction energies of two transformed neighboring particles along the x, y, z direction, respectively. They depend on the distance of two particles in the lattice, i.e. they depend on the volume fraction of the parent tetragonal ZrO_2 particles.

$$\sum_{(i,j)}^{x}, \sum_{(i,j)}^{y}, \sum_{(i,j)}^{z}$$

means the sums over all the neighboring particles along the x, y, z directions, respectively. Therefore, for a general lattice of untransformed particles, eq. (2) becomes

$$H = H_0 - h(\sigma^0,T)\sum_i \varphi(\mathbf{r}_i) - \sum_m J_m \sum_{(i,j)}^{x_m} \varphi(\mathbf{r}_i)\varphi(\mathbf{r}_j), \tag{7}$$

where J_m is the interaction energy of two transformed neighboring particles along the m-direction.

$$\sum_{(i,j)}^{x_m}$$

means the sum over all the neighboring particles along the m-direction.

Replacing each $\varphi(\mathbf{r}_i)$ in eq. (7) by $s(\mathbf{r}_i)$, where

$$s(\mathbf{r}_i) = 2\varphi(\mathbf{r}_i) - 1, \tag{8}$$

one obtains

$$H = \hat{H}_0 - \hat{h}(\sigma^0,T)\sum_i^N s(\mathbf{r}_i) - \sum_m \hat{J}_m \sum_{(i,j)}^{x_m} s(\mathbf{r}_i)s(\mathbf{r}_j), \tag{9}$$

where

$$\hat{H}_0 = H_0 - \frac{1}{4}N\sum_m J_m - \frac{1}{2}Nh(\sigma_0,T) \tag{10}$$

$$\hat{h}(\sigma_0,T) = \frac{1}{2}h(\sigma_0,T) + \frac{1}{2}\sum_m J_m \tag{11}$$

$$\hat{J}_m = \frac{1}{4}J_m, \tag{12}$$

where N is the total number of ZrO_2 particles. Thus, $s(\mathbf{r}_i) = -1$ if the particle at $\mathbf{r}_i$ does not transform from tetragonal to monoclinic phase, $s(\mathbf{r}_i) = 1$ if it has transformed. The system described by eq. (9) is the generalized Ising system, which has been studied in statistical physics extensively. Thus we can borrow some successful methods from statistical physics to deal with our problem.

Substitution of eq. (9) into eq. (5) yields

$$Z = \sum_{\{s\}} \exp\left\{\left[-\hat{H}_0 + \hat{h}(\sigma^0,T)\sum_i^N s(\mathbf{r}_i) + \sum_m \hat{J}_m \sum_{(i,j)}^{x_m} s(\mathbf{r}_i)s(\mathbf{r}_j)\right]/BT\right\}. \tag{13}$$

Since many interesting thermodynamic properties of the system can be derived from the partition function as we show below, the basic problem of equilibrium statistical mechanics is therefore to calculate the sum-over-states in eq. (13).

The Gibb's free energy of the system can be defined as

$$G = H - ST, \tag{14}$$

where S is the entropy of the system. According to statistical mechanics [7], we can derive

$$G = -BT\log Z. \tag{15}$$

Under the action of external stress field and temperature, the average volume fraction of the transformed particles can be derived as follows

$$\begin{aligned} C_f &= \lim_{N\to\infty} C_f^0 \frac{1}{N}\left\langle \sum_i^N \varphi_i \right\rangle \\ &= \frac{1}{2}C_f^0\left(1 + \lim_{N\to\infty}\frac{1}{N}\left\langle \sum_i^N S_i \right\rangle\right), \end{aligned} \tag{16}$$

where C_f^0 is the volume fraction of the parent phase of ZrO_2 particles, and

$$\begin{aligned} \lim_{N\to\infty}\frac{1}{N}\left\langle \sum_i^N S_i \right\rangle &= BT \lim_{N\to\infty}\frac{1}{N}\frac{\partial \log Z}{\partial \hat{h}} \\ &= -\frac{\partial}{\partial \hat{h}} \lim_{N\to\infty}\frac{G}{N}. \end{aligned} \tag{17}$$

In deriving eq. (17), we have used eq. (15).

The purpose for us to develop the microstructural statistical model is to predict the volume fraction of the transformed particles at a temperature and external stress field. More interestingly, we hope that we should be able to predict that the concentration of the transformed particles will suddenly and dramatically change as many people have observed in experiments at some temperature and pressure. In experiments, this dramatic change in volume fraction of the transformed particles manifests itself as occurrence of dramatic plastic strain in stress–strain curves [4]. The relation between the volume fraction of the transformed particles, external stress and temperature is called the equation of state in this paper; it can be predicted through the microstructure model, as Van der Waals equation of continuum fluid can be predicted through statistical physics.

Since we have reduced our system to the generalized Ising model [eq. (13)], we can show some specific characteristics of our system according to the results in statistical physics about the Ising model [8].

Following the remarkable result of Yang and Lee [9], we know, for arbitrary $J_m \geq 0$, all the thermodynamic and correlation functions determined by eq. (13) are analytic except those cases which satisfy $\hat{h} = 0$. It means that for $\hat{h} = 0$, the thermodynamic functions are not continuous. According to our model, the order parameter is $(cf - \frac{1}{2} c_f^0)/\frac{1}{2} c_f^0$, so we can expect that across $\hat{h} = 0$ which determines a condition of the external stress and temperature, the order parameter may take two values, for example, it may equal 1 or -1; the first case corresponds to when all the tetragonal particles have transformed to monoclinic phase, whereas the latter corresponds to when no tetragonal particles have transformed to monoclinic phase. Thus $\hat{h} = 0$ determines the condition of the sudden transformation of the material.

Another interesting point is that the discontinuity only occurs when $T < T_c$, where T_c is some critical temperature. Above it, the thermodynamic function is also analytic. So the point $(\hat{h} = 0, T_c)$ is called the critical point. Physicists have found many specific characteristics, e.g. the scaling law, universal class, etc., when a system approaches its critical point, and there are vast research works on this subject [7]. For our problem, at the critical point $c_f = \frac{1}{2} C_f^0$, which means that half of the total ZrO_2 particles has been transformed. Therefore, the configuration of the transformed particles should be in symmetry as the configuration of the non-transformed particles. In what follows, we also derive some specific characteristics of our system when it is near the critical point.

As shown above, the basic problem of our model is to calculate the sum-over-states in eq. (13). Unfortunately, for any realistic interesting system of macroscopic size including the one developed above, the exact evaluation of Z is extremely difficult. But we can use some approximation methods developed in statistical mechanics to deal with the partition function and we know that if the system is near the critical point, we can use the powerful renormalization group theory developed by Wilson [10, 11] to derive the scaling law and critical exponents etc. of the thermodynamic functions.

As an approximation used by Berlin and Kac [12], eq. (13) can be written in the form

$$Z_N = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \mathrm{d}s_1 \dots \mathrm{d}s_N \exp\left\{\left[\hat{h}\sum_{i=1}^{N} S_i + \sum_m \hat{J}_m \sum_{(i,j)}^{x_m} S_i S_j\right]/BT\right\}\delta\left(N - \sum_i s_i^2\right), \tag{18}$$

where we have neglected the constant which will not influence the behavior of the system. If a transformed particle configuration of the whole lattice may be represented by a point in a N-dimensional state-space consisting of N rectangular axes, one for each cell variable $s(r_i)$, for the above approximation, the allowed transformed particle configurations are represented by points on a hypersphere of radius $N^{1/2}$, so the approximation is also called the spherical model in statistical mechanics, while for the original model [eq. (13)], the representative points are the 2^N vertices of an inscribed hypercube.

Following the same procedure as in ref. [13] to carry out the integral in eq. (18), we can obtain

$$\lim_{N\to\infty} \frac{\log Z_N}{N} = \frac{1}{2}\log 2\pi - \frac{1}{2}\log\frac{J^*(\bar{0})}{BT} + \frac{J^*(\bar{0})}{2BT}\xi_s + \frac{\hat{h}^2}{2BTJ^*(\bar{0})(\xi_s - 1)}$$

$$- \frac{v_a}{2(2\pi)^3}\int \log[\xi_s - \lambda(\bar{k})]\mathrm{d}\bar{k}, \tag{19}$$

where

$$J^*(\bar{0}) = 2\sum_m \hat{J}_m \tag{20}$$

$$\lambda(\bar{k}) = \frac{J^*(\bar{k})}{J^*(\bar{0})}$$

$$= \frac{2}{J^*(\bar{0})} \sum_m \hat{J}_m \cos(\mathbf{k}\cdot\mathbf{m}) \tag{21}$$

and the saddle-point ξ_s is determined from the equation

$$\frac{J^*(\mathbf{0})}{BT} = \frac{\hat{h}^2}{J^*(\mathbf{0})(\xi_s - 1)^2 BT} + \frac{v_a}{(2\pi)^3} \int \frac{\mathrm{d}\mathbf{k}}{\xi_s - \lambda(\mathbf{k})}, \tag{22}$$

where v_a is the volume of a basic cell in the lattice.

Substitution of eq. (19) into eq. (17), then into eq. (16) gives the average volume fraction of the transformed particles

$$c_f - \frac{1}{2} c_f^0 = \frac{\hat{h}}{2J^*(\mathbf{0})(\xi_s - 1)} c_f^0. \tag{23}$$

In deriving eq. (23), we have used eq. (22). From eq. (23) we can obtain

$$(\xi_s - 1) = \frac{\hat{h}}{2J^*(\mathbf{0})(c_f - 1/2\, c_f^0)} c_f^0. \tag{24}$$

Substitution of eq. (24) into eq. (22) yields

$$J^*(\mathbf{0}) \left[1 - \frac{(c_f - 1/2 c_f^0)^2}{(1/2 c_f^0)^2} \right] = BTI\left(\frac{\hat{h} c_f^0}{2J^*(\mathbf{0})(c_f - 1/2\, c_f^0)} \right), \tag{25}$$

where

$$I(z) = \frac{v_a}{(2\pi)^3} \int_{-\pi}^{\pi} \frac{\mathrm{d}\mathbf{k}}{z + 1 - \lambda(\mathbf{k})}. \tag{26}$$

Equation (25) is the exact equation of state, i.e. the relation between the volume fraction of transformed particles, the external field which is included in $\hat{h}$ and the temperature.

It can be shown that the integral in eq. (26) has branch-point singularities at $z = 0$ or $\xi_s = 1$ in eqs (19) and (22). For a given real external field and temperature, there will be only one solution of ξ_s determined by eq. (22). If $\hat{h}(\sigma_{ij}^0, T) \neq 0$ in eq. (22), ξ_s which is a function of $\hat{h}(\sigma_{ij}^0, T)$ and T will never reach the branch-point $\xi_s = 1$ for any temperature. Only when $\hat{h}(\sigma_{ij}^0, T) = 0$, from eq. (22) we know ξ_s decreases monotonically to the branch-point where $c_f = 1/2\, c_f^0$ as the temperature is lowered. The corresponding critical temperature can be determined through eq. (22) as

$$\frac{J^*(\mathbf{0})}{BT_c} = \frac{v_a}{(2\pi)^3} \int \frac{\mathrm{d}\mathbf{k}}{1 - \lambda(\mathbf{k})}. \tag{27}$$

For convenience, we rewrite eq. (25) in the following form by using eq. (27)

$$I(0) - I\left(\frac{\hat{h} c_f^0}{2J^*(\mathbf{0})(c_f - 1/2\, c_f^0)} \right) = \frac{J^*(\mathbf{0})}{BT_c} \left[\frac{T - T_c}{T_c} + \frac{(c_f - 1/2 c_f^0)^2}{(1/2 c_f^0)^2} \right]. \tag{28}$$

For $\hat{h}(\sigma_{ij}^0, T) = 0$ and $T \leq T_c$, from the equation of state (28), we know that the saddle-point "sticks" at $\xi_s = 1$ [12]. Thus from eq. (24) we know that the left-hand-side of eq. (28) is zero. So the volume fraction of transformed particles may take two values

$$c_f - \frac{1}{2} c_f^0 = \pm \left(\frac{T_c - T}{T_c} \right)^{1/2} \frac{1}{2} c_f^0. \tag{29}$$

That means, at a given temperature T ($\leq T_c$), when the external field changes across $\hat{h}(\sigma_{ij}^0,T) = 0$, the volume fraction of transformed particles will change from

$$\frac{1}{2}c_f^0\left[1-\left(\frac{T_c-T}{T_c}\right)^{1/2}\right] \text{ to } \frac{1}{2}c_f^0\left[1+\left(\frac{T_c-T}{T_c}\right)^{1/2}\right]$$

abruptly. From the experimental observation of the stress–strain curve of ZrO_2 containing ceramics, we know that at a temperature, when the load reaches a critical value, a plastic-like strain will suddenly occur. This seems to be the result of the discontinuous change in the volume fraction of transformed particles predicted by this model. For TZP material which has a large value of c_f^0, this phenomenon is very striking. Thus in fact, we have determined the size of a nearly perfect plastic regime as a function of temperature T. According to the equilibrium statistical mechanics, this phenomena will appear both in the positive direction and in the reverse direction. In practice, people often observed that there was a loop of hysteresis in the stress–strain curve when the material was subjected to a cyclic load. This is due to during the loading process the material cannot always stay in an equilibrium state for the same reason as the loop of hysteresis in ferroelectricity.

For $\hat{h}(\sigma_{ij}^0,T) = 0$ and $T > T_c$, we have to determine the ξ_s value from eq. (22), then using eq. (23) to determine c_f.

The critical condition for the phase transition in ZrO_2 containing ceramics, which corresponds to the condition for the yielding in the stress–strain relation is determined by

$$\hat{h}(\sigma_{ij}^0,T) = 0. \tag{30}$$

When $\hat{h}(\sigma_{ij}^0,T)$ and $(T_c - T)/T_c$ are small, we can expand the integral in eq. (28) and obtain the critical equation of state

$$\hat{h}(\sigma_{ij}^0,T) \approx C\left(c_f - \frac{1}{2}c_f^0\right)\left[\frac{T-T_c}{T_c} + \left(\frac{c_f - 1/2c_f^0}{1/2c_f^0}\right)^2\right]^2. \tag{31}$$

Equation (31) is just the scaling relation between $\hat{h}(\sigma_{ij}^0,T)$, $(T_c - T)/T_c$ and $c_f - 1/2c_f^0$, which states that $\hat{h}(\sigma_{ij}^0,T)$ is a function of $(T_c - T)/T_c$ and $c_f - 1/2c_f^0$, which can be expressed in the general form of

$$\left(\frac{c_f - \frac{1}{2}c_f^0}{\frac{1}{2}c_f^0}\right)^{\delta} f(x), \text{ where } x = \frac{T-T_c}{T_c}\left(\frac{c_f - \frac{1}{2}c_f^0}{\frac{1}{2}c_f^0}\right)^{-1/\beta}.$$

From the modern phase transition theory [7] we know that when a system is very near its critical point, such a scaling law is generally true for all the thermodynamic functions, and the exponents which appear in these relations are believed to be universal in the sense that they do not depend on the detailed microstructure of the system, only on some general characteristics of the system, such as the components of the order parameter and dimension of the system. In the following part, we will study a specific system whose explicit form of $\hat{h}(\sigma_{ij}^0,T)$ and $\hat{J}$ can be obtained, and to predict its macroscopic characteristics.

3. THE EQUATION OF STATE OF ZrO_2 CONTAINING CERAMICS SUBJECTED TO AN APPLIED STRESS AND TEMPERATURE

To simplify the analysis, we introduce the following constraints about the system we studied.

(1) The non-transformed tetragonal ZrO_2 particles in ceramics are of spherical shape and they form a cubic lattice in the matrix (Fig. 2).

(2) Under an external load and temperature, some tetragonal ZrO_2 particles will transform to monoclinic phase. We assume that the matrix and non-transformed tetragonal ZrO_2 particles are isotropic and with a uniform elastic moduli, whereas the transformed monoclinic ZrO_2 particles are anisotropic and with a uniform eigenstrain ϵ_{ij}^p.

Under the above assumption, we can derive the change in the total elastic potential energy which constitutes the first term in eq. (3) when a tetragonal ZrO_2 particle transforms to monoclinic phase.

Consider a matrix **D** contains an inhomogeneous inclusion Ω with eigenstrain ϵ_{ij}^{p} under the action of an external load, the total potential energy of the body is defined by the sum of the elastic strain energy and the potential energy of the external load $\mathbf{F}_i$. According to Colonetti's theorem [14], the elastic strain energy W due to $\mathbf{F}_i$ and ϵ_{ij}^{p} is

$$W = W_{\mathrm{F}} + W_{\epsilon^{\mathrm{p}}}\,, \tag{32}$$

where W_{F} and $W_{\epsilon^{\mathrm{p}}}$ are the elastic energies due to the single action of $\mathbf{F}_i$ ($\epsilon_{ij}^{p} = 0$) and the single action ϵ_{ij}^{p} ($\mathbf{F}_i = 0$), respectively, and they are expressed as [14]

$$W_{\mathrm{F}} = \frac{1}{2}\int_{\mathbf{D}} \sigma_{ij}^{0}\epsilon_{ij}^{0}\mathrm{d}v + \frac{1}{2}\int_{\Omega} \sigma_{ij}^{0}\epsilon^{*}{}_{ij}\mathrm{d}v \tag{33}$$

$$W_{\epsilon^{\mathrm{p}}} = -\frac{1}{2}\int_{\Omega} \sigma_{ij}\epsilon_{ij}^{p}\mathrm{d}v, \tag{34}$$

where $\epsilon^{*}{}_{ij}$ is the fictitious eigenstrain introduced in the equivalent inclusion method by Eshelby [15]. If the material is homogeneous without the inclusion, the total potential energy is

$$W_0 = \frac{1}{2}\int_{\Omega} \sigma_{ij}\epsilon_{ij}^{0}\mathrm{d}v - \int_{s} F_i u_i^{0}\mathrm{d}s. \tag{35}$$

Thus, the change in the total elastic potential energy due to the existence of a transformed ZrO_2 particle is

$$\begin{aligned} E^{\mathrm{e}} &= W - \int_{s} F_i(u_i^{0} + u_i)\mathrm{d}s - W_0 \\ &= \frac{1}{2}\int_{\Omega} \sigma_{ij}^{0}\epsilon^{*}{}_{ij}\mathrm{d}v - \frac{1}{2}\int_{\Omega} \sigma_{ij}\epsilon_{ij}^{p}\mathrm{d}v - \int_{s} F_i u_i\mathrm{d}s. \end{aligned} \tag{36}$$

Finally, eq. (36) can be expressed in the form [14]

$$E^{\mathrm{e}} = -\frac{1}{2}v[\sigma_{ij}^{0}(\epsilon^{*}{}_{ij} + 2\epsilon_{ij}^{p}) + \sigma_{ij}\epsilon_{ij}^{p}] \tag{37}$$

and $v = \frac{4}{3}\pi a^3$, a is the radius of the tetragonal ZrO_2 particle. $\epsilon^{*}{}_{ij}$, σ_{ij} are determined by the following equations

$$C_{ijkl}(\epsilon_{kl}^{0} + S_{klmn}\epsilon^{*}{}_{mn}) = C_{ijkl}^{0}(\epsilon_{kl}^{0} + S_{klmn}\epsilon^{*}{}_{mn} - \epsilon^{*}{}_{kl}) \tag{38}$$

$$\sigma_{ij} = C_{ijkl}^{0}[S_{klmn}(\epsilon_{mn}^{p} + \epsilon^{*}{}_{mn}) - (\epsilon_{kl}^{p} + \epsilon^{*}{}_{kl})] \tag{39}$$

and C_{ijkl}, C_{ijkl}^{0} are elastic moduli of the monoclinic ZrO_2 particle, ceramic matrix, respectively. S_{ijkl} is Eshelby's tensor, which is shown in Appendix A for spherical inclusion.

The second term in eq. (3) is the chemical free energy change, which is a function of the test temperature T [16]

$$E^{\mathrm{c}}(T) = \Delta S(T_0 - T)v, \tag{40}$$

where ΔS is the transformational entropy change per unit volume and T_0 is the temperature at which the unconstrained tetragonal phase begins to transform to the monoclinic phase. The addition of certain solutes (e.g. MgO_2, CeO_2) will lower T_0. If we neglect the surface energy change, substitution of eqs (37) and (40) into eq. (3) gives

$$h(\sigma^{0},T) = \frac{1}{2}v[\sigma_{ij}^{0}(\epsilon^{*}{}_{ij} + 2\epsilon_{ij}^{p}) + \sigma_{ij}\epsilon_{ij}^{p}] - \Delta S(T_0 - T)v. \tag{41}$$

To derive an expression for $J(\mathbf{r}_i - \mathbf{r}_j)$ in eq. (2), one has to calculate the total elastic energy of two inhomogeneous inclusions in the matrix. Consider that there are two inclusions in a body, each of them has a uniform eigenstrain ϵ^p_{ij} (Fig. 3).

According to Colonetti's theorem [14] the total elastic energy W^s of a body containing two inhomogeneous inclusions with an eigenstrain ϵ^p_{ij} can be expressed in the form as

$$W^s = W_1 + W_2, \tag{42}$$

where W_1 is the total elastic potential energy created only by the external load without the eigenstrain and W_2 is the total elastic potential energy created only by the eigenstrain without external load.

Consider a body with two inhomogeneous inclusions without any eigenstrain, the strain energy W^*_1 is

$$W^*_1 = \frac{1}{2}\int_D (\sigma^0_{ij}+\sigma^1_{ij}+\sigma^2_{ij})(\epsilon^0_{ij}+\epsilon^1_{ij}+\epsilon^2_{ij})\mathrm{d}v =$$

$$\frac{1}{2}\int_D \sigma^0_{ij}\epsilon^0_{ij}\mathrm{d}v + \frac{1}{2}\int_D (\sigma^1_{ij}+\sigma^2_{ij})(\epsilon^0_{ij}+\epsilon^1_{ij}+\epsilon^2_{ij})\mathrm{d}v + \frac{1}{2}\int_D \sigma^0_{ij}(\epsilon^1_{ij}+\epsilon^2_{ij})\mathrm{d}v, \tag{43}$$

where ϵ^1_{ij}, σ^1_{ij} are strain and stress perturbations due to the existence of Ω_1 inclusion. ϵ^2_{ij}, σ^2_{ij} are strain and stress perturbations due to the existence of Ω_2 inclusion.

$$\int_D (\sigma^1_{ij}+\sigma^2_{ij})(\epsilon^0_{ij}+\epsilon^1_{ij}+\epsilon^2_{ij})\mathrm{d}v = \int_s u_i n_j(\sigma^1_{ij}+\sigma^2_{ij})\mathrm{d}s - \int_D u_i(\sigma^1_{ij}+\sigma^2_{ij})_{,j}\mathrm{d}v = 0, \tag{44}$$

since $n_j(\sigma^1_{ij} + \sigma^2_{ij}) = 0$ on S and $(\sigma^1_{ij} + \sigma^2_{ij})_{,j} = 0$ in D.

$$\int_D \sigma^0_{ij}(\epsilon^1_{ij}+\epsilon^2_{ij})\mathrm{d}v = \int_D \sigma^0_{ij}[\epsilon^1_{ij}+\epsilon^2_{ij} - \epsilon^*_{ij}H(\Omega_1) - \epsilon^*_{ij}H(\Omega_2) + \epsilon^*_{ij}H(\Omega_1) + \epsilon^*_{ij}(\Omega_2)]\mathrm{d}v$$

$$= \int_D C^0_{ijkl}\epsilon^0_{kl}[\epsilon^1_{ij} + \epsilon^2_{ij} - \epsilon^*_{ij}H(\Omega_1) - \epsilon^*_{ij}H(\Omega_2)]\mathrm{d}v + \int_{\Omega_1} \sigma^0_{ij}\epsilon^*_{ij}\mathrm{d}v + \int_{\Omega_2} \sigma^0_{ij}\epsilon^*_{ij}\mathrm{d}v, \tag{45}$$

where ϵ^*_{ij} is the equivalent eigenstrain and

$$H(\Omega) = \begin{cases} 1 & x \in \Omega \\ 0 & \text{others.} \end{cases} \tag{46}$$

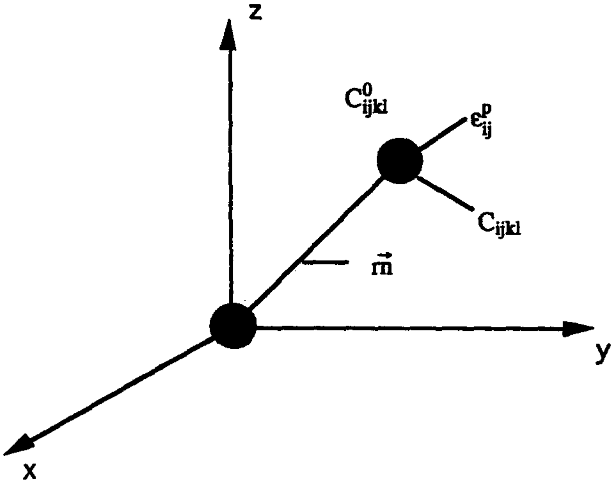

Fig. 3. Schematic of two inhomogeneous inclusions.

If we replace the inhomogeneous inclusion by a homogeneous inclusion according to Eshelby [15], then

$$C^0_{ijkl}[\epsilon^1_{kl} + \epsilon^2_{kl} - \epsilon^*{}_{kl}H(\Omega_1) - \epsilon^*{}_{kl}H(\Omega_2)] = \sigma^1_{ij} + \sigma^2_{ij}. \tag{47}$$

By using eq. (44) we obtain

$$\int_D \sigma^0_{ij}(\epsilon^1_{ij} + \epsilon^2_{ij})\mathrm{d}v = \int_{\Omega_1} \sigma^0_{ij}\epsilon^*{}_{ij}\mathrm{d}v + \int_{\Omega_2} \sigma^0_{ij}\epsilon^*{}_{ij}\mathrm{d}v. \tag{48}$$

Substitution of eqs (44) and (48) into eq. (43) yields

$$W^*{}_1 = \frac{1}{2}\int_D \sigma^0_{ij}\epsilon^0_{ij}\mathrm{d}v + \frac{1}{2}\int_{\Omega_1} \sigma^0_{ij}\epsilon^*{}_{ij}\mathrm{d}v + \frac{1}{2}\int_{\Omega_2} \sigma^0_{ij}\epsilon^*{}_{ij}\mathrm{d}v. \tag{49}$$

The total potential energy of the body is

$$W_1 = W^*{}_1 - \int_s F_i(u^0_i + u^1_i + u^2_i)\mathrm{d}s, \tag{50}$$

where u^1_i, u^2_i are displacements due to Ω_1 and Ω_2.

The other part of energy comes from the eigenstrain in the inclusions.

$$W_2 = \frac{1}{2}\int_D (\sigma^{1\mathrm{p}}_{ij} + \sigma^{2\mathrm{p}}_{ij})e_{ij}\mathrm{d}v, \tag{51}$$

where $\sigma^{1\mathrm{p}}_{ij}$, $\sigma^{2\mathrm{p}}_{ij}$ are stress fields created by $\epsilon^{\mathrm{p}}_{ij}$ at Ω_1 and Ω_2, respectively. e_{ij} is the elastic strain, which can be written as

$$e_{ij} = \epsilon_{ij} - \epsilon^{\mathrm{p}}_{ij}H(\Omega_1) - \epsilon^{\mathrm{p}}_{ij}H(\Omega_2). \tag{52}$$

Substitution of eq. (52) into eq. (51) gives

$$W_2 = -\frac{1}{2}\int_{\Omega_1} \sigma^{1\mathrm{p}}_{ij}\epsilon^{\mathrm{p}}_{ij}\mathrm{d}v - \frac{1}{2}\int_{\Omega_2} \sigma^{2\mathrm{p}}_{ij}\epsilon^{\mathrm{p}}_{ij}\mathrm{d}v - \int_{\Omega_1} \sigma^{2\mathrm{p}}_{ij}\epsilon^{\mathrm{p}}_{ij}\mathrm{d}v. \tag{53}$$

In deriving eq. (53), we have used

$$\int_D (\sigma^{2\mathrm{p}}_{ij} + \sigma^{2\mathrm{p}}_{ij})\epsilon_{ij}\mathrm{d}v = 0, \tag{54}$$

which can be approved as eq. (44).

According to eq. (42), the total elastic energy W of a body containing two inhomogeneous inclusions with an eigenstrain $\epsilon^{\mathrm{p}}_{ij}$ is

$$\begin{aligned} W = \frac{1}{2}\int_D \sigma^0_{ij}\epsilon^0_{ij}\mathrm{d}v + \frac{1}{2}\int_{\Omega_1} \sigma^0_{ij}\epsilon^*{}_{ij}\mathrm{d}v + \int_{\Omega_2} \sigma^0_{ij}\epsilon^*{}_{ij}\mathrm{d}v - \int_S F_i(u^0_i + u^1_i + u^2_i)\mathrm{d}s \\ - \frac{1}{2}\int_{\Omega_1} \sigma^{1\mathrm{p}}_{ij}\epsilon^{\mathrm{p}}_{ij}\mathrm{d}v - \frac{1}{2}\int_{\Omega_2} \sigma^{2\mathrm{p}}_{ij}\epsilon^{\mathrm{p}}_{ij}\mathrm{d}v - \int_{\Omega_1} \sigma^{2\mathrm{p}}_{ij}\epsilon^{\mathrm{p}}_{ij}\mathrm{d}v. \end{aligned} \tag{55}$$

The additional change in interaction energy due to two neighboring tetragonal particles transforming to monoclinic phase is

$$J(\mathbf{r}_i - \mathbf{r}_j) = -(W - E^{\mathrm{e}}_1 - E^{\mathrm{e}}_2 - W_0), \tag{56}$$

where W_0 is determined by eq. (35), and E^{e}_1 and E^{e}_2 can be determined by eq. (36).

Since there is no exact solution for a body containing two inhomogeneous inclusions, we have to make some assumption to obtain the interaction energy. We assume that ϵ_{ij}^* in eq. (55) can be determined by a single inclusion problem, i.e. ϵ_{ij}^* is given by eq. (38). Substitution of eqs (35), (36) and (55) into eq. (56) yields

$$J(\mathbf{r}_i - \mathbf{r}_j) = \int_{\Omega_1} \sigma_{ij}^{2p}\epsilon_{ij}^{p}\mathrm{d}v. \tag{57}$$

Since σ_{ij}^{2p} is the stress field created by ϵ_{ij}^p at Ω_2, according to Mura [14], we know

$$\sigma_{ij}^{2p} = C_{ijkl}D_{klmn}(\mathbf{x})(\epsilon^*{}_{mn} + \epsilon_{mn}^{p}), \tag{58}$$

where $\mathbf{x}$ is a point outside the inclusion Ω_2. C_{ijkl} is the elastic moduli of monoclinic ZrO_2 particles, ϵ_{mn}^* can be determined by eq. (38), and

$$\begin{aligned} 8\pi(1-\gamma)D_{ijkl}(\mathbf{x}) = {} & \frac{4\pi a^3}{r^3}\left[\frac{1-2\gamma}{3}(\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{kl} - \delta_{ij}\delta_{kl}) + \frac{a^2}{5r^2}(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il}) - 2\gamma n_i n_j \delta_{kl}\right. \\ & -(1-\gamma)(n_k n_j \delta_{il} + n_i n_k \delta_{jl} + n_l n_j \delta_{ik} + n_i n_l \delta_{jk}) \\ & \left. -\left(\frac{a^2}{r^2} - 1\right)(n_l n_k \delta_{ij} + n_j n_l \delta_{ik} + n_i n_l \delta_{jk} + n_j n_k \delta_{il} + n_i n_k \delta_{jl} + n_i n_j \delta_{kl})\right] + \left(\frac{7a^2}{r^2} - 5\right) n_i n_j n_k n_l \, , \end{aligned} \tag{59}$$

where a is the radius of the particles, r is the distance between the centers of the two neighboring inclusions, γ is Poisson's ratio of the matrix. The integral in eq. (57) can be done directly by substituting eq. (58) into eq. (57) [17], the final result is [18]

$$J(\mathbf{r}_i - \mathbf{r}_j) = \frac{4}{3}\pi a^3 C_{ijkl}\left[D_{klmn}(\mathbf{r}_i - \mathbf{r}_j) + \frac{3a^5}{10(1-\gamma)r^5} f_{klmn}(\mathbf{n})\right](\epsilon^*{}_{mn} + \epsilon_{mn}^{p})\epsilon_{ij}^{p} \, , \tag{60}$$

where

$$\begin{aligned} f_{klmn}(\mathbf{n}) = {} & \delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il} - 5(n_k n_l \delta_{ij} + n_j n_l \delta_{ik} + n_i n_l \delta_{jk} - n_j n_k \delta_{il} - n_i n_j \delta_{kl} - n_i n_k \delta_{jl}) \\ & + 5 n_i n_j n_k n_l \, . \end{aligned} \tag{61}$$

Since we assumed that the non-transformed tetragonal particles in ceramics formed a cubic lattice (Fig. 3), $J(\mathbf{r}_i - \mathbf{r}_j)$ might take three different values according to the relative positions of the neighboring inclusions. They are J_x, J_y and J_z, and J_x is determined by substituting $\mathbf{n} = (1,0,0)$ into eq. (60), J_y is determined by substituting $\mathbf{n} = (0,1,0)$ into eq. (60) and J_z is determined by substituting $\mathbf{n} = (0,0,1)$ into eq. (60). Substitution of eqs (41) and (60) into eq. (11) gives the critical condition for transformation or the yield condition in the stress–strain relation

$$\hat{h} = \frac{1}{3}\pi a^3[\sigma_{ij}^0(\epsilon^*{}_{ij} + 2\epsilon_{ij}^p) + \sigma_{ij}\epsilon_{ij}^p] - \frac{2}{3}\pi a^3 \Delta S(T_0 - T) + \frac{1}{2}(J_x + J_y + J_z) = 0. \tag{62}$$

Since we divided the body into many cubic cells and assumed that there is a ZrO_2 particle in each cell, the distance r between the centers of two neighboring inclusions is the size of the cubic cell. If we know that the original volume fraction of tetragonal ZrO_2 particle is c_f^0, r in eq. (60) can be determined by

$$r = \frac{a}{(3c_f^0/4\pi)^{1/3}} \, . \tag{63}$$

Given the transformation strain ϵ_{ij}^p, eq. (62) is a function of external load and temperature. According to the discussion in Section 2, we know that when external load and temperature satisfy eq. (62), the volume fraction of transformed particles takes two values [eq. (29)], one value is smaller than $\frac{1}{2}c_f^0$ and the other value is larger than $\frac{1}{2}c_f^0$ for $T < T_c$. So eq. (62) in fact determines a peuso-yielding condition for ZrO_2 particles containing ceramics.

To get a deep understanding of the transformation phenomena, we should derive the critical temperature by using eq. (27), where $\frac{1}{2}c_f^0$ particles will transform from one phase to the other. For cubic lattice, $\lambda(\mathbf{k})$ in eq. (27) can be determined from eq. (21) by summing over the sets of vectors $\{(\pm 1,0,0),\ (0,\pm 1,0),\ (0,0,\pm 1)\}$

$$\lambda(\mathbf{k}) = 2[J^*(\mathbf{0})]^{-1}(\hat{J}_x\cos k_1 + \hat{J}_y\cos k_2 + \hat{J}_z\cos k_3) \tag{64}$$

and $J^*(\mathbf{0})$ can be determined by eq. (20) as

$$J^*(\mathbf{0}) = 2(\hat{J}_x + \hat{J}_y + \hat{J}_z) = \frac{1}{2}(J_x + J_y + J_z), \tag{65}$$

in which we have used eq. (12). Thus from eq. (27), the critical temperature is given by

$$T_c = \frac{3\pi^2 c_f^0}{Ba^3}\left[\iiint_{-\pi}^{\pi} \frac{\mathrm{d}k_1\mathrm{d}k_2\mathrm{d}k_3}{J_x(1-\cos k_1) + J_y(1-\cos k_2) + J_z(1-\cos k_3)}\right]^{-1}, \tag{66}$$

where B is a material constant, and in statistical physics, it is Boltzmann's constant. J_x, J_y, J_z are functions of external load and transformation strain, and they can be determined by eq. (60). But the external load in eq. (66) must satisfy eq. (62). The two conditions determine a critical point according to the above discussion.

By substituting T in eq. (62) by T_c in eq. (66), we can obtain

$$\frac{1}{3}\pi a^3[\sigma_{ij}^0(\epsilon^*_{ij} + 2\epsilon_{ij}^{p}) + \sigma_{ij}\epsilon_{ij}^{p}] - \frac{2}{3}\pi a^3 \Delta S\left\{T_0 - \frac{3\pi^2 c_f^0}{Ba^3}\right.$$
$$\left.\left[\iiint_{-\pi}^{\pi} \frac{\mathrm{d}k_1\mathrm{d}k_2\mathrm{d}k_3}{J_x(1-\cos k_1) + J_y(1-\cos k_2) + J_z(1-\cos k_3)}\right]^{-1}\right\} + \frac{1}{2}(J_x + J_y + J_z) = 0. \tag{67}$$

Equation (67) represents a surface in stress space under the condition of given transformation strain. Any point on this surface is a critical point of the system. When a system is at a critical point, it has some specific characteristics. For example, the volume fraction of transformed particles equals $\frac{1}{2}c_f^0$ (or the order parameter is zero). When the system is near the critical point, some scaling laws such as eq. (31) are generally true for all the thermodynamics functions and the exponents which appear in them are believed to be universal.

Substitution of eqs (11), (41), (64) and (65) into eq. (25) yields the final state equation

$$\left[1 - \frac{(c_f - 1/2c_f^0)^2}{(1/2c_f^0)^2}\right] = BTI\left(\frac{\frac{1}{3}\pi a^3[\sigma_{ij}^0(\epsilon^*_{ij} + 2\epsilon_{ij}^{p}) + \sigma_{ij}\epsilon_{ij}^{p}] - \frac{2}{3}\pi a^3\Delta S(T_0 - T) + \frac{1}{2}(J_x + J_y + J_z)}{(J_x + J_y + J_z)(c_f - \frac{1}{2}c_f^0)/c_f^0}\right), \tag{68}$$

where

$$I(u) = \frac{a^3}{3\pi^2 c_f^0}\left[\iiint_{-\pi}^{\pi} \frac{\mathrm{d}k_1\mathrm{d}k_2\mathrm{d}k_3}{u(J_x + J_x + J_x) + J_x(1-\cos k_1) + J_y(1-\cos k_2) + J_z(1-\cos k_3)}\right]. \tag{69}$$

If we know the external load and temperature, we can determine the volume fraction of transformed particles from eq. (68). On the other hand, to obtain some amount of transformed particles, we can also determine the needed external load under given working temperature T from eq. (68). Equation (68) is an analytical relation between the volume fraction of transformed particles, the external load and temperature. We call it the equation of state.

4. SIMPLIFICATION OF RESULTS

To simplify the results obtained in the third part, we use some dramatic assumptions, but we hope that these assumptions will not change the properties of the material qualitatively. The key assumption we make in this part is that the elastic constants of the transformed particles are the same as the matrix and they can be treated as isotropic materials. Thus from eqs (38) and (39), we know

$$\epsilon^*_{ij} = 0 \tag{70}$$

$$\sigma_{ij} = C^0_{ijkl}(S_{klmn} - I_{klmn})\epsilon^{\mathrm{p}}_{mn} = \left[\frac{\mu(5\gamma - 7)}{15(1-\gamma)}(\delta_{im}\delta_{jn} + \delta_{in}\delta_{jm}) - \frac{2\mu(5\gamma + 1)}{15(1-\gamma)}\delta_{ij}\delta_{mn} \right]\epsilon^{\mathrm{p}}_{mn}\,, \tag{71}$$

where μ, γ are shear modulus and Poisson's ratio of the material, and I_{klmn} is the identity tensor. If we further assume that non-zero components of $\epsilon^{\mathrm{p}}_{mn}$ are $\epsilon^{\mathrm{p}}_{11} = \epsilon^{\mathrm{p}}_{22} = \epsilon^{\mathrm{p}}_{33} \neq 0$, $\epsilon^{\mathrm{p}}_{13} = \epsilon^{\mathrm{p}}_{31} \neq 0$, $\epsilon^{\mathrm{p}}_{mn}$ can be expressed in the form

$$\epsilon^{\mathrm{p}}_{ij} = \frac{1}{3}\epsilon^{\mathrm{p}}_{kk}\delta_{ij} + \epsilon^{\mathrm{p}}_{13}(\delta_{i1}\delta_{j3} + \delta_{i3}\delta_{j1}), \tag{72}$$

where $\epsilon^{\mathrm{p}}_{kk} = \epsilon^{\mathrm{p}}_{11} + \epsilon^{\mathrm{p}}_{22} + \epsilon^{\mathrm{p}}_{33}$.

Substitution of eqs (70)–(72) into eq. (41) gives

$$h(\sigma^0,T) = \frac{4\pi a^3}{3}\left[\frac{1}{3}\sigma^0_{ii}\epsilon^{\mathrm{p}}_{kk} + 2\sigma^0_{13}\epsilon^{\mathrm{p}}_{13} - \frac{2\mu(\gamma+1)}{9(1-\gamma)}(\epsilon^{\mathrm{p}}_{kk})^2 + \frac{\mu(5\gamma - 7)}{15(1-\gamma)}(\epsilon^{\mathrm{p}}_{13})^2 \right] - \frac{4\pi a^3}{3}\Delta S(T_0 - T), \tag{73}$$

where $\sigma^0_{ii} = \sigma^0_{11} + \sigma^0_{22} + \sigma^0_{33}$.

By substituting eqs (70) and (72) into eq. (60), after some cumbersome mathematics, we can obtain

$$J(\mathbf{r}_i - \mathbf{r}_j) = \frac{8\pi a^6}{3(1-\gamma)r^3}\left\{\left[k\left(2\gamma - 1 - \frac{3a^2}{r^2}\right) + \frac{\mu}{3}\left(\frac{6a^2}{r^2} - \gamma - 1\right)\right] n_1 n_3 \epsilon^{\mathrm{p}}_{kk}\epsilon^{\mathrm{p}}_{13} \right.$$

$$\left. + \mu\left[\frac{1-2\gamma}{3} + \frac{4a^2}{5r^2} + \left(\gamma - \frac{a^2}{r^2}\right)(n_1^2 + n_3^2) + 5\left(\frac{2a^2}{r^2} - 1\right) n_1^2 n_3^2 \right](\epsilon^{\mathrm{p}}_{13})^2 \right\}, \tag{74}$$

where k is the bulk modulus and r is the distance between the centers of two inclusions. n_1, n_2, n_3 denote the relative orientations of one inclusion with respect to the other (Fig. 3). If the center positions of the two inclusions are on the x-axial, i.e. $n_1 = 1$, $n_2 = n_3 = 0$, from eq. (74), we can obtain

$$J_x = \frac{8\pi\mu a^6}{9(1-\gamma)r^3}\left(1 + \gamma - \frac{3a^2}{5r^2}\right)(\epsilon^{\mathrm{p}}_{13})^2, \tag{75}$$

where r is given by eq. (63) if we know c^0_f.

If the two inclusions are on the y-axial, i.e. $n_2 = 1$, $n_1 = n_3 = 0$, one obtains

$$J_y = \frac{8\pi\mu a^6}{3(1-\gamma)r^3}\left(\frac{1-2\gamma}{3} + \frac{4a^2}{5r^2}\right)(\epsilon^{\mathrm{p}}_{13})^2. \tag{76}$$

If the two inclusions are on the z-axial, i.e. $n_3 = 1$, $n_1 = n_2 = 0$, one obtains

$$J_z = J_x = \frac{8\pi\mu a^6}{9(1-\gamma)r^3}\left(1 + \gamma - \frac{3a^2}{5r^2}\right)(\epsilon^{\mathrm{p}}_{13})^2. \tag{77}$$

Substitution of eqs (73), (75), (76) and (77) into eq. (62) gives the condition for half of the tetragonal particles transforming to monoclinic particles, i.e. the yielding condition for the macroscopic stress–strain relation in the form

$$\frac{1}{6}\sigma^0_{ii}\epsilon^p_{kk} + \sigma^0_{13}\epsilon^p_{13} = \frac{(1+\gamma)\mu}{9(1-\gamma)}(\epsilon^p_{kk})^2 + \frac{1}{2}(T_0 - T)\Delta S - \left\{\frac{\mu(5\gamma-7)}{30(1-\gamma)} + \frac{3\mu c^0_f}{4\pi(1-\gamma)}\left[1 + \frac{1}{10}\left(\frac{3c^0_f}{4\pi}\right)^{2/3}\right]\right\}(\epsilon^p_{13})^2. \quad (78)$$

Equation (78) is a bilinear yielding condition, which is quite similar to the phenomenological one proposed by Chen [3].

Substitution of eqs (75)–(77) into eq. (66) gives the critical temperature

$$T_c = \frac{\mu(\epsilon^p_{13})^2 c^0_f a^3}{B(1-\gamma)}\left[1 + \frac{1}{10}\left(\frac{3c^0_f}{4\pi}\right)^{2/3}\right]K_c^{-1}(\eta), \quad (79)$$

where

$$K_c(\eta) = \frac{4}{\pi^2\eta^{1/2}}(2+\eta)[(\omega+1)^{1/2} - (\omega-1)^{1/2}]K(m_2)K(m_3) \quad (80)$$

$$m_2 = \frac{1}{2}[(\omega-1)^{1/2} - (\omega-3)^{1/2}]\,[(\omega+1)^{1/2} - (\omega-1)^{1/2}] \quad (81)$$

$$m_3 = \frac{1}{2}[(\omega-1)^{1/2} - (\omega-3)^{1/2}]\,[(\omega+1)^{1/2} - (\omega-1)^{1/2}] \quad (82)$$

$$\omega = \frac{4+3\eta}{\eta} \quad (83)$$

$$\eta = \frac{J_y}{J_x} = \left[1 - 2\gamma + \frac{12}{5}\left(\frac{3}{4\pi}c^0_f\right)^{2/3}\right]\left[1+\gamma - \frac{3}{5}\left(\frac{3}{4\pi}c^0_f\right)^{2/3}\right]^{-1} \quad (84)$$

and $K(m)$ is a complete elliptic integral of the first kind.

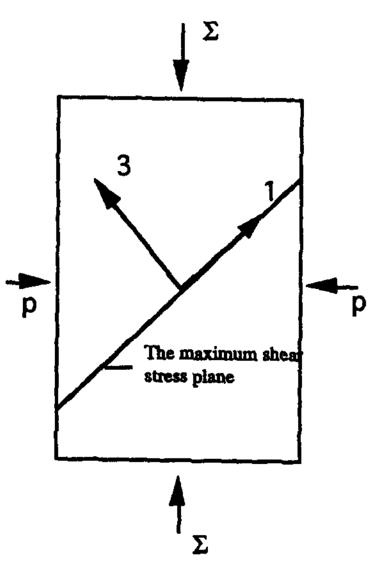

Fig. 4. Configuration of hydraulic compression test.

When $\hat{h}$, $(T_c - T)/T_c$ are small, the critical equation of state (31) can be written out explicitly

$$\frac{\hat{h}(\sigma_{ij}^0, T)}{BT_c} \approx \frac{2\eta\pi^2 K_c^3(\eta)}{(2+\eta)^3} \frac{(c_f - \frac{1}{2}c_f^0)}{\frac{1}{2}c_f^0} \left[\frac{T - T_c}{T_c} + \left(\frac{c_f - 1/2c_f^0}{1/2c_f^0} \right)^2 \right]^2, \tag{85}$$

where $K_c(\eta)$ is given by eq. (80) and η is determined by eq. (84).

5. AN EXAMPLE AND DISCUSSION

Since we do not have sufficient experimental data to determine some necessary parameters in the model such as B, T_0, etc., we can only obtain the qualitative prediction of the transformation behaviors on the example studied by Chen and Reyes Morel [3]. The material was Mg-PSZ cylinder, which was subjected to a hydraulic compression test (Fig. 4) under room temperature. In these experiments, a hydrostatic confining pressure P is provided in addition to a uniaxial compression Σ. Under such loading condition, the maximum shear stress plane is shown in the figure. Suppose we establish a coordinate system based on this plane as in Fig. 4, with 1- and 3-axes along the shear direction and perpendicular to the shear plane. Thus, if we further assume that all transformed particles have the same non-zero transformation strain $\epsilon_{11}^p = \epsilon_{22}^p = \epsilon_{33}^p \neq 0$, $\epsilon_{13}^p \neq 0$,

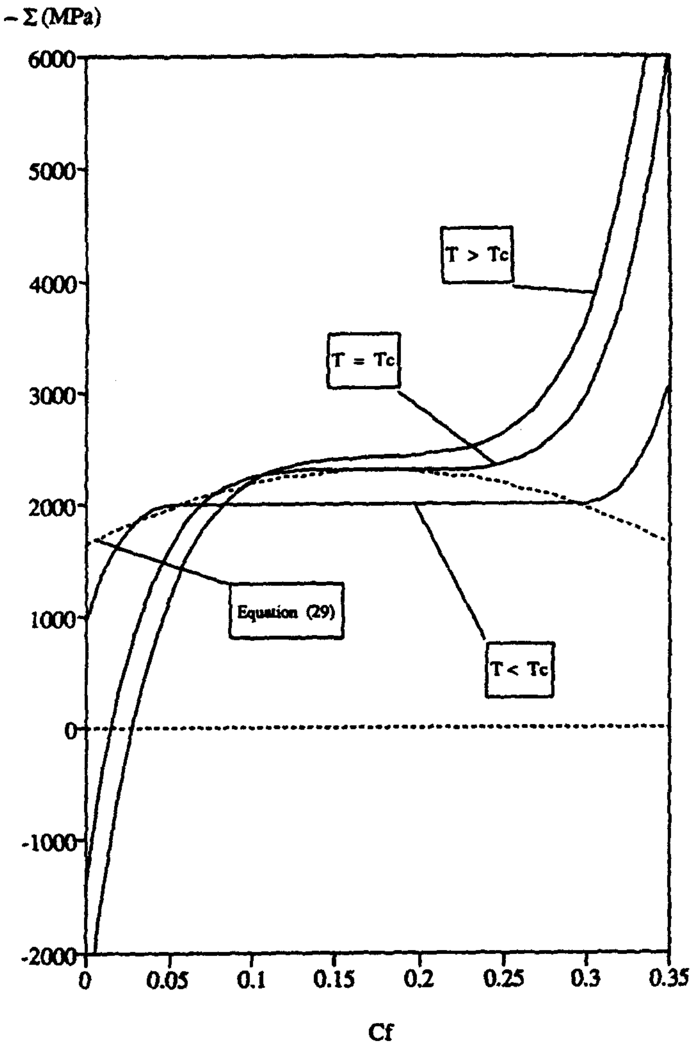

Fig. 5. The volume fraction of transformed particles vs temperature and external load.

and the tetragonal particles form a cubic lattice with respect to this coordinate system, we can use the results obtained in the last part to deal with such specimens. The external load which appeared in equations of the previous section are $\sigma^0_{ii} = \sigma^0_{11} + \sigma^0_{22} + \sigma^0_{33} = -(\Sigma + 3p)$, $\sigma^0_{13} = \Sigma_2$, and stress-free strain accompanying the transformation is $\epsilon^p_{kk} = 0.04$, $\epsilon^p_{13} = 0.15$. We cannot find the experimental data for T_0 which is the temperature for unconstrained tetragonal particles transforming to monoclinic phase. For pure zirconia, this temperature is about 1000°C, but the addition of certain solutes such as MgO will lower T_0. Therefore, we attempt to determine it from experimental data reported by Chen and Reyes Morel [3]. According to Chen and Reyes Morel, we know one yielding point where $c_f = \frac{1}{2} c_f^0$ and $\sigma^0_{11} = -2000$ MPa, $\sigma^0_{22} = \sigma^0_{33} = -200$ MPa, $T = 22°\mathrm{C}$. From eq. (78), we can determine T_0 as 557.6°C.

Another parameter which needs to be determined is B. In statistical mechanics, it is Boltzmann's constant, but here it is a material constant which should depend on the volume of a particle. At the present stage, we do not know how to calculate it. So we also determine its value by experimental data through eq. (25). It seems to be $B = 0.2v \times 10^6$ J/K. Therefore the critical temperature can be determined by eq. (79) as $T_c \approx 280°\mathrm{C}$. When the temperature is near its critical value T_c, eq. (85) is valid, which has been shown in Fig. 5.

The relation between the volume fraction of transformed particles, external load and temperature, which is shown in Fig. 5, is based on the assumption that any part of the material always stays in an equilibrium state when the external condition is changed. Therefore, it is suitable for both loading process and unloading process. In fact, it is almost impossible to make every part of the material always remain at equilibrium state under the loading. So in experiments, we often observed a loop of hysteresis when a specimen is first loading, then unloading. The explanation of this phenomenon is the same as that for the loop of hysteresis in ferroelectricity. Even when the temperature is lower than the critical temperature, it is not very easy to observe the flat part as shown in Fig. 5.

This research is an attempt to deal with a mesoscale problem by using the microscale statistical mechanics method and results. As an optimistic estimation, this may become an efficient approach of microstructural mechanics, since it can predict the macroscopic behavior of materials even if there is no such possibility to determine their changing, stochastic microstructure. However, there are some unsolved problems in this research at the present stage, e.g. how to determine the constant B? How to consider the effect of the irreversible transformation process? These problems will be considered in detail in the near future.

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APPENDIX

The non-zero components of Eshelby's tensor $S_{ijkl} = S_{jikl} = S_{ijlk}$ for spherical inclusion are

$$S_{1111} = S_{2222} = S_{3333} = \frac{7 - 5\gamma}{15(1 - \gamma)} \tag{A1}$$

$$S_{1122} = S_{2233} = S_{3311} = S_{1133} = S_{2211} = S_{3322} = \frac{5\gamma - 1}{15(1 - \gamma)} \tag{A2}$$

$$S_{1212} = S_{2323} = S_{3131} = \frac{4 - 5\gamma}{15(1 - \gamma)}. \tag{A3}$$