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DEFORMATION KINETICS OF STEADY-STATE CREEP IN METALS

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Abstract—The phenomenological constitutive equation given below, for uniaxial steady state creep, i.e.

$$\dot{\epsilon} = \frac{K_1{}^0 e^{-\epsilon_0/kT} \sinh K_2(\sigma - \sigma_0)}{\log \frac{16\epsilon_0}{kT} - \log K_2(\sigma - \sigma_0)},$$

has been derived from first principles and applied to AISI316 stainless steel, pure polycrystalline aluminum and copper. A single micromechanism has been found sufficient to predict the data throughout the entire test temperature and stress range.

The equation above has an intrinsically atomic basis as it has been obtained through the notion of internal variables in the context of the absolute reaction theory of Eyring. The physical meaning of the internal variables and the foundation of their associated evolution equations are established clearly in terms of averages of atomic motions over the energy barriers, under application of an external stress field. It is this concept that gives one hope that a sound thermodynamic and physical foundation of irreversible thermodynamics with internal variables has been found from microscopic considerations.

1. INTRODUCTION

Various theories of steady-state creep have been proposed in the literature in recent times. Four main approaches are worthy of mention: (a) that in which the creep process is presumed to depend on micromechanisms, such as vacancy diffusion, dislocation climb and microcreep in pure metals, dispersion-hardened alloys and solid solution alloys[1–3]; (b) that in which the main object is the analytical representation of available data leading to empirical formulae, such as the power law at low stress, the exponential law at high stress[4], or the hyperbolic sine law[5, 6]; (c) that in which analytical constitutive theories, derived from functional mathematical theories of visco-elasticity, are used as a basis for the analytical representation of the data[7]; (d) that in which phenomenological theories depend on a liaison between theories of micromechanisms and theories of continuum mechanics, such as the state variable theory proposed by Hart[8, 9], the reaction-rate theory proposed by Kanter, Kauzmann and Eyring[10] and the internal variable theory in conjunction with the absolute reaction rate theory proposed by Valanis[11] and Lalwani.

In this paper, the internal variable theory in the context of the absolutre reaction theory[11, 12] is extended and applied to the prediction of the effect of temperature and stress on the steady-state creep rate of metals. In the above theory, there are two fundamental postulates. The first lays the phenomenological foundations by stipulating that the Helmholtz free energy of a dissipative material system undergoing irreversible process is a state function of deformation, temperature and a set of internal variables[13] which are deemed necessary for the description of the inelastic behavior of a material undergoing a deformation process. The second establishes the *atomic* basis of the theory, according to which the inelastic strain is the result of a change in atomic configuration brought about by atoms crossing energy barriers.

The fundamental mechanisms of deformation proposed in theories of vacancy diffusion, dislocation climb, grain boundary glide, etc. are actually atomic motions in specific configurational conformations. In order to make possible an engineering analysis in terms of "deformation kinetics" at the atomic level, the theory presented here makes two stipulations and one hypothesis all of which are stated below:

(1) Creep is the result of diffusion of atoms over potential barriers. The height distribution of these barriers depends on the atomic arrangement in the material in question;

(2) The rate of change of an internal variable is equal to the average velocity of a group of atoms whose motion is impeded by an energy barrier of a specific height;

(3) The gradient of the Helmholtz free energy with respect to an internal variable acts as an internal force on the group of atoms associated with that variable.

The result theory and the ensuing analysis avoid some of the complexities that one finds in other theories of micromechanisms. It also leads to a phenomenological constitutive equation with an intrinsically atomic basis.

2. ANALYSIS

In phenomenological experiments one aims at obtaining laws of mechanical behavior of the materials in terms of a relation between stress, on one hand and strain, strain rate, etc. on the other. This approach is purely global and does not address itself to the micromechanisms in the material that contribute to the overall motion, though local micromotions. In this paper we present a theory in which we identify these micromotions as internal variables and propose laws that govern their evolution. A precise analysis of this point of view is presented in the remainder of this section.

The theory is presented in detail in Ref. [11]. Here we shall recount its essential points for the purposes of analysis.

In general, metals may contain a large number of point defects, dislocations, impurities, grain boundaries, etc. An atom in an environment of a disordered atomic structure, faces potential barriers of different shapes and heights. An atom will surpass a barrier in its path if and only if its energy is higher than the height of the barrier. When the reference state is stable, a large majority of atoms would be expected to be found oscillating in wells formed by the energy barriers. Some atoms may gain enough energy during their oscillations in the valleys and cross over the barriers. In order to ensure that the system is stable initially, it is sufficient to assume that the barriers are symmetric. This assumption will lead to an initially dynamic equilibrium in the system and will ensure that no net atomic motion in any particular direction will take place. The material is thus non-aging.

Following the point of view expressed in Ref. [11], we stipulate that the rate change of an internal variable is the average velocity of a group of atoms whose motion is impeded by a potential barrier of a specific height.

An internal variable q_r is then the statistical average of the displacements of a group of atoms r, whose motion is impeded by barriers whose *heights are all the same* and equal to $\epsilon_0{}^r$.

Certainly there may exist numerous but finite physically different potential barriers in the system. Thus a finite (yet possibly very large) set of internal variables corresponding to a finite number of barriers is needed to describe the material behavior in detail, by the scheme of thermodynamics of internal variables. In addition, it is quite natural that each internal variable has its own evolution equation pertinent to the deformation kinetics that apply at the atomic level. Thus a set of evolution equations corresponding to the set of the internal variables is expected at the phenomenological level at which the material behavior is to be given mathematical constitutive representation. For brevity only one typical internal variable and its associated evolution equation is analyzed here. Other internal variables and their associated evolution equations can be treated analogously in a fashion similar to the one presented in the text.

2.1 *Net number of atoms crossing a barrier*

The morphology of the potential surface of an atomic configuration is likely, in general, to be extremely complex. For the purposes of analysis the barriers are ordered according to their heights as follows:

$$\epsilon_1 < \epsilon_2 \cdots < \epsilon_\gamma \cdots < \epsilon_{n-1} < \epsilon_n.$$

If for every barrier height ϵ_γ there exist a number γ of atomic barriers, then it is possible to treat the motion of the group of atoms γ statistically. To avoid difficulties which arise in cases where γ is small, we shall deal with statistical averages in terms of an ensemble and in what follows we shall be dealing strictly with ensemble averages.

Consider N_γ atoms in the ensemble facing a potential barrier of the height $\epsilon_0{}^\gamma$. The fundamental hypothesis of irreversible thermodynamics in the context of the absolute reaction rate theory[11] is that the potential energy surface, in the vicinity of the atoms associated with the internal variable q_γ, suffers a local tilt ω_γ as a result of the application of the stress field σ. The local tilt ω_γ is assumed to be linearly related to the internal thermodynamic force $-(\partial\psi/\partial q_\gamma)$ acting on the group of atoms γ, where ψ is the Helmholtz free energy. This has the effect that the height of the front barrier is decreased by ω_γ while height of the rear barrier is increased by the same amount. Following Ref. [11], the net number N'_γ of atoms that partake in the forward motion is then that number of atoms whose energies ϵ_i are greater than $\epsilon_0{}^\gamma - \omega_\gamma$ but less than $\epsilon_0{}^\gamma + \omega_\gamma$.

In terms of Boltzmann statistics the probability of an atom being in an energy state ϵ_i is $\alpha\, e^{-\beta\epsilon_i}$ where α is the inverse of the sum over all energy states, β is the inverse of kT, k is the Boltzmann constant and T the absolute temperature. Thus

$$N'_\gamma = \alpha N_\gamma \sum_{\epsilon_i > \epsilon_0{}^\gamma - \omega_\gamma}^{\epsilon_i < \epsilon_0{}^\gamma + \omega_\gamma} e^{-\beta\epsilon_i}. \tag{2.1}$$

This expression maybe written in the form

$$N'_\gamma = \alpha N_\gamma \left(\sum_{\epsilon_i = \epsilon_1}^{\epsilon_i < \epsilon_0{}^\gamma + \omega_\gamma} e^{-\beta\epsilon_i} - \sum_{\epsilon_i = \epsilon_1}^{\epsilon_i < \epsilon_0{}^\gamma - \omega_\gamma} e^{-\beta\epsilon_i} \right). \tag{2.2}$$

Since in eqn (2.2) we are summing essentially over energies associated with the well, i.e. energies that are lower than the pertinent barrier height, we may with good approximation regard these as approximating those of a linear harmonic oscillator in which case

$$\epsilon_i = (i + \tfrac{1}{2})hv_\gamma \tag{2.3}$$

where ν_γ is the characteristic frequency associated with the well in question. Substitution of eqn (2.3) in eqn (2.2) yields the result

$$N'_\gamma = N_\gamma\, e^{-\beta\epsilon_0{}^\gamma} 2 \sinh \beta\omega_\gamma. \tag{2.4}$$

In view of the assumed linearity between ω_γ and $\partial\psi/\partial q_\gamma$ we propose the relation

$$\omega_\gamma = kTC^\gamma(Q_\gamma - Q_\gamma{}^0) \tag{2.5}$$

where the "internal force" $Q\gamma$ is defined as $Q_\gamma \equiv -(\partial\psi/\partial q_\gamma)$ and $Q_\gamma{}^0$ is some threshold value of Q_γ below which $\omega_\gamma = 0$. In general the coefficient of tilt C^γ will be a function of temperature.

With reference to the first author's previous paper[11], if $\bar{\tau}_\gamma$ is the "average time" for the group of atoms to tranverse the distance a_γ across a barrier, then the average velocity $\dot{q}_\gamma$ of the atoms in the forward direction is given by eqn (2.6), i.e.

$$\dot{q}_\gamma = \frac{a_\gamma N'_\gamma}{\bar{\tau}_\gamma N_\gamma}. \tag{2.6}$$

In Ref. [11] Valanis and Lalwani assumed that $\bar{\tau}_\gamma$ is independent of ω_γ as a first approximation. The following quantitative analysis, however, reveals that $\bar{\tau}_\gamma$ may be expressed more exactly as a function of ω_γ. With reference to Fig. 1, let $h(x)$ be the height of the barrier at a distance x from the lowest point in the well, such that,

$$h(a_\gamma) = \epsilon_0{}^\gamma - \omega_\gamma. \tag{2.7}$$

Consider an atom which is a candidate for going over the barrier on the right. This is an atom which prior to the application of the stress field was at an energy level ϵ_i (where i stands for "initial") such that

$$\epsilon_0{}^\gamma - \omega_\gamma < \epsilon_i < \epsilon_0{}^\gamma + \omega_\gamma. \tag{2.8}$$

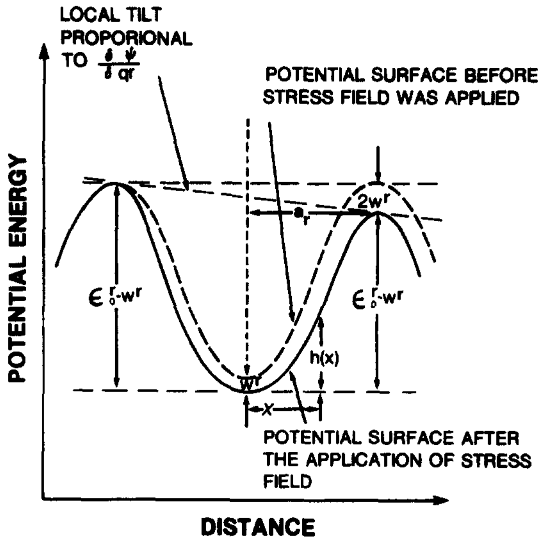

Fig. 1. Potential surface before stress field was applied.

Form considerations of energy conservation

$$h(x)+\tfrac{1}{2}V^2=\epsilon_i \tag{2.9}$$

where V is the velocity of an atom at position x. Thus

$$\frac{\mathrm{d}x}{\mathrm{d}t}=\sqrt{(2)}(\epsilon_i-h(x))^{1/2}. \tag{2.10}$$

It follows that the time τ_i to cross the barrier is given by eqn (2.11), i.e.

$$\tau_i=\frac{1}{\sqrt{2}}\int_0^{a_\gamma}\frac{\mathrm{d}x}{[\epsilon_i-h(x)]^{1/2}}. \tag{2.11}$$

In order to evaluate the integral on the r.h.s. of (2.11), we seek a convenient analytical expression for $h(x)$. We choose

$$h(x)=(\epsilon_0{}^\gamma-\omega_\gamma)\sin^2\frac{\pi x}{2a_\gamma}. \tag{2.12}$$

Upon substitution of eqn (2.12) in eqn (2.11), τ_i is found in terms of the complete elliptic integral F as shown in eqn (2.13).

$$\tau_i=\frac{2a_\gamma}{\pi\sqrt{(2\epsilon_i)}}F\left(\frac{\pi}{2},\sin^{-1}k_i\right) \tag{2.13}$$

where

$$k_i^2=\frac{\epsilon_0{}^\gamma-\omega_\gamma}{\epsilon_i}. \tag{2.14}$$

Equation (2.6) is derived on the basis of the following consideration. Omitting the subcript "γ" for the purposes of facilitating the notation

$$\dot{q}=\frac{\sum\limits_{\epsilon_0-\omega}^{\epsilon_0+\omega}N'_i v_i}{N_\gamma} \tag{2.15a}$$

where v_i is the average velocity of atom with energy† ϵ_i. Evidently

$$v_i = \frac{a}{\tau_i}. \tag{2.15b}$$

Hence:

$$\dot{q} = \frac{a \sum_{\epsilon_0-\omega}^{\epsilon_0+\omega} \frac{N'_i}{\tau_i}}{N_\gamma}. \tag{2.15c}$$

For sufficiently small ω one can write as a first approximation‡

$$\sum_{\epsilon_0-\omega}^{\epsilon_0+\omega} \frac{N'_i}{\tau_i} = \frac{1}{\tau_0} \sum_{\epsilon_0-\omega}^{\epsilon_0+\omega} N'_i \tag{2.15d}$$

where $\tau_0 = \tau|_{\epsilon_i=\epsilon_0}$. Thus restoring the subscript "γ" and as a result of eqn (2.15a)

$$\dot{q} = \frac{a_\gamma N'_\gamma}{\tau_0{}^\gamma N_\gamma}. \tag{2.16}$$

We mention that in eqn (2.6) $\bar{\tau}_\gamma$ has been equated approximately to $\tau_0{}^\gamma$. It follows therefore from eqn (2.13) that

$$\bar{\tau}_\gamma = \frac{2a_\gamma}{\pi\sqrt{(2\epsilon_0{}^\gamma)}} F\left(\frac{\pi}{2}, \sin^{-1} k_0{}^\gamma\right) \tag{2.17}$$

where

$$k_0{}^\gamma = \left(\frac{\epsilon_0{}^\gamma - \omega_\gamma}{\epsilon_0{}^\gamma}\right)^{1/2}. \tag{2.18}$$

Now using eqns (2.17), (2.6) and (2.4) we arrive at an important relation which links the time rate of change of q_γ to the potential distortion ω_γ. Specifically,

$$\dot{q}_\gamma = \frac{\sqrt{(2)}\,\pi\sqrt{(\epsilon_0{}^\gamma)}}{F} \mathrm{e}^{-\beta\epsilon_0{}^\gamma} \sinh \beta\omega_\gamma. \tag{2.19}$$

To obtain an equation for the evolution of the internal variable q_γ, we recall our earlier assumption according to which ω_γ is linearly related to $\partial\psi/\partial q_\gamma$. Recalling eqn (2.5) and substituting for ω_γ in eqn (2.19) we obtain the required eqn (2.20), i.e.

$$\dot{q}_\gamma = \frac{\sqrt{(2)}\,\pi\sqrt{(\epsilon_0{}^\gamma)}}{F} \mathrm{e}^{-\beta\epsilon_0{}^\gamma} \sinh C_\gamma(Q_\gamma - Q_\gamma{}^0) \tag{2.20}$$

subject to the constraint

$$\dot{q}_\gamma = 0, \qquad |Q_\gamma| \leq Q_\gamma^0. \tag{2.20a}$$

The appearance of $Q_\gamma{}^0$ has a sound physical explanation. It is well known that metals behave substantially elastically, below a stress level which is known as the yield stress. We

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†The limits of the sum in the numerator are consistent with the fact that only atoms in the indicated range partake in the forward motion.

‡Here we are essentially applying the mean value theorem to the sum.

expect therefore that no creep will take place unless the applied stress exceeds the yield stress at a particular temperature.

In eqn (2.20) Q_γ^0 has the meaning of an internal yield "stress" (force)† since no micromotion q_γ can take place unless the magnitude $|Q_\gamma|$ of the internal force exceeds Q_γ^0.

The limiting form of F. It is shown in Fig. 2 that for $0 \leq (\omega_\gamma/\epsilon_0^\gamma) \leq 0.35$, the function F can be approximated quite adequately by the relation (2.21), i.e.

$$F = \frac{1}{2}\log\left(\frac{16\epsilon_0^\gamma}{\omega_\gamma}\right). \tag{2.21}$$

The maximum error being less than 5%. Equation (2.20) may now be expressed in terms of standard functions.

2.2 *Relation between stress and steady rate of creep*

Following the application of stress, the creep process begins at its fastest rate and proceeds at a progressively slower rate until a constant creep rate (secondary creep) is achieved. The transition to tertiary creep and the circumstances surrounding the later will not be discussed here. In so far as creep in metals is the result of diffusion—by correlated atomic motion, interstial diffusion, vacancy diffusion or relaxation diffusion (motion by local atomic arrangement)—the characteristic shape of a creep curve suggests that initially high rate of creep must be associated with diffusion of atoms over low potential barriers. In their subsequent travel these atoms must by shear chance alone be progressively trapped in behind high barriers. So that *particles* that are available to diffuse over low barriers become less and less numerous. Furthermore trapped particles become obstacles to motion of mobile particles thereby increasing the population of high barriers. The implication is that "long term" (secondary creep) consists, essentially, of atoms climbing over the higher barriers.

It would appear therefore and it will be vindicated experimentally, that one internal variable corresponding to such high barriers will suffice to describe the process of deformation associated with steady state creep.

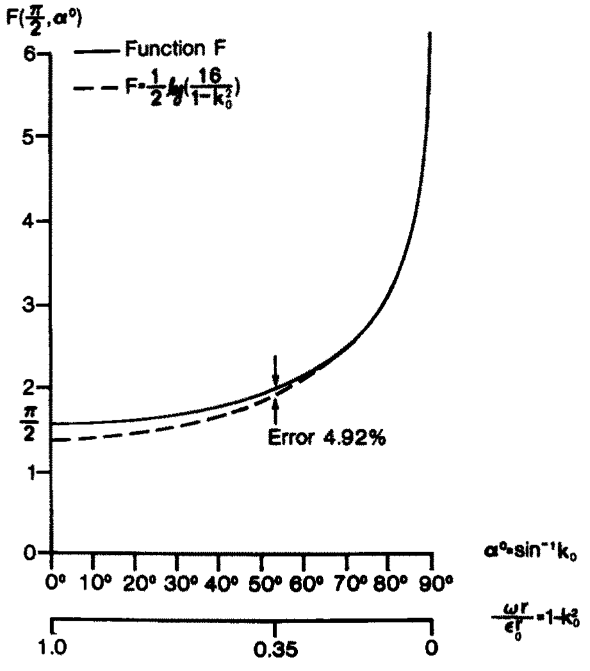

Fig. 2. The complete elliptic integral.

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†Physical concepts in this vein are already present in the literature. For instance Ashby in his construction of "deformation maps" admits stress thresholds below which no creep can occur as a result of the particular micromechanism dominant in a particular region of the homologous temperature-stress diagram. See Ref, [20]. Regions in which no creep can occur are called elastic regions.

With the above in mind and for the purposes of steady state creep we write the free energy density ψ in the form

$$\psi = \psi(\epsilon, q, T) \qquad (T = \text{const}). \tag{2.22}$$

The form of the function ψ merits discussion. We recall that the free energy is the mechanically stored (or recoverable) energy present in a thermodynamic system at any particular time. Energy is stored through mean displacement of atoms from their positions at the bottom of potential wells. To a good approximation the shape of a well may be regarded as parabolic for, its most part, leading to the model of linear harmonic oscillator. If an atom goes over a barrier its energy is no longer stored but is dissipated and thus it cannot contribute to the stored energy. Thus the free energy is the potential energy stored by virtue of atoms being displaced *within* potential well. The mean displacement generated as a result is directly related to the elastic strain. For instance in the case of a unidirectional equispaced atoms the elastic strain is exactly equal to the atomic displacement divided by the lattice spacing. Assuming parabolic wells, the potential energy is proportional to a quadratic function of the displacement, leading to the conclusion that the free energy is a quadratic function of the elastic strain.†

To relate the above discussion to eqn (2.22) we write ψ in the quadratic form

$$\psi = \tfrac{1}{2}A_{11}\epsilon^2 + A_{12}\epsilon q + \tfrac{1}{2}A_{22}q^2 \tag{2.23}$$

and insist that it is a perfect square, so that the squared linear term can then be identified with the elastic strain. This is possible if

$$A_{12}^2 = A_{11}A_{22} \tag{2.24}$$

in which case eqn (2.23) becomes

$$\psi = \tfrac{1}{2}A(\epsilon - Bq)^2 \tag{2.25}$$

where $A \equiv A_{11}$ and $B \equiv -(A_{12}/A)$. Thus since eqn (2.25) is the mathematization of the statement at the end of the last paragraph $\epsilon - Bq$ must be identified as an elastic strain. Note that A and B may be and are, in general, functions of temperature.

To obtain the desired analytical expression for creep we appear to a fundamental relation of irreversible thermodynamics according to which the stress is the gradient of free energy with respect to the strain, i.e.

$$\sigma = \frac{\partial\psi}{\partial\epsilon}. \tag{2.26}$$

Thus, as a result of eqns (2.25) and (2.26)

$$\sigma = A(\epsilon - Bq). \tag{2.27}$$

We also note at this juncture that $\partial\psi/\partial q$ which is essential in the determination of $\dot{q}$—see eqn (2.20)—is given by eqn (2.28):

$$\frac{\partial\psi}{\partial q} = -AB(\epsilon - Bq)$$

or

$$\frac{\partial\psi}{\partial q} = -B\sigma. \tag{2.28}$$

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†For a discussion see Appendix.

Equation (2.28) in conjunction with eqn (2.20) yields a relation between $\dot{q}$ and σ. The fact that during creep the stress is a constant, following the instant of its application, leads to a relation between the strain rate and $\dot{q}$. Specifically, as a result of eqn (2.27)

$$\dot{\epsilon} = B\dot{q} \tag{2.29}$$

upon substitution of eqns (2.28) and (2.29) in eqn (2.20) one obtained the following explicit relation between the creep rate and its stress:

$$\dot{\epsilon} = 2\sqrt{(2\epsilon_0)}\,\pi B\,\mathrm{e}^{-(\epsilon_0/kT)}\frac{\sinh K_2(\sigma-\sigma_0)}{\log\frac{16\epsilon_0}{kT}-\log K_2(\sigma-\sigma_0)} \tag{2.30}$$

where

$$K_2 = CB \tag{2.31}$$

and

$$\sigma_0 = B^{-1}Q^0. \tag{2.32}$$

Perusal of eqn (2.30) shows that σ_0 has the significance of a "threshold stress" below which the rate of secondary creep is zero. Experimental results give a strong indication of the existence of such a threshold (at least in an approximate sense). We have found that in the case of steel (AISI316 stainless steel) σ_0 is substantially independent of temperature. However, in the case of pure polycrystalline copper and aluminum σ_0 depends on temperature quite sensibley.

3. USE OF EQUATION (2.30) TO PREDICT SECONDARY CREEP

For the purposes of a discussion we write eqn (2.30) in the form

$$\dot{\epsilon} = \mathcal{F}(\sigma, T)\,\mathrm{e}^{-\epsilon_0/kT} \tag{3.1}$$

where

$$\mathcal{F}(\sigma, T) = \frac{K_1{}^0\sinh K_2(\sigma-\sigma_0)}{\log\frac{16\epsilon_0}{kT}-\log K_2(\sigma-\sigma_0)} \tag{3.2}$$

and

$$K_1{}^0 = 2\sqrt{(2\epsilon_0)}\,\pi B. \tag{3.3}$$

We note from the above equations that the dependence of $\dot{\epsilon}$ on σ and T is determined in terms of the parameters ϵ_0, σ_0, $K_1{}^0$ and K_2. To determine these parameters we use arguments based on the following physical considerations.

We presume that, since an increase in temperature increases the amplitude of oscillation of atoms about their mean position, only the mean kinetic energy is affected by a temperature change but not the potential surface configuration. Thus ϵ_0 is insensitive to temperature and is essentially constant. Perusal of the experimental data—AISI 316 stainless steel, pure polycrystalline aluminum and copper on the plot of σ vs $\log_{10}\dot{\epsilon}$, as shown in Figs. 3, 7 and 11—indicates that, under constant T, the data points converge asymptotically to a stress value σ_0 as $\dot{\epsilon}\to 0$. In general σ_0 is substantially constant or a sensitive function of T as the case may be. In addition, eqn (3.2) under constant T is dominated by $\sinh K_2(\sigma-\sigma_0)$ when $K_2(\sigma-\sigma_0)$ is high. As a result, at high stresses $\dot{\epsilon}$ is proportional to $\mathrm{e}^{K_2(\sigma-\sigma_0)}$ and the plot of σ vs $\log_{10}\dot{\epsilon}$ will be almost a straight line. This trend is confirmed by the Figs. 3, 7 and 11. Thus K_2 can be found by the relation

$$K_2 = \left.\frac{\partial \log \dot{\epsilon}}{\partial \sigma}\right|_T \quad (\sigma \text{ large}). \tag{3.4}$$

In fact K_2 is a function of T.

To determine ϵ_0 we are guided by the previous technical literature. The general practice has been to plot $\log_{10} \dot{\epsilon}$ vs $1/T$ at constant stress. In the case of common metals this "plot" is to a first approximation, a straight line. The implication is that in the temperature range of the test $\log_{10} \mathcal{F}$ is a weak function of temperature and as a result ϵ_0 may be obtained from the measured slope of the straight line. The expectation that ϵ_0 is independent of stress should lead to parallel straight lines, each corresponding to a different, constant stress level. This observation enabled us to determine a first (approximate) value of ϵ_0. Using the values of σ_0, ϵ_0 and K_2, eqn (3.1) can be readily applied and $K_1{}^0$ can be determined by the best fit of the theory to the experimental data. This procedure worked welled for steel and aluminum but a different approach had to be employed in the case of copper.

3.1 *Application to AISI* 316 *stainless steel*

Figures 3 and 4 are experimental data from Ref. [15]. From Fig. 3, the value of σ_0 is observed to be a constant, i.e. 2 ksi (140.6 kg/cm^2). The function $K_2(T)$ was found by use of eqn (3.4) and is shown in Fig. 5. The values of $K_2(T)$ over the indicated temperature range show $K_2(T)$ to be a fairly slowly varying function of T. In Fig. 4, we let a straight line pass through the data points and find ϵ_0 to be equal to 73.7 kcal/mole.† This is very close to the value of the "activation energy" in Ref. [15]. The values of $K_1{}^0(T)$ then found by using eqn (3.1) and are shown in Fig. 6. This figure shows that $K_1{}^0$ is a slowly varying function of T. Thus $\log_{10} \mathcal{F}$ is also a slowly varying function of T due to the slowly varying nature of $K_1{}^0(T)$ and $K_2(T)$. This shows that eqn (3.1) approximates an Arrhenius type relation as shown in Fig. 4, within the tolerance of experimental scatter.

The theoretical predictions are in good agreement with the experimental data as shown in Fig. 3.

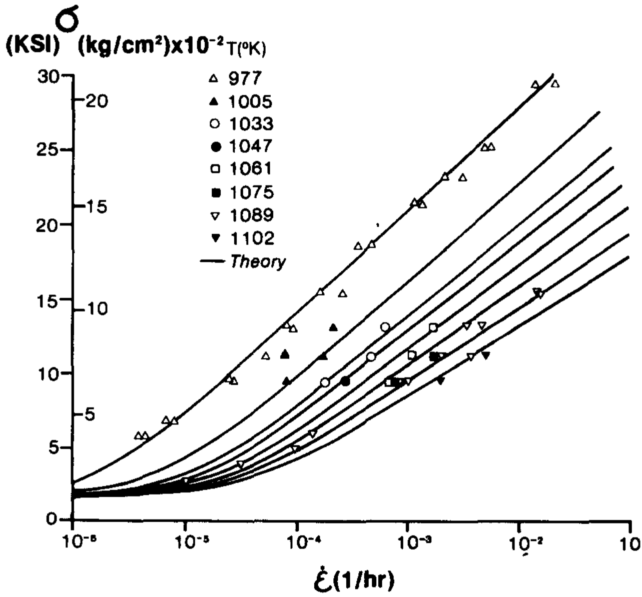

Fig. 3. AISI 316 stainless steel.

†According to Refs. [4, 15], this value is in good agreement with the activation energy for self diffusion in $\mathcal{T}$-iron which is the major constituent of AISI 316 stainless steel in the test temperature range.

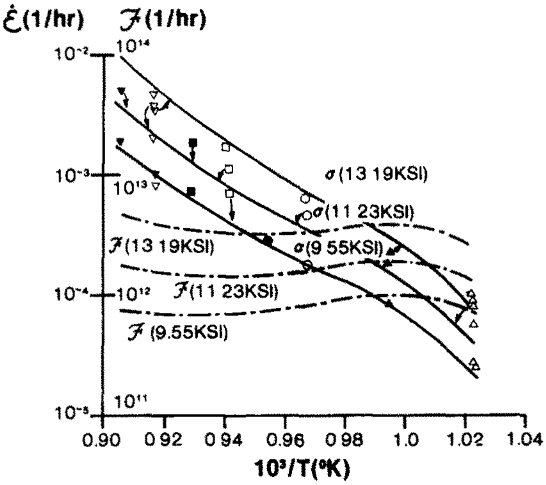

Fig. 4. AISI 316 stainless steel.

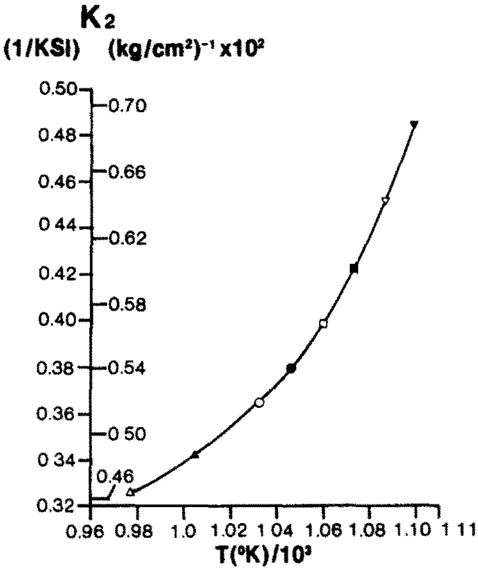

Fig. 5. AISI 316 stainless steel.

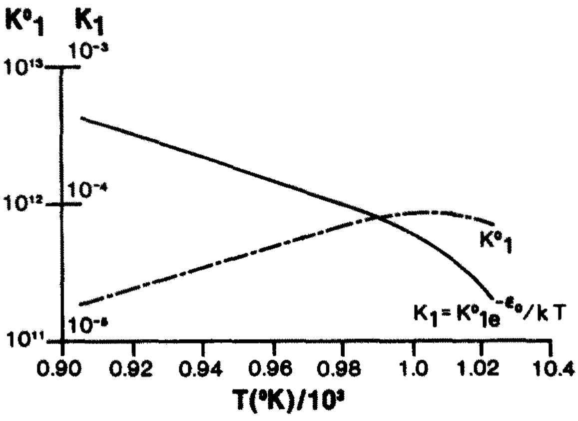

Fig. 6. AISI 316 stainless steel.

3.2 *Application to pure polycrystalline aluminum*

Figures 7 and 8 are experimental data from Ref. [16]. From Fig. 7, one concludes that σ_0 is a function of T shown in Fig. 9. The function K_2 given by eqn (3.4), is also a function of T as shown in Fig. 9. In Fig. 8 plots are shown of $\log \dot{\epsilon}$ vs $10^3/T$ at different constant stress levels. Though the number of points in the plots is small (two or three), they serve to establish approximate linear relations. We expect then that $\log_{10} \mathcal{F}$ (within these temperature ranges) will be a slowly varying function of T and, indeed, this is true as shown in Fig. 8. the value of ϵ_0 is found to be equal to 34 kcal/mole† which is the same value as the activation energy in Ref. [16]. The function $K_1^0(T)$ is then found by using eqn (3.1) and the result shown in Fig. 10. With the functions σ_0, K_1^0 and K_2 so found the dependence of $\log_{10} \mathcal{F}$ on T is now calculated throughout the range of the test temperature. As seen in Fig. 8 a strong dependence of $\log_{10} \mathcal{F}$ on T is indicated outside the temperature range of the experiment.

This accounts for the fact that when workers use an Arrhenius plot—thus assuming that $\log_{10} \mathcal{F}$ is constant—they find activation energies that are stress dependent. However we find that this is not the case when $\log_{10} \mathcal{F}$ is expressed properly as a function of T.

The resulting theoretical predictions are in good agreement with the experimental data as shown in Fig. 7.

3.3 *Application to pure polycrystalline copper*

In Figs. 11 and 12 we present experimental data from Ref. [17]. From Fig. 11, we deduce that σ_0 is a function of T as shown in Fig. 13. The value of K_2 is also found by the procedure previously discussed and is shown in Fig. 13. Only two to four data points under constant stress are shown in Fig. 12. Obviously these points can not be connected by parallel straight lines as was previously the case.

However, the experience accumulated from the previous cases lead to the following observations. Equation (3.1), under given σ_0 and K_2, depends on $K_1(= K_1^0\, e^{-\epsilon_0/kT})$ but not on ϵ_0 alone. The effect of changing ϵ_0 in eqn (3.1) is always offset by a corresponding change in K_1^0. As a result the theoretical curves predicted by eqn (3.1) on a plot of $\log_{10} \dot{\epsilon}$ vs $1/T$ are not sensitive to the change of ϵ_0. In addition, under conditions of high-temperature creep, ϵ_0 is in good agreement with the activation energy of self diffusion in pure metals or of the major constituent in solid solutions alloys. The same conclusion may be drawn from Dorn's observations[4]. As a result, ϵ_0 is set equal to 49 kcal/mole which is the activation energy of self

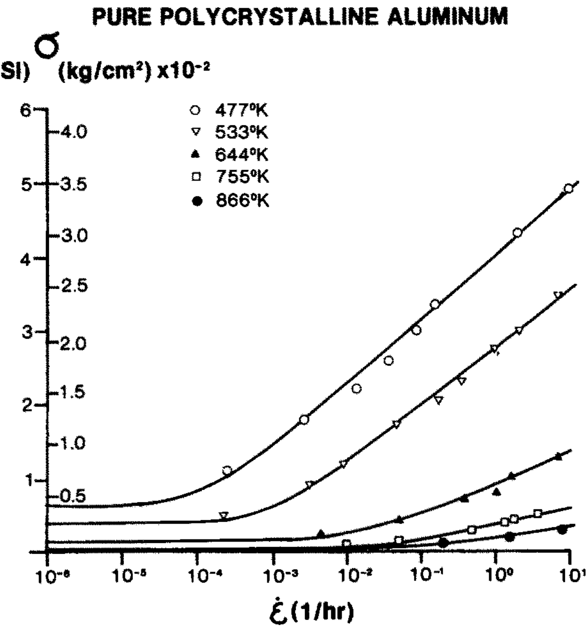

Fig. 7. Pure polycrystalline aluminum.

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†According to Refs. [4, 16], this value is in good agreement with the activation energy for self diffusion in aluminum.

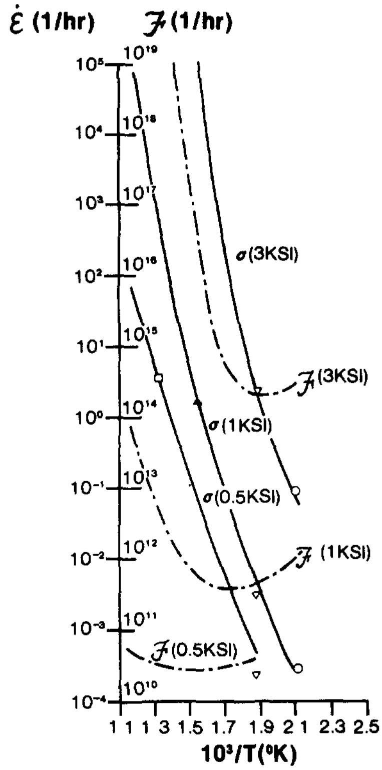

Fig. 8. Pure polycrystalline aluminum.

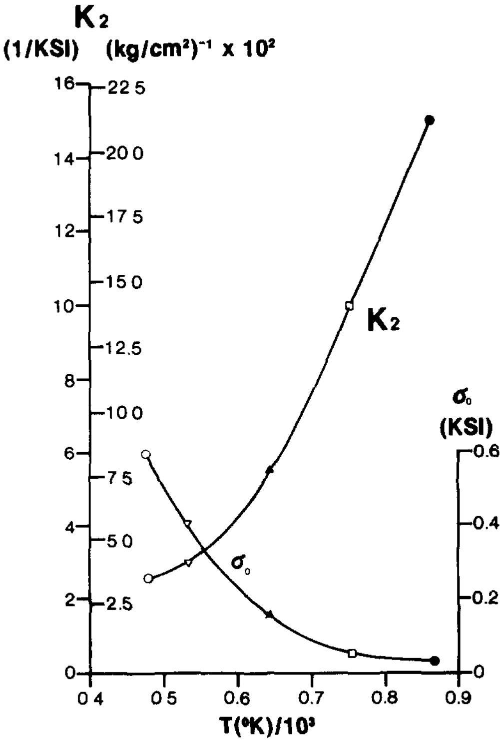

Fig. 9. Pure polycrystalline aluminum.

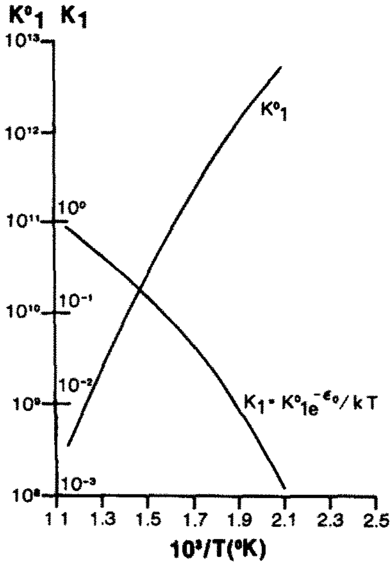

Fig. 10. Pure polycrystalline aluminum.

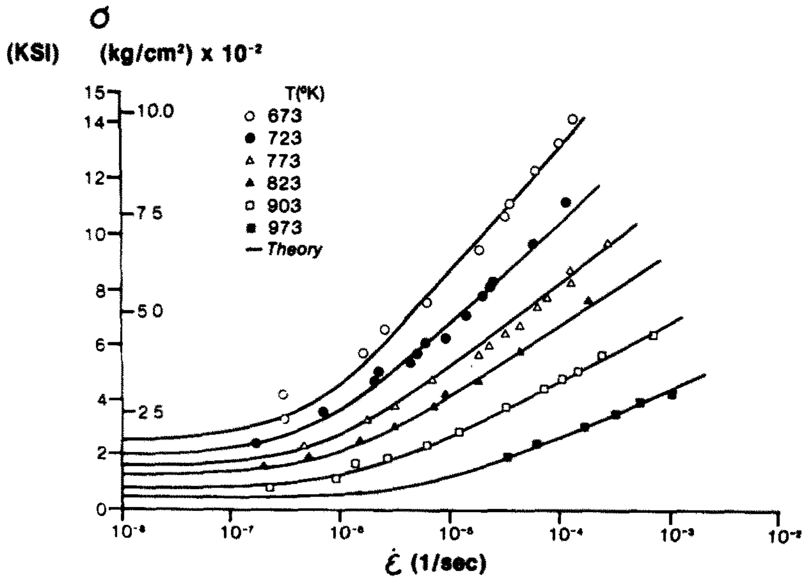

Fig. 11. Pure polycrystalline copper.

diffusion in copper. The value of ϵ_0 determined here is different from those temperature dependent values of activation energy, determined in Refs. [17, 19].

The function $K_1^0(T)$ is then determined from eqn (3.1) and is shown in Fig. 14. We show in Fig. 12 that $\log_{10} \mathscr{F}$ is a strong function of T due to the dependence of σ_0, K_1^0 and K_2 on T.

The theoretical predictions are in good agreement with experimental data as shown in Fig. 11.

4. CONCLUSIONS

A phenomenological constitutive equation has been derived on the basis of considerations at the atomic scale using deformation kinetics and irreversible thermodynamics of internal variables. The physical meaning of the internal variables and the foundation of their associated evolution equations have been determined very clearly in terms of the motion of atoms crossing potential energy barriers, distorted by the presence of local internal forces.

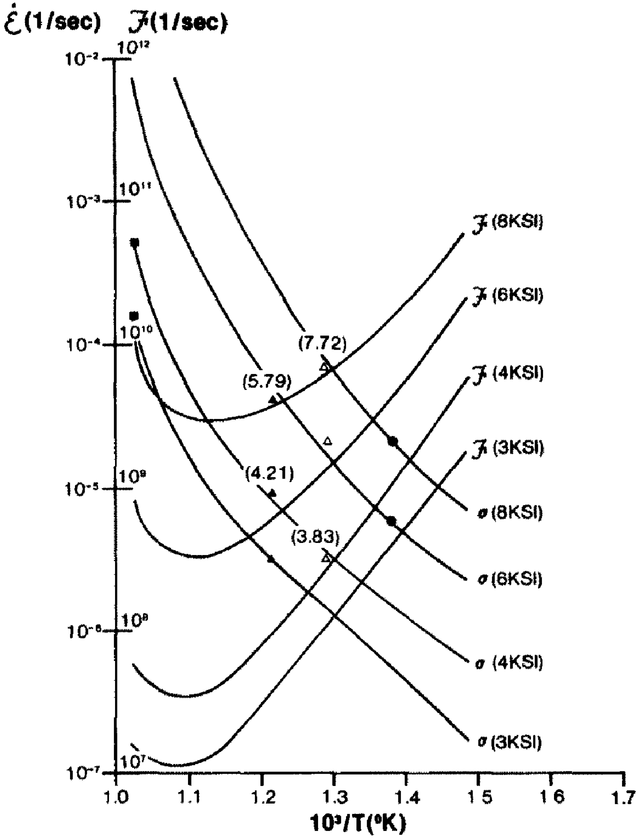

Fig. 12. Pure polycrystalline copper.

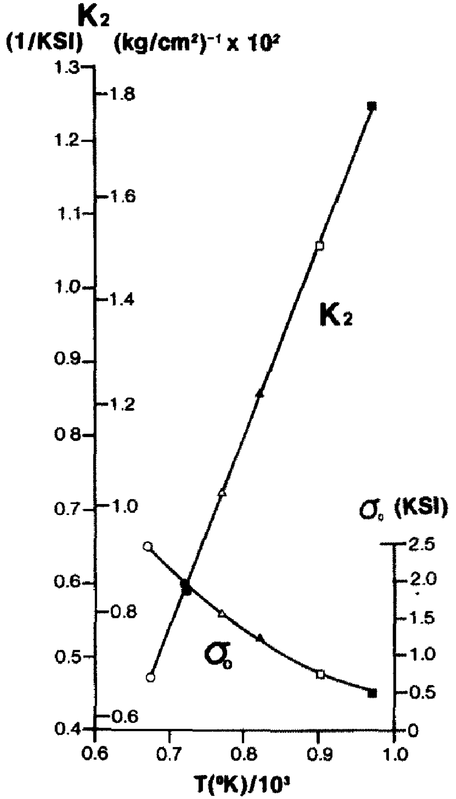

Fig. 13. Pure polycrystalline copper.

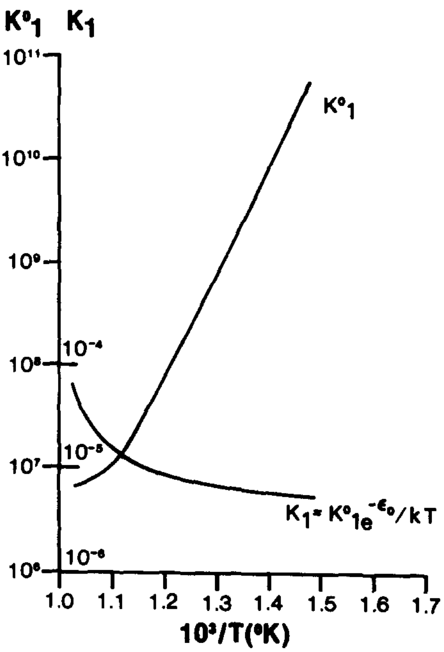

Fig. 14. Pure polycrystalline copper.

The theory is in good agreement with experimental observation of steady-state creep in metals such as AISI 316 stainless steel, pure polycrystalline aluminum and copper. A single micromechanism (i.e. one internal variable) is found sufficient to predict the data in the entire range of temperature of the tests.

It is expected that the theory, developed herein, will have wide applicability owing to its basic nature. The thermodynamic and physical foundations upon which this theory is based make it suitable for the study of general thermodynamic deformation processes in other materials.

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REFERENCES

1. A. J. Kennedy, *Processes of Creep and Fatigue in Metals*, p. 250. Wiley, New York (1963).
2. F. Garofalo, *Fundamentals of Creep and Creep-Rupture in Metals*, Chap. 6. MacMillan, New York (1965).
3. O. D. Sherby and P. M. Burke, Mechanical behavior of crystalline solids at elevated temperatur. In *Progress in Materials Science* (Edited by Chalmers and W. Hume-Rothery), Vol. 13. Pergamon Press, Oxford (1968).
4. J. E. Dorn, Some fundamental experiments on high temperature creep. *J. Mech. Phys. Solids* **3**, 85 (1954).
5. A. Nadai and P. G. McVetty, Hyperbolic sine chart for estimating working stresses of alloys at elevated temperature. *Proc. ASTM* **43**, 735 (1943).
6. F. Garofalo, An empirical relation refining the stress dependence of minimum creep rate in metals. *Trans. AIME* **227**, 351 (1963).
7. W. N. Findley, J. S. Lai and K. Onaran, *Creep and Relaxation of Nonlinear Viscoelastic Material.* North-Holland, New York (1976).
8. E. W. Hart, Constitutive relations for the nonelastic deformation of metals. *Trans. ASME J. Engng Mat. Tech.* Series H98, 3, 193 (1976).
9. F. H. Huang, H. Yamada and C. Y. Li, Constitutive relations based on state variables for nonelastic deformation in type 304 and 316 stainless steel. In *Characteristization of Materials for Services at Elevated Temperature* (Edited by G. V. Smith). ASME MPC-7 (1978).
10. A. S. Krausz and H. Eyring, *Deformation Kinetics.* Wiley, New York (1975).
11. K. C. Valanis and S. A. Lalwani, Themodynamics of internal variables in the context of absolute reaction rate theory. *J. Chem. Phys.* **67**, 3980 (1977).
12. C. P. Wei, Effects of temperature, irradiation and cold work on creep behavior of metals. Ph.D. Thesis, The Univ. of Iowa, Iowa City, Iowa, U.S.A. (1978).
13. K. C. Valanis, *Irreversible Thermodynamics of Continuous Media—Internal Variable Theory.* Springer-Verlag, New York (1972).
14. C. Hastings, Jr., *Approximations for Digital Computers*, p. 170. Princeton Univ. Press, Princeton, New Jersey (1955).
15. F. Garofalo, C. Richmond, W. F. Domis and R. von Gemmingen, Strain-time, rate-stress and rate-temperature relations

during large deformation in creep. In *Joint Int. Conf. on Creep* 1963. Papers, London, Inst. of Mech. Engrs, pp. 1–31 (1963).
16. I. S. Servi and N. J. Grant, Creep and stress rupture behavior of aluminum as a function of purity. *Trans. AIME* **191**, 909 (1951).
17. P. Feltham and J. D. Meakin, Creep in face-centered cubic metals with special reference to copper. *ACTA Met.* **7**, 614 (1959).
18. C. R. Barrett and O. D. Sherby, Steady-state creep characteristic of polycrystalline copper in the temperature range 400–900°C. *Trans. AIME* **230**, 1322 (1964).
19. E. R. Gilbert and D. E. Munson, Multistep reaction in the creep of copper. *Trans. AIME* **233**, 429 (1965).
20. M. F. Ashby, A first report on deformation-mechanism maps. *Acta Met.* **20**, 887 (1972).
21. J. Meixner and H. G. Reik, Thermodynamik der irreversiblen prozesse. In *Handbuch der Physik* (Edited by S. Flügge), Vol. III/2, pp. 413–523. Springer-Verlag, Berlin (1959).
22. M. A. Biot, *Mechanics of Incremental Deformations*, p. 346. Wiley, New York (1965).
23. R. A. Schapery, Application of thermodynamics to thermomechanical fracture and birefringent phenomena in viscoelastic media. *J. Appl. Phys.* **35**, 1451 (1964).
24. J. Kestin, *A Course in Thermodynamics*, Vol. II, p. 447. Blaisdell, London (1968).

APPENDIX

Quadratic function in ϵ and q of the free energy has been discussed in the literature extensively (see for instance Meixner and Reik[21], Biot[22], Schapery[23], Valanis[13], Kestin[24] *et al.*). These functions satisfy the principle of thermodynamic stability as discussed by the above authors provided that certain constraints are imposed to insure ellipticity of the function in the sense that the free energy is positive definite.

With reference to eqn (2.23) the constraints are

$$A_{11} > 0, \quad A_{22} > 0 \quad A_{12}^2 - A_{22}A_{11} < 0. \tag{A1a,b,c}$$

The constraint (A1c) is somewhat too stringent in that it excludes the possibility of (A1c) be an equality. This is a physically admissible possibility and pertains, in the case of viscoelasticity, to simple models such as the Maxwell model, which exhibits a fluid equilibrium configuration.

In this paper we admit the possibility of (A1c) being an equality. We note in passing that if this were not so, steady state creep would not be possible.