Thermoelastic Fluctuations in Solids¹

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Adiabatic thermoelastic heating can be used to monitor stress fluctuations in solids. Previous studies of the effects on the temperature fluctuations both of applied static stress and of the finite amplitude of the stress fluctuations have used approximate theory. The present rigorous thermodynamic treatment distinguishes between adiabatic second-order derivatives needed for finite amplitude and mixed derivatives needed for static applied stress. A detailed analysis is given for purely compressive stress, followed by computations for KCl, NaCl, Al, Cu, Ti, and the alloy Ti-6Al-4V. Additional terms revealed by the new analysis prove to be substantial, including the difference between the adiabatic and mixed derivatives. Revised forms are then proposed for earlier approximations. For unidirectional stress, expressions are taken from an analysis given elsewhere; and computations made for Al, Cu, Ti and Ti-6Al-4V. Corrections to earlier approximations are relatively smaller than for compressive stress, and of opposite sign because the shear component of the unidirectional stress dominates the second order effects.

KEY WORDS: aluminium; compressive thermoelasticity; copper; potassium chloride; shear thermoelasticity; sodium chloride; thermal stress analysis; Ti-6Al-4V; titanium.

1. INTRODUCTION

Oscillating stresses in solids give rise to oscillations in temperature. This provides a means of monitoring stress fluctuations in a material; the associated temperature fluctuations are scanned over the surface of the material with the aid of a sensitive infrared detector [1].

¹ Paper presented at the Fourteeenth Symposium on Thermophysical Properties, June 25–30, 2000, Boulder, Colorado, U.S.A.

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Although important effects can arise in applications from frictional processes and from heat flow, the phenomenon is essentially adiabatic. It is sometimes characterized by a "thermoelastic constant," defined by [2]

$$K = -\frac{1}{T_0} \left(\frac{\Delta T}{\Delta \sigma}\right)_S \tag{1}$$

where T_0 is the mean temperature and ΔT is the amplitude of the adiabatic cyclic change in temperature caused by a cyclic change in the sum of the principal stresses of amplitude $\Delta \sigma$. We may note, however, that Eq. (1) defines K uniquely only for isotropic or cubic materials under hydrostatic pressure, since otherwise ΔT depends upon the directions of the principal stresses and how $\Delta \sigma$ is distributed among them. Furthermore, even these materials lose their symmetry as soon as an anisotropic stress is applied, and so the derivatives of K with respect to such stresses are ill-defined. We shall therefore retain K only for isotropic or cubic materials under isotropic pressure, and redefine it as the "thermoelastic coefficient"

$$K = \frac{1}{3T} \left(\frac{\partial T}{\partial P} \right)_{S} \tag{2}$$

For anisotropic stresses we shall refer only to the stress derivatives of T.

In any case, to refer to K as a "constant" can be misleading, because a stress derivative of T is itself stress-dependent [3, 4]. This gives rise to two second-order effects: (i) the temperature response to stress fluctuations about a mean stress σ_m varies with σ_m ; and (ii) the temperature response to a sinusoidally varying stress includes a second harmonic of double the applied frequency.

Wong et al. [4, 5] developed a method for calculating the magnitude of these effects from other properties of the material. Although they started with time-dependent equations which took account both of heat flow and of internal heat sources, they discarded all such nonequilibrium processes before reaching their result, which was thus purely thermodynamic. They tested the method experimentally for unidirectional stress fluctuations in the titanium alloy Ti-6Al-4V, obtaining good agreement with experiment [5]. However, their theory employed a number of approximations in the thermodynamics which were not discussed or assessed; in particular, the distinction between adiabatic and isothermal second derivatives was largely ignored.

Subsequently Ledbetter et al. [6] considered the effect of pressure rather than unidirectional stress. They used three different expressions for the pressure dependence of K; one was derived by rough approximations

from a Mie–Grüneisen pair potential, another from the theory of Wong et al., and the third from the second by further approximations due to Chang [7] which are not always reliable [8]. These expressions gave values which agreed with each other in order of magnitude for each of eight metals studied, differing by 20 to 50%.

In the present paper we derive exact thermodynamic expressions for the temperature response of a material subjected to oscillating stress or pressure. We investigate for various materials the importance of terms neglected in the approximations of Wong et al. and Ledbetter et al. In Section 2 we point out that it is the isothermal stress derivative of $(\partial T/\partial \sigma)_S$ which determines the effect of the mean stress σ_m , and the adiabatic stress derivative which determines the amplitude of the second harmonic response. In Section 3 rigorous thermodynamic expressions are derived for the pressure effects, and the approximations of Ledbetter et al. are modified accordingly. Calculations on various materials show that terms neglected in the method of Wong et al. make substantial contributions. In Section 4 expressions for unidirectional stress are quoted from a more general analysis for orthorhombic symmetry given elsewhere [9]. Calculations show that corrections to the theory of Wong et al. are still appreciable, but much less important than for purely compressional stress.

2. STEADY-STATE RESPONSE TO FLUCTUATING STRESS

Wong et al. [5] applied their theory to a unidirectional stress, denoted here by σ_U , with both static and sinusoidal components:

$$\sigma_U = \sigma_m + \Delta \sigma \sin \omega t \tag{3}$$

where σ_m and $\Delta \sigma$ are constants. We start by taking a more general form,

$$\sigma_U = \sigma_m + \sigma_v \tag{4}$$

where σ_m is the mean stress and σ_v is an oscillating component of arbitrary shape, so that

$$\langle \sigma_U \rangle = \sigma_m, \qquad \langle \sigma_v \rangle = 0$$
 (5)

where $\langle \cdots \rangle$ denotes averaging over an oscillation. After a sufficiently long time, the mean temperature will approach a limiting value T_m ; if lossy processes are neglected, T_m is given by the ambient temperature T_0 . The steady-state response is thus purely oscillatory, and is determined by $(\partial T/\partial \sigma_U)_S$, which is itself stress-dependent. Moreover, the effects of σ_m and σ_v on $(\partial T/\partial \sigma_U)_S$ must be considered separately. In the steady-state, σ_m has

no effect upon the temperature, so that its effect on $(\partial T/\partial \sigma_U)_S$ is isothermal; whereas in the limit of rapid oscillations the effect of σ_v is adiabatic. To the first order in the stress, therefore,

$$\left(\frac{\partial T}{\partial \sigma_U}\right)_{S} = \left(\frac{\partial T}{\partial \sigma_U}\right)_{S;0} + \left[\frac{\partial}{\partial \sigma_U}\left(\frac{\partial T}{\partial \sigma_U}\right)_{S}\right]_{T;0} \sigma_m + \left[\frac{\partial^2 T}{\partial \sigma_U^2}\right]_{S;0} \sigma_v \qquad (6)$$

where the subscript 0 denotes evaluation at $\sigma_U = 0$, $T = T_0$. Integration with respect to σ_v then gives

$$T - T_{0} = \left\{ \left(\frac{\partial T}{\partial \sigma_{U}} \right)_{S; 0} + \left[\frac{\partial}{\partial \sigma_{U}} \left(\frac{\partial T}{\partial \sigma_{U}} \right)_{S} \right]_{T; 0} \sigma_{m} \right\} \sigma_{v} + \frac{1}{2} \left[\frac{\partial^{2} T}{\partial \sigma_{U}^{2}} \right]_{S; 0} \left\{ (\sigma_{v})^{2} - \langle (\sigma_{v})^{2} \rangle \right\}$$
(7)

where the constant term is fixed by the steady-state condition $\langle T \rangle = T_0$.

For the sinusoidal oscillation $\sigma_v = \Delta \sigma \sin \omega t$, this becomes

$$T - T_{0} = \left\{ \left(\frac{\partial T}{\partial \sigma_{U}} \right)_{S; 0} + \left[\frac{\partial}{\partial \sigma_{U}} \left(\frac{\partial T}{\partial \sigma_{U}} \right)_{S} \right]_{T; 0} \sigma_{m} \right\} \Delta \sigma \sin \omega t$$
$$- \frac{1}{4} \left[\frac{\partial^{2} T}{\partial \sigma_{U}^{2}} \right]_{S; 0} (\Delta \sigma)^{2} \cos 2\omega t \tag{8}$$

The response to an applied pressure $P = P_m + \Delta P \sin \omega t$ is similarly

$$T - T_{0} = \left\{ \left(\frac{\partial T}{\partial P} \right)_{S;0} + \left[\frac{\partial}{\partial P} \left(\frac{\partial T}{\partial P} \right)_{S} \right]_{T;0} P_{m} \right\} \Delta P \sin \omega t$$
$$- \frac{1}{4} \left[\frac{\partial^{2} T}{\partial P^{2}} \right]_{S;0} (\Delta P)^{2} \cos 2\omega t \tag{9}$$

In Eqs. (8) and (9) the small second-order terms in $\cos 2\omega t$ do not alter the amplitude ΔT of the cyclic change in T, since they raise the maximum and minimum temperatures by the same amount. To this approximation, therefore, the thermoelastic "constant" of Eq. (1) is independent of the amplitude of the fluctuations; and its dependence on the mean stress is given by a mixed isothermal/adiabatic derivative of T. On the other hand, the magnitude of the second harmonic response depends on the square of the amplitude $(\Delta \sigma)^2$ or $(\Delta P)^2$ as given by the purely adiabatic second derivative $\left[\frac{\partial^2 T}{\partial \sigma_{II}^2} \right]_S$ or $\left[\frac{\partial^2 T}{\partial P^2} \right]_S$.

The result of Wong et al. [5] for unidirectional stress is given by their Eq. (2.6), which may be written in the present notation as

$$\frac{C_{\eta}}{V} \left(\frac{T - T_0}{T_0} \right) = -\left(\alpha - \frac{1}{E^2} \frac{\partial E}{\partial T} \sigma_m \right) \Delta \sigma \sin \omega t - \frac{1}{4E^2} \frac{\partial E}{\partial T} (\Delta \sigma)^2 \cos 2\omega t$$
(10)

where C_{η} is the heat capacity at constant strain, V is the volume, α is the coefficient of linear expansion in the direction of the stress, and E is Young's modulus.⁵ Comparison of Eq. (10) with Eq. (8) shows that Wong et al. do not distinguish between the different kinds of second-order derivatives. For unidirectional stress their approximations are equivalent to taking

$$\left(\frac{\partial T}{\partial \sigma_U}\right)_{S;0} \approx -\alpha T V / C_\eta \tag{11}$$

and

$$\left[\frac{\partial}{\partial\sigma_{U}}\left(\frac{\partial T}{\partial\sigma_{U}}\right)_{S}\right]_{T;0} \approx \left[\frac{\partial^{2}T}{\partial\sigma_{U}^{2}}\right]_{S;0} \approx -\frac{TV}{C_{\eta}}\left[\frac{\partial}{\partial T}\left(\frac{1}{E}\right)\right]_{\sigma;0}$$
(12)

However, such approximations are unnecessary, because exact thermodynamic expressions for the various stress derivatives are obtainable. In the next section the general method is illustrated in detail by its simplest application, viz. to a solid under fluctuating hydrostatic pressure. Unidirectional stress is treated briefly in Section 4.

3. TEMPERATURE RESPONSE TO FLUCTUATING PRESSURE

3.1. Thermodynamic Expressions

Experimental quantities from which thermoelastic pressure effects can be derived are the volume V, the adiabatic compressibility χ_S (or bulk modulus B_S)

$$\chi_{S} = (1/B_{S}) = -(1/V)(\partial V/\partial P)_{S}$$
(13)

the coefficient of volumetric expansion β , and the heat capacity at constant pressure C_P , together with their temperature derivatives at constant

⁵ Wong et al. do not distinguish between E_s and E_T . The difference between them is small, because Young's modulus determines the response to a stress in which shear is the dominant component.

pressure; alternatively, C_P and V may be replaced by the specific heat per unit mass c_P and the density ρ , since they are needed only in the combination $C_P/V = \rho c_P$. The derivatives in Eq. (9) are then obtained from the following thermodynamic analysis.

A Maxwell relation,

$$(\partial T/\partial P)_{S} = (\partial V/\partial S)_{P} \tag{14}$$

gives immediately

$$\left[\frac{\partial T}{\partial P}\right]_{S} = \left[\frac{\partial V}{\partial T}\right]_{P} \left[\frac{\partial T}{\partial S}\right]_{P} = \frac{\beta VT}{C_{P}} = \gamma \chi_{S} T$$
(15)

where γ is the thermodynamic Grüneisen function defined by (see, e.g., Refs. 10 and 11)

$$\gamma \equiv \left[\frac{\partial P}{\partial (U/V)}\right]_{V} = -\left[\frac{\partial \ln T}{\partial \ln V}\right]_{S} = \frac{\beta V}{\chi_{S} C_{P}}$$
(16)

Equations (13) and (14) then give for the adiabatic second pressure derivative

$$\begin{bmatrix} \frac{\partial^2 T}{\partial P^2} \end{bmatrix}_{S} = \frac{\partial^2 V}{\partial P \partial S} = -\begin{bmatrix} \frac{\partial}{\partial S} (V\chi_S) \end{bmatrix}_{P}$$
$$= -\frac{T}{C_P} \begin{bmatrix} \frac{\partial}{\partial T} (V\chi_S) \end{bmatrix}_{P}$$
$$= -\frac{VT}{C_P} \left\{ \begin{bmatrix} \frac{\partial \chi_S}{\partial T} \end{bmatrix}_{P} + \beta \chi_S \right\}$$
(17)

$$= -\left(\beta VT\chi_S/C_P\right)(\delta_S + 1) \tag{18}$$

where δ_s is the adiabatic Anderson–Grüneisen function defined by Bassett et al. [12]:

$$\delta_{S} = -\left[\frac{\partial \ln B_{S}}{\partial \ln V}\right]_{P} = \left[\frac{\partial \ln \chi_{S}}{\partial \ln V}\right]_{P} = -\frac{1}{\beta B_{S}}\left[\frac{\partial B_{S}}{\partial T}\right]_{P}$$
(19)

The isothermal pressure derivative may then be obtained from the identity

$$\left[\frac{\partial}{\partial P}\left(\frac{\partial T}{\partial P}\right)_{S}\right]_{T} = \left[\frac{\partial^{2}T}{\partial P^{2}}\right]_{S} - \left[\frac{\partial}{\partial T}\left(\frac{\partial T}{\partial P}\right)_{S}\right]_{P}\left(\frac{\partial T}{\partial P}\right)_{S}$$
(20)

which with the aid of Eqs. (15) and (17) gives the derivative explicitly in terms of primary experimental quantities:

$$\begin{bmatrix} \frac{\partial}{\partial P} \left(\frac{\partial T}{\partial P} \right)_{S} \end{bmatrix}_{T} = -\frac{VT}{C_{P}} \left\{ \begin{bmatrix} \frac{\partial \chi_{S}}{\partial T} \end{bmatrix}_{P} + \beta \chi_{S} + \frac{V\beta}{C_{P}} \left(\beta + \beta^{2}T + T \begin{bmatrix} \frac{\partial \beta}{\partial T} \end{bmatrix}_{P} - \frac{\beta T}{C_{P}} \begin{bmatrix} \frac{\partial C_{P}}{\partial T} \end{bmatrix}_{P} \right) \right\}$$
(21)

In contrast, the method of Wong et al. gives for the second derivatives (cf. Eq. (12))

$$\left[\frac{\partial^2 T}{\partial P^2}\right]_{\mathcal{S}} \approx \left[\frac{\partial}{\partial P} \left(\frac{\partial T}{\partial P}\right)_{\mathcal{S}}\right]_{T} \approx -\frac{VT}{C_{V}} \left[\frac{\partial \chi}{\partial T}\right]_{P}$$
(22)

Equation (17) shows that it is the adiabatic compressibility whose isobaric temperature derivative is required, that the denominator should be C_P (rather than C_η or C_V), and that there is an additional term in $(\partial^2 T/\partial P^2)_S$. Equation (21) shows that there are further additional terms in $[(\partial/\partial P)(\partial T/\partial P)_S]_T$.

The results obtained in this subsection apply not only to isotropic material but also to any homogeneous material under hydrostatic pressure.

3.2. Pressure Derivative of the Thermoelastic Coefficient

For a cubic or isotropic material, the thermoelastic coefficient of Eq. (2) is given by

$$K = \frac{1}{3} \left(\frac{\partial \ln T}{\partial P} \right)_{S} = \frac{1}{3} \beta V / C_{P} = \frac{1}{3} \gamma \chi_{S}$$
(23)

Approximate thermodynamic expressions for its pressure derivative have been suggested by Ledbetter et al.:⁶

$$\frac{1}{K_0} \left(\frac{\partial K}{\partial P} \right) \approx -\frac{\delta}{B_0} \approx -\frac{1}{B_0} \left(\frac{dB_T}{dP} - 1 \right) \approx -\frac{1}{B_0} \left(\frac{dB_S}{dP} - 1 \right)$$
(24)

Like those of Wong et al., these expressions do not distinguish fully between adiabatic and isothermal processes. We have seen in Section 2 that it is the mixed second derivative of Eq. (21) that is relevant to the pressure

⁶ A correction factor of one third has been applied.

dependence of K. Using this derivative, and also by direct differentiation of the last of Eqs. (23) [13], exact expressions can be obtained in place of those of Eqs. (24):

$$\frac{1}{K} \left(\frac{\partial K}{\partial P} \right)_T = -\frac{\delta_S}{B_T} - \frac{1}{B_S} \left\{ 1 + \gamma + (\partial \gamma / \partial \ln T)_P \right\}$$
(25)

$$= -\frac{\delta_T}{B_T} - \frac{1}{B_S} \left\{ 1 - (VT/C_P)(\partial\beta/\partial T)_P \right\}$$
(26)

$$= -\frac{1}{B_{S}} \left(\left[\frac{\partial B_{S}}{\partial P} \right]_{T} + (1 + \beta \gamma T) q \right)$$
(27)

where B_T is the isothermal bulk modulus $B_S/(1 + \beta \gamma T)$, δ_T is the isothermal Anderson–Grüneisen function $(\partial \ln \chi_T/\partial \ln V)_P$ (see Ref. 12), and

$$q = (\partial \ln \gamma / \partial \ln V)_T = (V/\gamma)(\partial \gamma / \partial V)_T$$
(28)

sometimes called the second Grüneisen function.7

At high temperatures $(\partial \beta / \partial T)_P$ and $(\partial \gamma / \partial T)_P$ are usually fairly small, $\beta \gamma T$ and the difference between B_S and B_T seldom exceed 10%, and (less reliably) q is often about unity. Equations (25)–(27) thus suggest the following rough approximations as modifications of Eqs. (24):

$$\frac{1}{K} \left(\frac{\partial K}{\partial P} \right)_T \approx -\frac{\delta_S + 1 + \gamma}{B_S} \approx -\frac{\delta_T + 1}{B_S} \approx -\frac{(\partial B_S / \partial P)_T + 1}{B_S}$$
(29)

3.3. Experimental Magnitudes and Discussion

We have used Eqs. (15), (17), and (21) to calculate pressure derivatives of T for several of the materials considered by Wong et al. and Ledbetter et al., and also for two alkali halides. It is difficult to estimate error in the primary data, and different measurements often disagree, especially at room temperature where high and low temperature ranges meet. The values we have adopted are good enough to let us assess the relative importance of different terms in the thermodynamic expressions, but we have not attempted a critical assessment of all available data. We give only the room temperature values (Table I), although for all the materials except the titanium alloy we have calculated pressure derivatives and Kover a range of temperatures. Table II lists values for room temperature and one higher and one lower temperature, together with the quantity

⁷ At any point where the thermal expansion changes sign, β , γ and K are zero and δ_s and q infinite. Equation (18) is then indeterminate, although the equivalent Eq. (17) is still valid.

Material	χs	α	Cp	$\left(\frac{\partial \chi_S}{\partial \ln T}\right)_P$	$\left(\frac{\partial \ln \alpha}{\partial \ln T}\right)_P$	$\left(\frac{\partial \ln C_P}{\partial \ln T}\right)_P$
	(TPa ⁻ 1)	$(10^{-6} K^{-1})$	$(J\cdot kg^{-1}\cdot K^{-1})$	(TPa^{-1})		
NaCl	39.9	39.0	864	4.70	0.257	0.145
KCl	56.1	36.3	686	5.60	0.485	0.057
Al	13.1	16.7	906	0.924	0.179	0.154
Cu	7.16	16.7	386	0.378	0.181	0.156
Ti	9.33	8.30	520	0.290	0.322	0.176
Ti-6Al-4V	9.43	9.14	529	0.281	0.199	0.245

Table I. Experimental Data for Pressure Analysis

 $W2P = -(VT/C_P)(\partial \chi_S/\partial T)_P$. W2P is the first term in Eq. (17), and gives the value obtained by the method of Wong et al., except for the factor C_V/C_P which is close to unity. Table II shows that at all temperatures the mixed derivative is larger than the adiabatic derivative, typically by a factor of about 1.5, although less (about 1.25) for Ti and Ti-6Al-4V. Neither derivative is approximated closely by W2P; the adiabatic and mixed derivatives are greater by factors of about 1.3 and 1.8, respectively.

Material	Т	$\left(\frac{\partial T}{\partial P}\right)_{S}$	K	$\left(\frac{\partial^2 T}{\partial P^2}\right)_{S}$	$\left[\frac{\partial}{\partial P}\left(\frac{\partial T}{\partial P}\right)_{S}\right]_{T}$	W2P ^a
	(K)	$(K \cdot GPa^{-1})$	(TPa^{-1})	$(K \cdot GPa^{-2})$	$(K \cdot GPa^{-2})$	$(K\cdot GPa^{-2})$
NaCl	160	9.01	18.77	-1.50	-2.06	-1.15
NaCl	294	18.73	21.23	-3.30	-4.67	-2.56
NaCl	675	53.90	26.62	-11.8	-17.9	-9.22
KC1	160	12.12	25.24	-3.50	-4.53	-2.85
KC1	300	24.08	26.75	-5.46	-8.28	-4.11
KC1	550	53.03	32.14	-16.40	-23.59	-13.13
Al	160	3.52	7.32	-0.229	-0.294	-0.184
Al	300	6.12	6.80	-0.457	-0.587	-0.377
Al	550	16.68	10.11	-1.08	-1.49	-0.845
Cu	160	2.25	4.69	-0.065	-0.098	-0.050
Cu	295	4.28	4.84	-0.140	-0.205	-0.110
Cu	673	10.37	5.14	-0.368	-0.546	-0.287
Ti	223	2.34	3.49	-0.117	-0.139	-0.095
Ti	293	3.11	3.54	-0.153	-0.191	-0.124
Ti	673	8.00	3.96	-0.402	-0.507	-0.324
Ti-6Al-4V	295	3.46	3.91	-0.153	-0.192	-0.120

Table II. Calculated Pressure Derivatives

^{*a*} W2P is the approximation used by Ledbetter et al. [6]: $W2P = -(VT/C_P)[\partial \chi_S/\partial T]_P$.

Material	$\left(\frac{\partial B_S}{\partial P}\right)_T$	$\left(\frac{\partial \ln K}{\partial P}\right)_T$ (TPa^{-1})	$-\frac{\delta_{S}+1+\gamma}{B_{S}}$ (TPa ⁻¹)	$-\frac{\delta_T + 1}{B_S}$ (TPa^{-1})	$-\frac{(\partial B_S/\partial P)_T + 1}{B_S}$ (TPa ⁻¹)
NaCl	5.3	-249	-240	-254	-251
KC1	5.1	-344	-307	-368	-342
Al	4.9	-96	-95	-98	-78
Cu	5.5	-48	-47	-49	-47
Ti		-61	-60	-64	
Ti-6Al-4V	—	-55	-56	-57	

Table III. Modified Approximations for $(\partial \ln K / \partial P)_T$ at Room Temperature

Table III gives room temperature isothermal pressure derivatives of ln K, compared with the approximations of Eqs. (29). The approximations have errors of about 10% or less, except for Al, where the 20% error for the third approximation appears to stem from a high value of q. Similar calculations made at other temperatures showed that K and its isothermal pressure derivative increase fairly slowly with temperature, typically by about 10% every 100 K. The first two approximations of Eqs. (29) remained accurate to within about 10%, the first approximation being closest at low temperatures and the second at high temperatures. The third approximation was tested only at room temperature, because for other temperatures the values of $(\partial B_S/\partial P)_T$ were not readily available.

4. RESPONSE TO FLUCTUATING UNIDIRECTIONAL STRESS

4.1. Thermodynamic Expressions

The derivation of expressions for second-order stress derivatives is more complex than for pressure derivatives, mainly because there are no finite strain coordinates thermodynamically conjugate to elements of the Cauchy stress tensor $\sigma_{\alpha\beta}$. A rigorous analysis for orthorhombic symmetry is given elsewhere [9], which includes as a special case unidirectional stress σ_U in an isotropic material. This gives

$$\left(\frac{\partial T}{\partial \sigma_U}\right) = -\frac{1}{3} \left(\frac{\partial T}{\partial P}\right) = -\left(\frac{VT}{C_P}\right) \alpha \tag{30}$$

$$\left[\frac{\partial^2 T}{\partial \sigma_U^2}\right]_{S;0} = -\left(\frac{VT}{C_P}\right) \left[\left(\frac{\partial (1/E_S)}{\partial T}\right)_P - \alpha \left(\frac{1+4v_S}{E_S}\right)\right]$$
(31)

$$\begin{bmatrix} \frac{\partial}{\partial \sigma_{U}} \left(\frac{\partial T}{\partial \sigma_{U}} \right)_{S} \end{bmatrix}_{T;0} = \begin{bmatrix} \frac{\partial^{2} T}{\partial \sigma_{U}^{2}} \end{bmatrix}_{S;0} - \left(\frac{TV^{2} \alpha^{2}}{C_{P}^{2}} \right) \\ \times \begin{bmatrix} 1 + \beta T - \left(\frac{\partial \ln C_{P}}{\partial \ln T} \right)_{P} + \left(\frac{\partial \ln \beta}{\partial \ln T} \right)_{P} \end{bmatrix}$$
(32)

where E_s and v_s are, respectively, the adiabatic Young's modulus and Poisson's ratio. Comparing these with Wong's approximations of Eqs. (11) and (12), we see that C_{η} should be replaced by C_P , that the Young's modulus required is E_s , and that there are additional terms in the second derivatives which then differ from each other.

4.2. Experimental Magnitudes and Discussion

We have used Eqs. (31) and (32) to compute second-order unidirectional stress derivatives of T for some metals, including the alloy studied by Wong [5]. Table IV gives some results, together with E_s and its temperature derivative (other data are in Table I). The most obvious features of these results compared with those for hydrostatic pressure is that the additional terms reduce instead of enhancing the magnitudes given by the Wong approximation $W2U = -(VT/C_P)[\partial(1/E_S)/\partial T]_P$, and also that the difference between the adiabatic and mixed second derivatives is relatively much smaller than that between the analogous pressure derivatives. This can be explained by expressing σ_U as a combination of a strong shear stress σ_{SH} and a comparatively weak negative pressure. Up to the second order, in an isotropic material these components affect the temperature independently. Although the first-order shear derivative $(\partial T/\partial \sigma_{SH})_P$ is zero, the

Material	E_s^{-1} (TPa ⁻¹)	$\left(\frac{\partial (E_s^{-1})}{\partial \ln T}\right)_P$ (TPa ⁻¹)	$\left(\frac{\partial^2 T}{\partial \sigma_U^2}\right)_S$ (K · GPa ⁻²)	$\left[\frac{\partial}{\partial \sigma_U} \left(\frac{\partial T}{\partial \sigma_U}\right)_S\right]_T$ (K · GPa ⁻²)	$W2U^a$ (K · GPa ⁻²)
Al	14.3	2.44	-0.923 -0.200	-0.937	-0.993
Ti Ti-6Al-4V	8.68 9.00	1.55 1.18	-0.642 -0.481	-0.646 -0.485	-0.662 -0.505

Table IV. Calculated Stress Derivatives at Room Temperature

^{*a*} W2U is the approximation used by Wong et al. [5]: $W2U = -(VT/C_P)[\partial(1/E_S)/\partial T]_P$.

second derivatives are large and dominate the unidirectional stress derivatives. If σ_{SH} has strength equivalent to $\sigma_{23} = \sigma_{SH}$, then [9]

$$(\partial^2 T/\partial \sigma_{SH}^2)_S = (-VT/C_P) \{ [\partial(1/G)/\partial T]_P - \beta(1/G) \}$$
(33)

where $G = G_S = G_T$ is the rigidity modulus; moreover, there is no difference between the adiabatic and mixed second differentives because $(\partial T/\partial \sigma_{SH})_S = 0$. The second term of Eq. (33) is of opposite sign to the Wong approximation (given by the first term), reducing the magnitude. For unidirectional stress derivatives this is partially compensated by the additional terms in the small pressure contributions, which therefore lessen differences from the Wong approximation and also produce a small difference between the adiabatic and mixed derivatives. Corrections to W2U are particularly small for Ti and Ti-6Al-4V, which may explain why Wong et al. [5] obtained good agreement with their experimental results for unidirectional stress despite their neglect of terms important for other types of stress.

5. CONCLUSION

We have found that errors in earlier approximations for second-order thermoelastic effects in isotropic materials are substantial for compressive stress but much smaller for unidirectional stress. Elsewhere [9] we discuss (i) more complex stress fields in isotropic materials, including whether it is possible to deduce from temperature fluctuations the separate contributions of compressive and shear stress; and (ii) anisotropic materials.

ACKNOWLEDGMENT

We thank the referee for comments and suggestions. A. Padmaja thanks the Commonwealth Scholarship Commission U.K. for financial support.

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