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On the equilibrium transition temperature of thermoelastic martensitic transformations

Recently, the thermodynamics of thermoelastic martensitic transformations have been studied by several investigators [1–6]. Although it is well known that the M_s^\dagger temperature should always lie below the T_0 temperature, there still exists an uncertainty in the location of the A_f temperature relative to T_0 [7–10]. An exact knowledge of the location of A_f relative to T_0 would be necessary if one attempts to determine approximately T_0 by bracketing it between M_s and A_f . Tong and Wayman [7, 8] and Olson and Cohen [9, 10] have analysed the thermodynamics of the process of formation of a single isolated martensite plate at M_s and its complete reversion to the HTP at A_f : However, different conclusions have been reached about the location of A_f relative to T_0 . Tong and Wayman have assumed that the contribution of elastic strain energy to the total free energy difference between M and HTP is negligible at M_s and considered the internal frictional forces to be substantial. This necessarily led to the conclusion that $A_f > T_0$. They then proposed that T_0 can be approximated by:

$$T_0 = \frac{1}{2} [M_s + A_f].$$

However, the assumption of negligible elastic strain energy at M_s cannot be justified in view of the expected comparatively small chemical free energy difference.

In contrast, Olson and Cohen took into con-

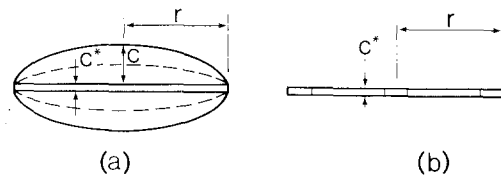


Figure 1 (a) Progressive thinning of an oblate spheroid of martensite with fixed radius during heating until a critical thickness C^* is attained. (b) Radial shrinkage of a plate of thickness C^* .

sideration the elastic strain energy and concluded that A_f could lie below T_0 ; therefore, the bracketing procedure proposed by Tong and Wayman cannot be generalized. They considered the case of an oblate spheroid of martensite having radius r and semithickness C , where $C \ll r$. (See Fig. 1). The total free energy difference (ΔG) accompanying formation of such martensite (in the absence of internal friction) can be written [11] as:

$$\Delta G(T) (\text{HTP} \rightarrow \text{M}) = \frac{4}{3} \pi r^2 C \Delta g_{\text{ch}} (\text{HTP} \rightarrow \text{M}) + \frac{4}{3} \pi r C^2 A + 2 \pi r^2 \sigma \quad (1)$$

where A is an elastic strain energy constant such that (AC/r) is an elastic strain energy per unit volume and σ is an interfacial energy per unit area. The conclusion that $A_f < T_0$ was derived from the condition $\partial \Delta G / \partial r = 0$ and $\partial \Delta G / \partial C = 0$. That is, the martensite becomes completely unstable when the net forces (chemical and non-chemical) acting upon it vanish [9, 10].

However, this condition is expected to be satisfied at any temperature where thermoelastic equilibrium between M and HTP can be estab-

† M = martensite; HTP = high temperature phase; M_s = temperature at which transformation to M starts during cooling; T_0 = temperature at which $\Delta g_{\text{ch}} (\text{M} \rightarrow \text{HTP}, \text{HTP} \rightarrow \text{M}) = 0$, where Δg_{ch} is the chemical free energy difference per unit volume; A_f = temperature at which reversion of M to HTP is completed during heating.

lished. Consider, for example that the heating process is interrupted at a temperature below the A_f and the temperature is held constant. The martensite plate with a fixed radius [9, 10] and a thickness characteristic of that temperature, remains in thermoelastic equilibrium with the HTP and no further thinning takes place until the temperature is raised. This requires the condition $\partial\Delta G/\partial r = 0$ and $\partial\Delta G/\partial C = 0$ to be satisfied.

In this note, the conditions that determine the A_f temperature relative to T_0 are examined and a simple method of bracketing T_0 is proposed. For perfect thermoelastic behaviour, the elastic strain and interfacial energies would be expected to totally assist the reversion of M to HTP during heating. Therefore, from Equation 1 the free energy of reversion can be written as:

$$\Delta G(T) (M \rightarrow \text{HTP}) = \frac{4}{3}\pi r^2 C \Delta g_{\text{ch}} (M \rightarrow \text{HTP}) - [\frac{4}{3}\pi r C^2 A + 2\pi r^2 \sigma] \quad (2)$$

Now, consider shrinkage of the martensite plate under a fixed radius [9, 10]. This is shown schematically in Fig. 1. As a critical thickness C^* is reached during heating, the plate shrinks radially until it completely disappears at the A_f [9, 10]. This state of unstable equilibrium requires the condition $(\partial^2 \Delta G/\partial r^2) \leq 0$ ($M \rightarrow \text{HTP}$) to be satisfied rather than $\partial\Delta G/\partial r = 0$ and $\partial\Delta G/\partial C = 0$. From Equation 2, this is satisfied when:

$$\Delta g_{\text{ch}} (M \rightarrow \text{HTP}) \leq 3\sigma/2C^* \quad (3)$$

Since C^* has a finite positive value and σ is positive, it follows from Equation 3 that the A_f temperature is reached while $\Delta g_{\text{ch}} (M \rightarrow \text{HTP})$ is still positive. Since $\Delta g_{\text{ch}} (M \rightarrow \text{HTP})$ can only be positive at temperatures below T_0 ($\Delta g_{\text{ch}}(T) (\text{HTP} \rightarrow M) = -\Delta g_{\text{ch}}(T) (M \rightarrow \text{HTP})$) it follows that for perfect thermoelastic behaviour $A_f < T_0$. If now the effect of internal frictional forces is introduced, such that the elastic strain and interfacial energies do not totally assist the reversion of martensite, the A_f is expected to shift to a higher temperature. Therefore, in general, the A_f temperature could lie below, above or even coincide with, the T_0 . In all cases, however, the driving force of reversion of martensite would be expected to be larger than that of its formation, due to the

assistance imparted by elastic strain energy and energy associated with reversible defects (e.g. twins). Therefore, even if the A_f temperature is shifted to a temperature higher than T_0 , the interval $A_f - T_0$ would be expected to be smaller than the interval $T_0 - M_s$.

The above effects are reflected in the asymmetry of experimentally obtained thermal hysteresis loops [12]. A typical thermal hysteresis loop is shown schematically in Fig. 2. If the forces opposing formation of martensite are exactly the same as those opposing its reversion, a perfectly symmetrical loop would be obtained. From the above argument the following simple method of bracketing T_0 using experimentally obtained thermal hysteresis loops is proposed.

A line is drawn parallel to line ba from point C (Fig. 2). The end point (d') of this line defines a temperature A'_f at which martensite becomes completely unstable if the forces opposing its reversion to HTP were the same as those opposing its formation. In this case, the interval $A'_f - T_0$ equals the interval $T_0 - M_s$. T_0 can then be determined to a good approximation from:

$$T_0 = \frac{1}{2}[M_s + A'_f] = M_s + \frac{1}{2}[A_s - M_f] \quad (4)$$

where M_s , A_s and M_f are all experimentally measurable temperatures. This would lead to an approximate T_0 temperature that lies above the M_s and could lie below, above or even coincide with the A_f temperature consistent with the above thermodynamic arguments.

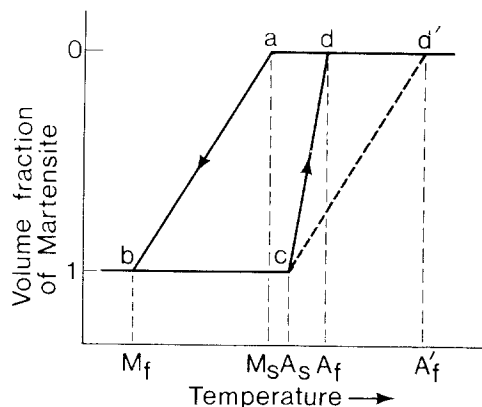


Figure 2 Thermal hysteresis loop. M_f is the temperature at which transformation to martensite finishes and A_s is the temperature at which the reverse transformation starts. For definition of M_s , A_f and A'_f see the text.

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Welding of magnesium oxide single crystals by H_3PO_4

Bicrystals of magnesium oxides have been fabricated by hot pressing [1, 2] from single crystals or by heating at very high temperatures [3]. For some purposes, however, it is useful simply to weld crystals with an appropriate binder. This note describes the welding of magnesium oxide single crystals by orthophosphoric acid.

Sheets approximately 2mm thick were cleaved on {100} faces from crystals purchased from the Tateho company. H_3PO_4 solution at 120°C was

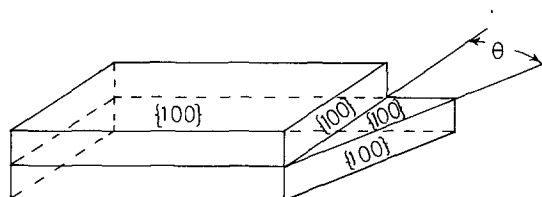


Figure 1 Schematic diagram of welding samples of magnesium oxide single crystals.

applied with a brush made of glass fibres to crystals heated to the same temperature. After cooling the crystals to room temperature, they were bound with Pt wire, as shown in Fig. 1. The values of θ vary from 5° to 45°. The crystals were

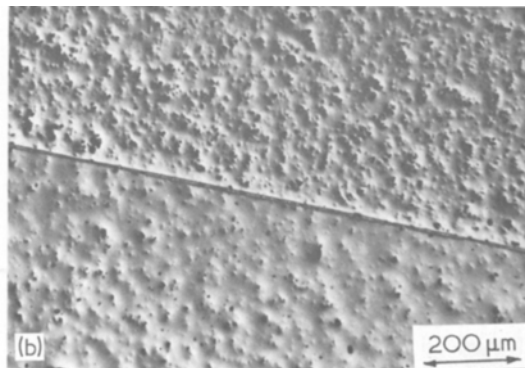
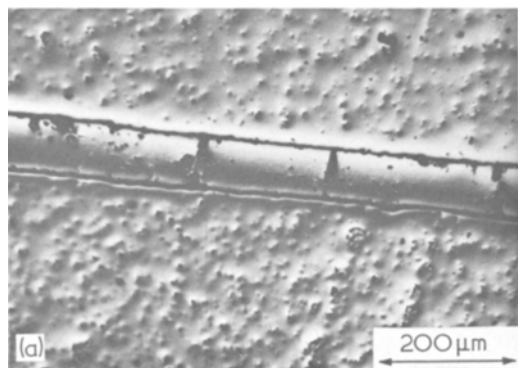


Figure 2 Photomicrographs of polished surface in a sample heated at 1400°C for 20 h in air. θ is 20°.