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The equilibrium of martensite shear stress at phase transitions in TiNi-based alloy

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ABSTRACT

Thermoelastic martensitic transformations play a fundamental role in the shape memory effect and related phenomena. Owing to their unique crystallographic and thermomechanical behaviour, martensitic transformations have generated considerable research in the areas of crystallography, thermodynamics and mechanical behaviour. In the area of thermodynamics a theoretical approach is now added which provides the basis for thermoelastic behaviour through consideration of the Gibbs energy change. In this paper, the interrelation of internal elastic stresses and martensite shear stresses in phase transitions has been defined. A thermoelastic stress equilibrium equation for a wide range of martensitic transformation temperatures has been presented. On the basis of the calculations made, an estimation of dislocation defects formation energy for the TiNi-based alloy has been made. For TiNi-based composition made of TN-10 brand alloy, commercially produced for medical goals, the energy of vacancy formation is about 0.06 kcal/mol. The study and calculations are shown to make clear, using a new approach, the considering of phase transitions in terms of external and internal stresses. Copyright © 2015 VBRI Press.

Keywords: martensite transition; equilibrium equation; TiNi-based alloy; Gibbs energy change.



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His current research interests are (i) Phase transitions in solids, (ii) Shape memory alloys, (iii) Martensite transitions in TiNi-based alloys, and (iv) High level studies in wide range of porous and porousless TiNi-based medical implants.



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TiNi-based alloys.

Introduction

The term "martensite transition" (martensite transformation) was originally introduced to characterize the processes of hardening during steels quenching. Currently, the term has a broader meaning. Martensite transformations include all diffusionless cooperative phase transitions in solids. Modern ideas about the regular nature of lattice restructuring at martensite transformations – the majority of atoms before and after the transition have the same "neighbors" – suggests the shear nature of changes in the lattice shape of the transformed area in a solid [1]. A shear (a change in shape) is a result of the interface movement and can be caused by change in temperature (T), pressure (p), strain (ϵ) and entropy (s). When cooling or loading the interface moves in one direction (martensite transformation), when heating or unloading it moves the reverse direction (austenite transformation), leading to a reverse shear and shape recovering. Experimentally, the surface relief appears and disappears on a solid's polished surface [2].

At martensite transformation, the new phase areas appear as crystals, which growth may stop when the interface is no longer coherent or the removing of the accumulated stresses by plastic flow happens. Simultaneously, the transition involves many interrelated areas (crystals) of the product phase, which interaction is in constant evolution and could be determined by internal

stresses and the shear of the produced area, by the nature of heat release absorption during phase transitions [3].

TiNi-based alloys are increasingly being used in medical applications because of their ability to survive large loads at a constant stress without permanent plastic strain [3]. Recently, medical design engineers are also interested in various shapes and forms of the material for use in components for new medical goals, e.g. surgical technologies [4]. For these engineers, it's critically important to understand and characterize the properties of the material as well as to predict the criteria of stress-strain dependence and dynamic behavior. However, the previous research work [5] conducted on the investigating the stress-induced martensitic transformation as energy-dissipative processes, i.e. hysteretic between the forward and reverse processes in TiNi-based alloys and to draw general rules governing the hysteretic behavior of these alloys, was preliminary and needed further study. Moreover, only limited research works on the fundamental mechanism of deformation behavior of TiNi-based alloys in terms of external and internal stresses have been reported in the open literatures [6]. The objective of the present work is to continue a moving from theoretical consideration to practical aspect and to explore, using the Gibbs energy change, the martensite transformation in TiNi-based alloys in terms of external and internal stresses.

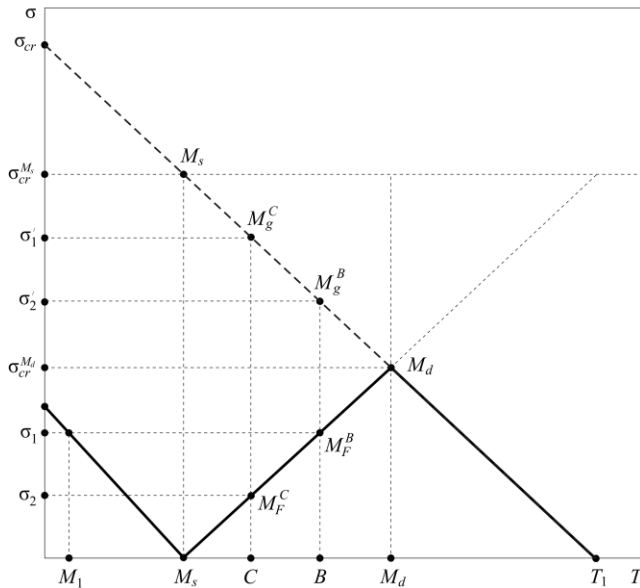


Fig. 1. Temperature dependence of martensite shear stress and yield strength of alloys showing martensite transformation.

Theoretical analysis

Main features of solids' macroscopic behavior, where the martensite phase transition takes place, are described by the thermodynamic equilibrium equation, which establishes the relationship between the functions of the state in a solid: temperature (T), pressure (p), volume (V) and entropy (s).

Generally, during phase transitions, the thermoelastic equilibrium equation may be represented as [7]:

$$\Delta G^{A \rightarrow M} = \Delta G^{MT} + \Delta G^{elast} = 0 \quad (1)$$

Where, $\Delta G^{A \rightarrow M}$ is Gibbs energy change (Gibbs functional) at the transition from the parent phase (the A phase), to the produced one (the M phase); ΔG^{MT} is Gibbs energy change associated with the martensite transformation (MT); ΔG^{elast} is Gibbs energy change associated with a change of elastic energy at the transition from the A to the M phase (when the first dislocations appear).

In the general case, equation (1) is satisfied throughout the range of temperatures both in the A and the M phases, including the double-phase state temperature area.

Analyzing the temperature dependence of martensite shear stress (within $M_1 \div M_d$ range) on Fig. 1 and the temperature dependence of yield strength (within $M_d \div T_1$ range), one can estimate the level of ΔG^{MT} and ΔG^{elast} .

The greatest interest for the thermoelastic equilibrium equation analysis is the M_d point, which is the maximum temperature when the martensite phase transition under the stress σ_{cr} occurs. But the temperature M_d is, at the same time, the minimum temperature when applying the critical stress σ_{cr} first dislocations appear, i.e. the plastic strain takes place.

Let's consider Gibbs energy change ΔG^{MT} ($\Delta G^{MT} = G_F^A - G_F^M$) for the temperature range $M_s \div M_d$ under conditions of independent variables of temperature and pressure (T and σ).

For the parent phase (the A phase), Gibbs energy change G^A under conditions of the phase transition in a differential form [8, 9] can be represented as the following equation:

$$dG_F^A = -S_F^A \cdot dT + V_F^A \cdot dp. \quad (2)$$

For the martensite phase (the M phase), at the phase transition, differential record of Gibbs function change will look like:

$$dG_F^M = -S_F^M \cdot dT + V_F^M \cdot dp. \quad (3)$$

Under the conditions of phases equilibrium

$$dG_F^A \approx dG_F^M,$$

Then,

$$-S_F^A dT + V_F^A dp \approx -S_F^M dT + V_F^M dp$$

or

$$(V_F^A - V_F^M) dp = +(S_F^A - S_F^M) dT,$$

i.e.

$$dp_F = \frac{\Delta S_F^{A \rightarrow M}}{\Delta V_F^{A \rightarrow M}} dT. \quad (4)$$

At constant pressure in both phases

$$\Delta S = \frac{\Delta H_F^M}{T},$$

Where, ΔH_F^M is the enthalpy of a transition from the A to the M phase; $T \approx T_0$ corresponds to the equilibrium temperature.

Formula (1) becomes:

$$dp_F = \frac{\Delta H_F^{A \rightarrow M}}{T_0 \cdot \Delta V_F^{A \rightarrow M}} \cdot dT .$$

For solids the pressure change Δp corresponds to the stress change $\Delta \sigma$, and the change in volume ΔV corresponds to the change of deformation $\Delta \epsilon$, therefore

$$d\sigma_F = \frac{\Delta H_F^{A \rightarrow M}}{T_0 \cdot \Delta \epsilon_F^{A \rightarrow M}} \cdot dT . \quad (5)$$

Temperature T_0 implicitly corresponds to the temperature M_s of phase equilibrium under conditions when no load applied.

Equation (5) describes the set of points of the line $M_1 \div M_d$ on the temperature dependence of martensitic shear stress (**Fig. 1**). Specifically for point M_d , equation (5) in the integral form will look like:

$$\Delta \sigma_{Fcr}^{Md} = \frac{\Delta H_F^{A \rightarrow M}}{M_s \cdot \Delta \epsilon_{max}^{A \rightarrow M}} \cdot \Delta T ,$$

Where: $\Delta \sigma_{Fcr}^{Md} = \sigma_{Fcr}^{Md} - 0 = \sigma_{Fcr}^{Md}$, $\Delta T = M_d - M_s$.

Thus,

$$\Delta \sigma_{Fcr}^{Md} = \frac{\Delta H_F^{A \rightarrow M}}{M_s \cdot \Delta \epsilon_{max}^{A \rightarrow M}} (M_d - M_s) . \quad (6)$$

Critical stress σ_{Fcr}^{Md} of formula (6) corresponds at M_d temperature to maximum stress induced of martensite phase under load.

In the temperature range $M_d \div T_1$ under the load no phase transition occurs. Deformation in this temperature range is carried out by plastic shear, i.e. critical stress on line $M_d \div T_1$ (**Fig. 1**) corresponds to the internal stress and critical stresses of dislocations occurrence. Temperature M_d characterizes the maximum level of stresses σ_{cr}^M of dislocations occurrence at a temperature near M_d .

Using Gibbs functional we can calculate the stress at which dislocations appear, and calculate the energy of dislocations formation for the plot $M_d \div T_1$ as well.

When a load is applied, Gibbs energy change in the transition from the A to the M phase, caused by overcoming internal stresses and formation of dislocations at the area $T_1 \div M_d$ (**Fig. 1**) can be represented as:

$$\Delta G^{elast} = G_g^A - G_g^M , \quad (7)$$

Where, G_g^A – is Gibbs energy corresponding to the A phase before stress induced dislocations appearing; G_g^M – is Gibbs energy corresponding to the M phase at the moment stress induced dislocations appearing.

In differential form, changes of the energy states of G_g^A and G_g^M can be represented as:

$$dG_g^A = -S_g^A dT + V_g^A dp ,$$

$$dG_g^M = -S_g^M dT + V_g^M dp .$$

Assuming that at the boundary conditions $dG_g^A \approx dG_g^M$, then

$$-S_g^A dT + V_g^A dp = -S_g^M dT + V_g^M dp ,$$

or

$$(V_g^A - V_g^M) dp = (S_g^A - S_g^M) dT ,$$

i.e.

$$dp = \frac{\Delta S_g^{A \rightarrow M}}{\Delta V_g^{A \rightarrow M}} dT . \quad (8)$$

When the pressure is the same both in the A and the M phase

$$\Delta S_g^{A \rightarrow M} = \frac{\Delta H_g^{A \rightarrow M}}{T_0} ,$$

Where, $\Delta H_g^{A \rightarrow M}$ – is enthalpy of transition from the A to the M phase; T_0 – corresponds to the equilibrium temperature.

Formula (8) will look in the following way:

$$dp = \frac{\Delta H_g^{A \rightarrow M}}{T_0 \Delta V_g^{A \rightarrow M}} \cdot dT . \quad (9)$$

As for solids, $\Delta p = \Delta \sigma$, and ΔV – corresponds to $\Delta \epsilon_{max}$, equation (9) can be represented as

$$d\sigma = \frac{\Delta H_g^{A \rightarrow M}}{T_0 \Delta \epsilon_g^{A \rightarrow M}} dT , \quad (10)$$

Equation (10) describes the set of points of the line $T_1 \div M_d$ on the temperature dependence of dislocations occurrence stresses (**Fig. 1**).

Specifically for point M_d , equation (10) in the integral form will look like:

$$\Delta\sigma_{g_{cr}}^{Md} = \frac{\Delta H_g^{A \rightarrow M}}{T_1 \cdot \Delta \varepsilon_g^{A \rightarrow M}} \cdot \Delta T,$$

Where: $\Delta\sigma_{g_{cr}}^{Md} = \sigma_{cr}^{Md} - 0 = \sigma_{g_{cr}}^{Md}$; $\Delta T = M_d - T_1$.

Thus

$$\sigma_{g_{cr}}^{Md} = \frac{\Delta H_g^{A \rightarrow M}}{T_1 \cdot \Delta \varepsilon_g^{A \rightarrow M}} (M_d - T_1). \quad (11)$$

Critical stress $\sigma_{g_{cr}}^{Md}$ of formula (11) corresponds at M_d temperature to maximum level of stresses of dislocation defects occurrence without participation of the M phase under load.

Based on equations (6) and (11) and analyzing the **Fig. 1**, the following entry can be presented:

$$\sigma_{cr}^{Md} = \sigma_{F_{cr}}^{Md} = \sigma_{g_{cr}}^{Md},$$

i.e.,

$$\begin{aligned} \sigma_{cr}^{Md} &= \frac{\Delta H_F^{A \rightarrow M}}{M_S \Delta \varepsilon_{F_{max}}^{A \rightarrow M}} (M_d - M_S) = \\ &- \frac{\Delta H_g^{A \rightarrow M}}{T_1 \Delta \varepsilon_{g_{max}}^{A \rightarrow M}} (T_1 - M_d) = 0, \end{aligned} \quad (12)$$

or

$$\begin{aligned} \sigma_{cr}^{Md} &= \frac{\Delta H_F^{A \rightarrow M}}{M_S \Delta \varepsilon_{F_{max}}^{A \rightarrow M}} (M_d - M_S) + \\ &\frac{\Delta H_g^{A \rightarrow M}}{T_1 \Delta \varepsilon_{g_{max}}^{A \rightarrow M}} (T_1 - M_d) = 0, \end{aligned} \quad (13)$$

Where,

$$\left| \sigma_{F_{cr}}^{Md} \right| = \left| \sigma_{g_{cr}}^{Md} \right|.$$

Equation (13) is the equation of thermoelastic stresses equilibrium in point M_d in **Fig. 1** when the stresses caused by martensite phase transition are balanced by elastic stresses at this point.

But this equation also evidences the fact that the martensite transition can take place without load applied in the event when contribution of elastic stresses in equation (13) corresponds to the value σ_{cr}^{Ms} (see **Fig. 1**), i.e. when $\sigma_{cr}^{Ms} = 2\sigma_{g_{cr}}^{Md}$.

Equation (13) allows to perform a very important calculation that will estimate $\Delta H_g^{A \rightarrow M}$ – the latent energy of dislocations occurrence, as the rest values in equation (13) can be determined from experimental data.

Thus,

$$\frac{\Delta H_F^{A \rightarrow M}}{M_S \Delta \varepsilon_{F_{max}}^{A \rightarrow M}} (M_d - M_S) = \frac{\Delta H_g^{A \rightarrow M}}{T_1 \Delta \varepsilon_{g_{max}}^{A \rightarrow M}} (M_d - T_1) \quad (14)$$

Calculation

For TiNi-based composition made of TH-10 brand alloy commercially produced [3, 10, 11]

$$\Delta H_F^{A \rightarrow M} \approx 2.2 \text{ kcal/mol};$$

$$M_S \approx 300 \text{ K};$$

$$\varepsilon_{F_{max}}^{A \rightarrow M} \approx 10\% = 0.1;$$

$$M_d \approx 600 \text{ K};$$

$$T_1 \approx 900 \text{ K};$$

$$\varepsilon_{g_{max}}^{A \rightarrow M} \approx 0.1\% = 0.001;$$

$$\begin{aligned} \Delta H_g^{A \rightarrow M} &= \frac{\Delta H_F^{A \rightarrow M}}{M_S \Delta \varepsilon_{F_{max}}^{A \rightarrow M}} \frac{(M_d - M_S) \cdot T_1 \Delta \varepsilon_{g_{max}}^{A \rightarrow M}}{(M_d - T_1)}; \\ \Delta H_g^{A \rightarrow M} &= -\Delta H_F^{A \rightarrow M} \frac{300 \text{ K} \cdot 900 \text{ K} \cdot 0.001}{300 \text{ K} \cdot 0.1 \cdot 300 \text{ K}}; \end{aligned} \quad (15)$$

$$\Delta H_g^{A \rightarrow M} = -\Delta H_F^{A \rightarrow M} \cdot 0.03;$$

i.e.

$$\Delta H_g^{A \rightarrow M} = 0.03 \cdot \Delta H_F^{A \rightarrow M};$$

as $H_F^{A \rightarrow M} \approx 2.2 \text{ kcal/mol}$,

Then $\Delta H_g^{A \rightarrow M} \approx 0.03 \cdot 2.2 \text{ kcal/mol}$,

$$\Delta H_g^{A \rightarrow M} \approx 0.066 \text{ kcal/mol}. \quad (16)$$

Therefore, considering that in equation (15) the minus sign evidences that vacancies formation goes with heat absorption, the energy of vacancy formation is about 0.06 kcal/mol.

Summary

Gibbs potentials thermodynamic equilibrium equation (1) and thermoelastic stresses equilibrium equation derived in this paper establishes a relationship of internal elastic stresses and external phase stresses responsible for martensite transformations in solids.

Temperature M_d is a critical temperature in relation to internal elastic stresses and external stresses, which are balanced and in accordance with the equilibrium thermoelastic equation create local stresses, which correspond to the sum of the absolute stresses $\left| \sigma_{F_{cr}}^{Md} \right| + \left| \sigma_{g_{cr}}^{Md} \right|$.

Temperature M_S is a critical temperature at which elastic stress reaches also values that correspond to the absolute value $\left| \sigma_{F_{cr}}^{Md} \right| + \left| \sigma_{g_{cr}}^{Md} \right|$, and the martensite transition occurs spontaneously without external load applied.

Throughout the temperature range $M_s \div M_d$ the condition of thermoelastic equilibrium of stresses is fulfilled, i.e. maintaining the constancy of stresses in the critical points, for example at temperatures C and B corresponding to M_F^C and M_g^C , M_F^B and M_g^B points:

$$|\sigma_1| + |\sigma'_1| = |\sigma_2| + |\sigma'_2| .$$

This also results in the following relation

$$|\sigma_{cr}^{Ms}| = 2|\sigma_{cr}^{Md}| .$$

The above study and calculations are shown to make clear, using a new approach, the considering of phase transitions in terms of external and internal stresses. Of particular importance to thermoelastic behaviour is the change in Gibbs' energy accompanying the transformation and the frictional work required to propagate the martensite-parent phase interface during the transformation.

A general methodology of complex considering and understanding of the martensite transformation is necessary to obtain the reliable knowledge on TiNi-based alloys studying. The procedure must define the paradigm and approaches to explore, analyze, and combine data acquired for the further design, processing and control best adapted to the SMA developed application. If the basis of the procedure is correctly set, new devices for their use in medicine or industries can successfully be designed and manufactured.

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