

IMPROVEMENT OF THE O-P THERMODYNAMIC MODEL OF THERMOELASTIC MARTENSITIC TRANSFORMATION^①

Yang, Guanjun[†] * Hao, Shiming^{*}

[†] Northwest Institute for Nonferrous Metal Research, Baoji 721014

* Northeastern University, Shenyang 110006

ABSTRACT Based on analysis on the O-P thermodynamic model, raised by Ortin and Planes, of thermal measurements in thermoelastic martensitic transformation, the authors have pointed out shortcomings of the model, and proposed amendments. On the basis of new assumptions made by the authors, the equation of the latent heat of the transformation is derived by application of the first and second thermodynamic principles to a complete cycle, which can be used to separate the latent heat of the transformation from calorimetric data.

Key words: thermoelastic martensitic transformation thermodynamic model calorimetric experiment

1 INTRODUCTION

Since the beginning of 1950s, thermoelastic martensitic transformation have received considerable attention because the thermoelastic character of the growth and reversion of the martensite phase is generally acknowledged to be responsible for the interesting mechanical features of pseudoelasticity and shape memory effect, as reviewed by Delaey *et al*^[1]. Among the different alloy systems displaying this effect, Ti-Ni, Cu-Zn-Al, Cu-Al-Ni and Au-Cd are the best studied.

The martensitic transformation is a first-order transition in the solid state. Consequently, there is coexistence of the two phases in the transformation region and an associated latent heat of transformation. So far, the latent heat of thermoelastic martensitic transformation cannot be determined directly, but it can be separated from the heat measured by the calorimeter. In a calorimetric run of a thermally-induced thermoelastic transformation the heat measured by the calorimeter is the sum of (i) the latent heat of transformation, (ii) the elastic strain energy, and (iii) the frictional work.

The latent heat of transformation arises from the difference in Gibbs free energy between austenite and martensite, and acts as a driving force promoting the phase with lower energy at each temperature. Both the elastic strain energy and the frictional work belong to non-chemical forces. The former is the need to accommodate the transformational shape and volume changes, which opposes the forward transformation and promotes the reverse one. The latter is the energy dissipated in the specimen as internal work during the transformation. The internal work is mainly devoted to overcome frictional barriers opposing interfacial motion, either during growth or during shrinkage of the martensite plates. This contribution represents the irreversible part of the non-chemical energies and is responsible for the thermal hysteresis observed in many thermoelastic transformations.

The latent heat of transformation, elastic strain energy and frictional work are measured at the same time and consequently it is not correct (although it is often done) to equate the latent

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heat with the heat measured in the transformation. This fact has been earlier recognized by Olson and Cohen^[2] who indicate that separation of chemical and non-chemical contributions in thermodynamics of thermoelastic martensites requires independent measurement of one term or the other. Since this idea was stated, several works^[3-7] have appeared attempting to separate the different contributions from the heat measured in the transformation. Recently, Ortin and Planes^[8] have analyzed, from the thermodynamic viewpoint, the information given by calorimetric experiments in thermoelastic martensitic transformation, and put forward a thermodynamic model (O-P thermodynamic model) to separate the different contributions from the heat measured by the calorimeter. However, the O-P model have some deficiencies which must be improved. The attempt of this paper is to improve the O-P thermodynamic model, based on analysis on the model.

2 THE SYNOPSIS ON THE O-P MODEL

2.1 Symbols

Q_M : the absolute value of the total heat measured in a forward transformation.

Q_A : the absolute value of the total heat measured in a reverse transformation.

ΔS_M : the entropy change of the specimen in a forward transformation.

ΔS_A : the entropy change of the specimen in a reverse transformation.

ΔH_{ch} : the latent heat of transformation.

ΔH_{el} : the elastic strain energy.

E_{fr} : the frictional work.

C_p^M : the heat capacity of the martensite phase.

C_p^A : the heat capacity of the austenite phase.

2.2 Basic Assumptions

In order to separate the different contributions from Q_M and Q_A , four basic assumptions are made by Ortin and Planes as follows.

Assumption 1: The sample recovers its original thermodynamic state at A_i after a complete transformation cycle which starts at A_i , includes cooling down to M_f and heating up again to A_i , is finished. Writing this assumption explicitly

$$\oint dU = 0 \quad (1)$$

$$\oint dS = 0 \quad (2)$$

Assumption 2: Ortin and Planes introduce the concept of thermoelastic equilibrium through what they call "the entropy argument", which is that the condition of thermoelastic equilibrium is equivalent to a null change in the entropy of the universe. This assumption can be expressed

$$-\Delta S_M = \int_{M_i}^{M_f} \frac{dQ_M}{T} \quad (3)$$

$$\Delta S_A = \int_{A_i}^{A_f} \frac{dQ_A}{T} \quad (4)$$

Assumptions 3: The heat capacity of specimen is assumed to be independent of temperature.

Assumption 4: Q_M and Q_A denote the absolute values of the total heat enclosed between the thermal curves and the horizontal base-line given by a null thermal power, between the extreme temperatures M_f and A_i , respectively.

2.3 Basic Method to Separate Q_M and Q_A

They separate the different contributions from Q_M and Q_A by comparing the change in internal energy U and entropy S of the specimen, on going from A_i and M_i following the three different paths, represented in Fig. 1, joining the initial and final state of the specimen:

- (1) is the actual path of the transformation,
- (2) is a reversible path without frictional work, and
- (3) is a reversible path without frictional and without elastic strain contributions, and hence proceeding isothermally at the equilibrium temperature T_0 .

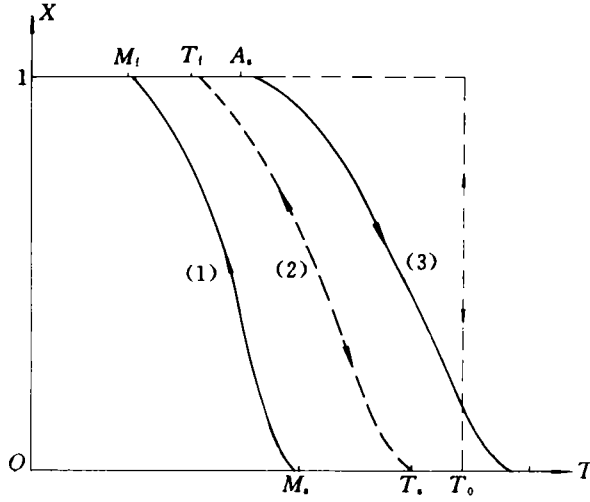


Fig. 1 Hysteresis cycle of the martensitic transformation in the volume fraction of martensite(X) vs temperature(T) coordinates, and three alternative paths for the forward and reverse transformations joining the same initial and final states

2.4 Main Equation

For the forward transformation, the heat measured is given by

$$-Q_M = -\Delta H_{ch}^{P \rightarrow M} + \Delta H_{el}^{P \rightarrow M} + E_{fr}^{P \rightarrow M} \quad (5)$$

where

$$\begin{aligned} \Delta H_{ch}^{P \rightarrow M} &= T_0 \left[\int_{A_i}^{M_i} \frac{1}{T} dQ_M + C_p^A \ln \frac{T_0}{A_i} + C_p^M \ln \frac{M_i}{T_0} \right] \\ &\quad - C_p^A (T_0 - A_i) - C_p^M (M_i - T_0) \end{aligned} \quad (6)$$

$$\Delta H_{el}^{P \rightarrow M} = -Q_M + \Delta H_{ch}^{P \rightarrow M} - E_{fr}^{P \rightarrow M} \quad (7)$$

For the reverse transformation, the heat measured is given by

$$Q_A = \Delta H_{ch}^{M \rightarrow P} - \Delta H_{el}^{M \rightarrow P} + E_{fr}^{M \rightarrow P} \quad (8)$$

where

$$\begin{aligned} \Delta H_{ch}^{M \rightarrow P} &= T_0 \left[\int_{M_i}^{A_i} \frac{1}{T} dQ_A - C_p^M \ln \frac{T_0}{M_i} - C_p^A \ln \frac{A_i}{T_0} \right] \\ &\quad + C_p^M (T_0 - M_i) + C_p^A (A_i - T_0) \end{aligned} \quad (9)$$

Moreover

$$E_{fr}^{P \rightarrow M} + E_{fr}^{M \rightarrow P} = Q_A - Q_M \quad (10)$$

3 MAIN PROBLEMS IN THE O-P MODEL

It should be pointed out that the O-P thermodynamic model is a successful thermodynamic model in the thermodynamic theory of thermoelastic martensitic transformation. By means of this model, the latent heat of transformation, elastic strain energy and frictional work can be separated from the calorimetric data. As other thermodynamic models^[3-7], however, the O-P model have some shortcomings to revise. We hold that among basic assumptions in the O-P model assumptions 3 and 4 do not coincide with the actual conditions. Moreover, internal energy U in assumption 1 should be replaced by enthalpy H , so as to tally with following treatment.

First, we discuss assumption 3. It is clear that establishing of this assumption is to simplify the treatment. However, it is well known that the heat capacity of solid is closely dependent of temperature, except temperature of solid is more higher than the characteristic temperature. It is obvious that this assumption is incorrect, especially for low temperature. Second, according to assumption 4, the heats measured, Q_M and Q_A , include at the same time the contributions due to the transformation itself and the contributions due to the change in temperature of the specimen in the forward and reverse transformations, respectively. From thermal measurement, however, Q_M and Q_A should be the energies enclosed between the calorimetric curves and the base-line, so assumption 4 does not coincide with the common principle that in a calorimetric run of a thermally-induced thermoelastic transformation the heat measured by the calorimeter is the sum of the latent heat of transformation, elastic strain energy and frictional work. Therefore, we revise assumptions 1, 3 and 4, and re-separate the different contributions from Q_M and Q_A .

4 THERMODYNAMIC ANALYSIS OF CALORIMETRIC CURVES

As we are dealing with calorimetric curves, let us discuss first the amendments for assumptions 3 and 4. It is well known that the heat capacity of the specimen is closely dependent of temperature, and the heat capacity *vs* temperature curve can be measured by the adiabatic calorimeter^[9]. During the transformation the heat capacity of the sample should be the mixed one of the austenite and martensite, and let C_p^{AM} and C_p^{MA} denote the mixed heat capacity in the forward and reverse transformations, respectively. Moreover, when transformations take place along path (3), as shown in Fig. 1, the heat capacity of the austenite and martensite can be obtained by extrapolating C_p *vs* T curves measured by the adiabatic calorimeter to the equilibrium temperature T_0 . For assumption 4, we will recover its original meaning. As shown in Fig. 2, we define $-Q_M$ and Q_A (heats measured in the calorimetric run) as the energies enclosed between the thermal curves and the base-line.

(i) The condition $\oint dH = 0$ gives

$$\begin{aligned} \int_{A_i}^{M_s} C_p^A(T) dT + \int_{M_s}^{M_i} C_p^{AM}(T) dT - Q_M - E_{tr}^{P \rightarrow M} + \int_{M_i}^{A_s} C_p^M(T) dT \\ + Q_A - E_{tr}^{M \rightarrow P} + \int_{A_s}^{A_i} C_p^{MA}(T) dT = 0 \end{aligned} \quad (12)$$

(ii) The condition $\oint dS = 0$ gives

$$\begin{aligned} \int_{A_i}^{M_s} \frac{C_p^A(T)}{T} dT + \int_{M_s}^{M_i} \frac{C_p^{AM}(T)}{T} dT - \Delta S_M + \int_{M_i}^{A_s} \frac{C_p^M(T)}{T} dT \\ + \int_{A_s}^{A_i} \frac{C_p^{MA}(T)}{T} dT + \Delta S_A = 0 \end{aligned} \quad (13)$$

Our next objective is to separate the different contributions from Q_M and Q_A . To do this, we

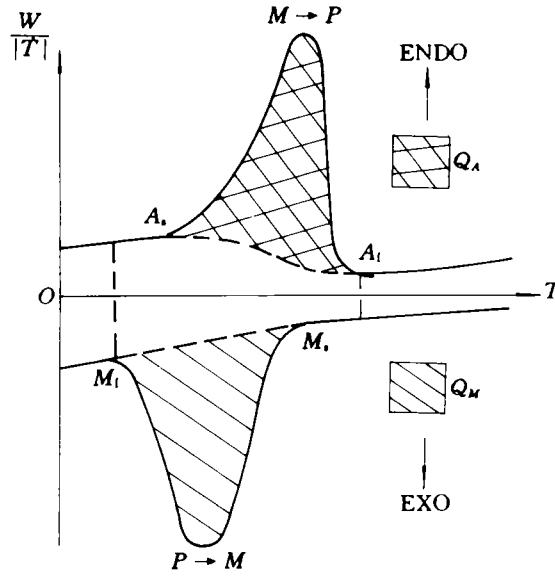


Fig. 2 Schematic representation of the calorimetric curves corresponding to a forward ($P \rightarrow M$) and reverse ($M \rightarrow P$) martensitic transformation induced on changing the temperature of the specimen. The thermal power W in the ordinates is rescaled by the absolute value of the cooling or heating rate $|\dot{T}|$

first consider the forward transformation and three different transformation paths represented in Fig. 1. We compare now the changes in enthalpy and entropy of the specimen, on going from A_i to M_i following the different paths. For simplicity, we momentarily omit the superscripts $P \rightarrow M$ from our notation.

(a) Comparison of paths (2) and (3) gives

$$\begin{aligned} & \int_{A_i}^{T_s} C_p^A(T) dT + \int_{T_s}^{T_f} d(-\Delta H_{ch} + \Delta H_{el})_{(2)} + \int_{T_f}^{M_i} C_p^M(T) dT \\ &= \int_{A_i}^{T_0} C_p^A(T) dT - \Delta H_{ch(3)} + \Delta H_{el} + \int_{T_0}^{M_i} C_p^M(T) dT \end{aligned} \quad (14)$$

where ΔH_{el} is introduced as an additional external work which has to be done on the specimen, when following path(3), to bring it to a final strained state at M_i , and

$$\begin{aligned} & \int_{A_i}^{T_s} \frac{C_p^A(T)}{T} dT + \int_{T_s}^{T_f} \frac{1}{T} d(-\Delta H_{ch} + \Delta H_{el})_{(2)} + \int_{T_f}^{M_i} \frac{C_p^M(T)}{T} dT \\ &= \int_{A_i}^{T_0} \frac{C_p^A(T)}{T} dT - \frac{\Delta H_{ch(3)}}{T_0} + \int_{T_0}^{M_i} \frac{C_p^M(T)}{T} dT \end{aligned} \quad (15)$$

(b) Comparison of paths (1) and (2) gives

$$\begin{aligned} & \int_{A_i}^{M_s} C_p^A(T) dT + \int_{M_s}^{M_i} C_p^{AM}(T) dT - Q_M - E_{fr} \\ &= \int_{A_i}^{T_s} C_p^A(T) dT + \int_{T_s}^{T_f} d(-\Delta H_{ch} + \Delta H_{el})_{(2)} + \int_{T_f}^{M_i} C_p^M(T) dT \end{aligned} \quad (16)$$

where E_{fr} is the work done by the specimen through the frictional path (1), and

$$\int_{A_i}^{M_s} \frac{C_p^A(T)}{T} dT + \int_{M_s}^{M_i} \frac{C_p^{AM}(T)}{T} dT - \Delta S_M$$

$$= \int_{A_f}^{T_s} \frac{C_p^A(T)}{T} dT + \int_{T_s}^{T_f} \frac{1}{T} d(-\Delta H_{ch} + \Delta H_{el})_{(2)} + \int_{T_f}^{M_f} \frac{C_p^M(T)}{T} dT \quad (17)$$

From equations (14) and (16)

$$\Delta H_{ch} = \Delta H_{ch(3)} + \int_{A_f}^{M_s} C_p^A(T) dT + \int_{M_s}^{M_f} C_p^{AM}(T) dT - \int_{A_f}^{T_0} C_p^A(T) dT - \int_{T_0}^{M_f} C_p^M(T) dT \quad (18)$$

and from equations (15) and (17)

$$\Delta H_{ch(3)} = T_0 \left[\int_{A_f}^{T_0} \frac{C_p^A(T)}{T} dT + \int_{T_0}^{M_f} \frac{C_p^M(T)}{T} dT - \int_{A_f}^{M_s} \frac{C_p^A(T)}{T} dT - \int_{M_s}^{M_f} \frac{C_p^{AM}(T)}{T} dT + \Delta S_M \right] \quad (19)$$

From the last two equations, it follows immediately (using again the superscripts $P \rightarrow M$) that the latent heat of transformation is given by

$$\begin{aligned} \Delta H_{ch}^{P \rightarrow M} = T_0 & \left[\int_{A_f}^{T_0} \frac{C_p^A(T)}{T} dT + \int_{T_0}^{M_f} \frac{C_p^M(T)}{T} dT - \int_{A_f}^{M_s} \frac{C_p^A(T)}{T} dT - \int_{M_s}^{M_f} \frac{C_p^{AM}(T)}{T} dT + \Delta S_M \right] \\ & + \int_{A_f}^{M_s} C_p^A(T) dT + \int_{M_s}^{M_f} C_p^{AM}(T) dT - \int_{A_f}^{T_0} C_p^A(T) dT - \int_{T_0}^{M_f} C_p^M(T) dT \end{aligned} \quad (20)$$

and the elastic energy is

$$\Delta H_{el}^{P \rightarrow M} = -Q_M + \Delta H_{ch}^{P \rightarrow M} - E_{fr}^{P \rightarrow M} \quad (21)$$

For the reverse transformation, the corresponding equations read

$$\begin{aligned} \Delta H_{ch}^{M \rightarrow P} = T_0 & \left[\int_{M_f}^{A_s} \frac{C_p^M(T)}{T} dT + \int_{A_s}^{A_f} \frac{C_p^{MA}(T)}{T} dT - \int_{M_f}^{T_0} \frac{C_p^M(T)}{T} dT - \int_{T_0}^{A_f} \frac{C_p^A(T)}{T} dT + \Delta S_A \right] \\ & + \int_{M_f}^{T_0} C_p^M(T) dT + \int_{T_0}^{A_f} C_p^A(T) dT - \int_{M_f}^{A_s} C_p^M(T) dT - \int_{A_s}^{A_f} C_p^{MA}(T) dT \end{aligned} \quad (22)$$

$$\Delta H_{el}^{M \rightarrow P} = -Q_A + \Delta H_{ch}^{M \rightarrow P} + E_{fr}^{M \rightarrow P} \quad (23)$$

Moreover, the frictional work can be determined by the O-P model as follows:

$$E_{fr}^{P \rightarrow M} + E_{fr}^{M \rightarrow P} = Q_A' - Q_M' \quad (24)$$

5 CONCLUSIONS

The O-P thermodynamic model is undoubtedly a successful model in thermodynamic theory of thermoelastic martensitic transformation. As other thermodynamic models, the O-P model have some shortcomings to revise. According to the theories concerned, we improve the O-P model, and derive the equations (20) and (22) of the latent heat of transformation by application of the first and second thermodynamic principles to a complete cycle. The latent heat of transformation, elastic strain energy and frictional work can be directly separated from calorimetric data by means of the improving model raised by the authors, which has contributed to a thorough understanding for the nature of thermoelastic martensitic transformation.

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