## Hysteresis in shape memory alloys. Is it always a constant?

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Shape Memory Alloys (SMAs) have been used in many applications due to their unique shape memory behavior. These materials can be "plastically" deformed at a low temperature, and then return to their shape prior to the deformation upon heating. This is known as the shape memory effect. If they are deformed at a high temperature, upon releasing the applied load, the original shape can be fully recovered. This is superelasticity. The underlying mechanism of these phenomena is the phase transformation between the high temperature austenite phase (A) and the low temperature martensite phase (M) and reorientation among marteniste variants, which are crystallographically equivalent, but oriented along different directions.

Hysteresis means the difference between the forward and reverse transformations. It is intrinsic in SMAs due to the energy dissipation in a full transformation cycle. In the case of thermal cycling with any external load, it is the difference in temperature between the forward transformation upon cooling  $(A \rightarrow M)$  and the reverse transformation upon heating  $(M \rightarrow A)$  [1]. Under a constant external load, it is the temperature difference in the temperature vs. displacement curves upon heating and cooling. For a superelastic SMA, the difference in stress (force) in the load vs. displacement curves upon loading and unloading is hysteresis.

In general, hysteresis is considered as a constant in a particular type of cyclic condition. However, is it always a constant? This paper aims to answer this question.

For simplicity, we consider an austenite SMA single crystal, which has *m* martensite variants that are associated with *m* transformation strains. The complementary free energy of a unit volume of SMA is given by [2]

$$\Psi(\Sigma_{ij}, T, \xi) = -[\Phi(\Sigma_{ij}, T, \xi) - \Sigma_{ij} E_{ij}] \quad (1)$$

where  $\Sigma_{ij}$  is the macroscopic stress tensor and  $E_{ij}$  is the macroscopic strain tensor, which can be divided into two parts as a first-order estimation, i.e., elastic strain  $E_{ij}^{e}$  and transformation strain  $E_{ij}^{t}$  ( $E_{ij} = E_{ij}^{e} + E_{ij}^{t}$ ). *T* is the temperature. In this expression Helmoltz free energy is defined as

$$\Phi(\Sigma_{ij}, T, \xi) = \Delta G_{\rm ch}(T) + W_{\rm mech} + W_{\rm surf} \quad (2)$$

where  $\Delta G_{ch}$  is the change of the chemical free energy due to the phase transformation,  $W_{surf}$  is the surface energy at the interphase between austenite and martensite and interface between martensite variants.  $W_{mech}$  is the mechanical energy.  $W_{surf}$  is small. As a traditional practice, it can be ignored.

According to the second law of thermodynamics, for any transformation process we have

$$d\Psi = dE_{A \to M} \ge 0 \tag{3}$$

Here,  $E_{A \to M}$  is the energy dissipation in the forward transformation. Assume that it is a constant for a transformation from an austenite to any martensite variant.

For a material that is uniform and homogeneous, the chemical-free energy is a function of temperature only. At a temperature T, the change of chemical energy due to the  $A \rightarrow M$  transformation may be written as

$$\Delta G_{\rm ch}(T) = G_{\rm ch}^M(T) - G_{\rm ch}^A(T) = \Delta G_{\rm ch}(T) \qquad (4)$$

It is reasonably accurate to use a linear approximation for the temperature range around the equilibrium temperature  $T_{equ}$ . This yields

$$\Delta G_{\rm ch} = \Delta \bar{G}_{\rm ch} (T - T_{\rm equ}) \tag{5}$$

where  $\Delta \bar{G}_{ch}$  is a constant. The mechanical energy is given by

$$W_{\rm mech} = \frac{1}{2} \Sigma_{ij} C_{ijkl} \Sigma_{kl} + W_{\rm int}$$
(6)

where  $C_{ijkl}$  is the elastic compliance tensor.  $W_{int}$  is the internal energy, which can be removed if the whole grain transforms into one marteniste variant instantly.

As the applied stress is greater than a certain value, stress induced martensitic transformation occurs. If the deformation is carried out at an extremely slow speed, the variation of temperature is very small. Assuming that the whole grain transforms into one particular martensite variant  $(M^i)$ , one has [2],

$$-\frac{1}{2}\Sigma_{ij}\left(C_{ijkl}^{A}-C_{ijkl}^{M^{i}}\right)\Sigma_{kl}+\Sigma_{ij}E_{ij}^{t}=K_{A\to M}\quad(7)$$

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where  $K_{A\to M} = E_{A\to M} + \Delta \bar{G}_{ch}(T - T_{equ})$ , is the driving energy (or driving force) for the forward transformation at temperature *T*.  $C_{ijkl}^A$  and  $C_{ijkl}^{M^i}$  are elastic compliance tensors of austenite and martensite variant *i*, respectively. Among *m* possible variants, the favorite one is the one with the largest phase transformation strain along the direction of the applied stress.

Similarly, we can obtain the expression for the reverse transformation  $(M \rightarrow A)$  at  $T^*$  as

$$\frac{1}{2} \sum_{ij}^{*} \left( C_{ijkl}^{A} - C_{ijkl}^{M^{i}} \right) \sum_{kl}^{*} - \sum_{ij}^{*} E_{ij}^{t}$$
$$= E_{M \to A} - \Delta \bar{G}_{ch} (T^{*} - T_{equ})$$
(8)

Consider the case of thermal cycling under a constant load, i.e.,

$$\Sigma_{ij} = \Sigma_{ij}^* \tag{9}$$

From Equations 11 and 12, one has

$$E_{A \to M} + \Delta \bar{G}_{ch}(T - T_{equ}) + E_{M \to A}$$
$$-\Delta \bar{G}_{ch}(T^* - T_{equ}) = 0 \qquad (10)$$

Hence, hysteresis ( $\Delta T$ )

$$\Delta T = T^* - T = \frac{E_{A \to M} + E_{M \to A}}{\Delta \bar{G}_{ch}}$$
(11)

It reveals that hysteresis is a constant in the case of thermal cycling under a constant load.

In the case of loading/unloading at a constant temperature (i.e.,  $T = T^*$ ), from Equations 7 and 8 we can obtain

$$-\frac{1}{2}\Sigma_{ij} (C^A_{ijkl} - C^{M^i}_{ijkl}) \Sigma_{kl} + \Sigma_{ij} E^t_{ij}$$
$$+ \frac{1}{2}\Sigma^*_{ij} (C^A_{ijkl} - C^{M^i}_{ijkl}) \Sigma^*_{kl} - \Sigma^*_{ij} E^t_{ij}$$
$$= E_{A \to M} + E_{M \to A}$$
(12)

It is apparent that hysteresis  $(\Delta \Sigma_{ij} = \Sigma_{ij} - \Sigma_{ij}^*)$  is not a constant anymore. Let us consider the simplest case of uniaxial tension. Under such a situation, as shown in [3], Equation 16 can be reduced to

$$\frac{1}{2} \left( \frac{1}{D_M} - \frac{1}{D_A} \right) (\sigma^2 - [\sigma^*]^2) + (\sigma - \sigma^*) \varepsilon^t$$
$$= E_{A \to M} + E_{M \to A}$$
(13)

where  $\sigma$  and  $\sigma^*$  are the transformation stress in loading and unloading,  $\varepsilon^t$  is the transformation strain,  $D_M$  and  $D_A$  are the Young's Moduli of martensite and austenite. Hysteresis can be obtained as

$$\Delta \sigma = (\sigma - \sigma^*) = \frac{E_{A \to M} + E_{M \to A}}{\left(\frac{1}{D_M} - \frac{1}{D_A}\right)\frac{(\sigma + \sigma^*)}{2} + \varepsilon^t} \quad (14)$$

This reveals that in the case of loading/unloading at a constant temperature, hysteresis is not a constant anymore, but depends on the temperature. Since at a higher temperature, the required transformation stress is higher,  $\frac{\sigma+\sigma^*}{2}$  is higher. Subsequently, hysteresis ( $\Delta\sigma$ ) becomes smaller.

To conclude, this paper demonstrates that hysteresis is not always a constant. In the case of thermal cycling under a constant load, hysteresis (in terms of temperature) is not only a constant, but also independent on the magnitude of the applied load. However, in the case of loading/unloading at a constant temperature, because of the difference in the elastic compliance tensors of austenite and martensite, hysteresis (in terms of stress) is temperature dependent. At a higher temperature, hysteresis is smaller.

## References

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