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Thermodynamics of martensite transformation hysteresis in Ni-Ti shape memory alloys①

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Abstract: A thermodynamic calculation method on the temperature hysteresis of thermoelastic martensite transformation in Ni-Ti shape memory alloys was developed. The thermodynamic analysis indicates that the irreversible consumed energy and the elastic energy are the important factors influencing transformation hysteresis. It is revealed that the wide inherent transformation hysteresis can be attributed to the higher irreversible consumed energy of martensite transformation in Ni-Ti-Nb based alloys than those of Ni-Ti binary alloys.

Key words: thermodynamics; thermoelastic martensite; temperature hysteresis; Ni-Ti alloys **Document code:** A

1 INTRODUCTION

Ni-Ti and Ni-Ti-Nb shape memory alloys are well known to exhibit different temperature hysteresis in an unstressed state[1,2], i.e. the inherent hysteresis of thermoelastic martensite transformation. The latter have wider transformation hysteresis than the former[3~5]. From the view point of the structure, their characteristic is that Ni-Ti-Nb based alloys consist of β-Nb and parent austenite phases, while Ni-Ti binary alloys only include the parent phase at room temperature after annealing. Although some work was reported[6,7], a general understanding of the criteria on determining the thermoelastic transformation hysteresis is unclear for Ni-Ti shape memory alloys. The purpose of the present work is to analyze the thermodynamic factors affecting transformation temperature hysteresis so as to offer a reference for shape memory alloys design.

2 THERMODYNAMIC PRESENTATION OF THERMOELASTIC MARTENSITIC TRANSFORMATION

According to the thermodynamic laws, the difference of free energy between martensite and parent austenite phases during forward and reverse martensitic transformation can be expressed as follows[8]:

$$\Delta G^{p-m} = \Delta G_c^{p-m} + \Delta E_e^{p-m} + \Delta E_i^{p-m} \quad (1)$$

$$\Delta G^{m-p} = \Delta G_c^{m-p} + \Delta E_e^{m-p} + \Delta E_i^{m-p} \quad (2)$$

where $\Delta G_c = \Delta H - T\Delta S$, is the change in chemical free energy associated with the corresponding transformation; $\Delta E_e = \Delta E_e^0 + \Delta E_e(f_m)$, ΔE_e^0 is the change in elastic energy caused by the nucleation of martensite and $\Delta E_e(f_m)$ the change in volume elastic energy during the transformation process which depends on the volume fraction of martensite f_m; ΔE_i is the energy consumed during the transformation process due to internal resistance for the movement of the interface between martensite and parent phases. It is reasonable that the consumed energy can be assumed equal for the forward and reverse martensitic transformation in Ni-Ti shape memory alloys, that is

$$\Delta E_i^{p-m} = \Delta E_i^{m-p} = \Delta E_i > 0.$$

At the beginning of the forward martensite transformation at M_s temperature, Eq.(1) can be written as

$$\Delta G_{M_s}^{p-m} = \Delta G_{c,M_s}^{p-m} + \Delta E_i^{p-m} + \Delta E_{e,M_s}^{p-m} = 0 \quad (3)$$

Since

$$\Delta G_{c,M_s}^{p-m} = \Delta H^{p-m} - M_s \cdot \Delta S^{p-m} \quad (4)$$

so

$$M_s = \frac{\Delta H^{p-m} - \Delta G_{c,M_s}^{p-m}}{\Delta S^{p-m}} = \frac{\Delta H^{p-m} + \Delta E_i^{p-m} + \Delta E_{e,M_s}^{p-m}}{\Delta S^{p-m}} \quad (5)$$

A similar deduction can be adopted for the reverse martensitic transformation:

$$A_s = \frac{\Delta H^{m-p} - \Delta G_{c,A_s}^{m-p}}{\Delta S^{m-p}} = \frac{\Delta H^{m-p} + \Delta E_{e,A_s}^{m-p} + \Delta E_i^{m-p}}{\Delta S^{m-p}} \quad (6)$$

Based on the above analysis, the inherent temperature hysteresis width for the forward and reverse thermoelastic martensitic transformation can be ex-

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pressed as

$$A_s - M_s = \frac{2\Delta E_i + \Delta E_{e,M_s}^{p-m} + \Delta E_{e,A_s}^{m-p}}{-\Delta S} \quad (7)$$

In Eq.(7) the change in elastic energy during forward martensitic transformation, $\Delta E_{e,M_s}^{p-m}$, is the elastic energy stored in the alloy above M_s temperature during cooling, it can be regarded as a constant in a given alloy because it is only a function of the substance state. The change in elastic energy during reverse martensite transformation, $\Delta E_{e,A_s}^{m-p}$, is the one on heating from M_f temperature to A_s temperature, which consists of two components: one is directly associated with martensite transformation as expressed by ΔE_e^{trans}, the other is related to the variation of temperature as expressed by ΔE_e^{temp}. The change in the elastic energy related to temperature can be assumed very small compared with the elastic energy caused by martensitic transformation. Therefore, Eq.(7) can be rewritten as

$$A_s - M_s = \frac{2\Delta E_i - \Delta E_e^{trans}}{-\Delta S} \quad (8)$$

From Eq.(8), it can be seen that the inherent temperature hysteresis width of thermoelastic martensitic transformation is controlled by two factors: the consumed energy ΔE_i and the elastic energy produced by martensitic transformation ΔE_e^{trans}. Applying the following condition[9]: $\Delta S < 0$, $\Delta E_e^{trans} > 0$, we can conclude that the temperature hysteresis width increases with the increase in the consumed energy and the decrease in the change in elastic energy.

3 ESTIMATION OF ELASTIC ENERGY IN Ni-Ti-Nb BASED ALLOYS

During the martensitic transformation in Ni-Ti-Nb based shape memory alloys, the change in the elastic energy can be expressed as[10]

$$\Delta E_e = -\frac{1}{2\rho}\int \sigma_{ij}^t \varepsilon_{ij}^t \mathrm{d}V/V - \frac{1}{\rho}\int (\sigma_{ij} + \sigma_{ij}^d)\varepsilon_{ij}^t \mathrm{d}V/V \quad (9)$$

where σ_{ij}, σ_{ij}^d and σ_{ij}^t are the applied stress, the internal elastic stress field due to the presence of the second particles and the internal stress field associated with the transformation, respectively; ε_{ij}^t is the transformation strain, ρ is the density and the integration is over the volume, V, of the specimen. The first term on the right side of Eq.9 presents the contribution from the elastic accommodation of the local transformation strain, expressed as ΔE_e^t. It can influence the whole transformation process. The second term is associated with the presence of the second phase, expressed as ΔE_e^d and can influence the magnitude of ΔE_e.

The elastic stress field may be caused by the lattice misfit and the thermal mismatch between the matrix and the β Nb particles in Ni-Ti-Nb based alloys. In this case, it should be noted that the matrix means the parent phase for the forward transformation and martensite for the reverse transformation respectively. This stress field will influence the character of σ_{ij}^d, consequently influence that of ΔE_e^d. The occurrence of thermally induced martensite will produce shear elastic stress field on cooling, which determines the character of ΔE_e^t. In general, ΔE_e^t will be a positive value, while ΔE_e^d may be positive or negative depending on the character of σ_{ij}^d. For Ni-Ti binary alloys without any defect, σ_{ij}^d generally tends to be zero, accordingly ΔE_e^d is zero; only ΔE_e^t can make contributions to the elastic energy, so $\Delta E_s = \Delta E_e^t$. For Ni-Ti-Nb based alloys, however, the β Nb particles are soft compared with the matrix, and can not strengthen the alloys, so ΔE_e^d should be negative, which will cause the decrease in elastic energy.

4 ESTIMATION OF CONSUMED ENERGY IN Ni-Ti-Nb BASED ALLOYS

There is no thermal mismatch stress in Ni-Ti binary alloys due to being a single solid solution. However, for Ni-Ti-Nb based alloys, the matrix subjected to an internal stress exhibits an enthalpy ΔH^σ different from that of the unstressed alloy due to the presence of the thermal mismatch stress between the matrix and the β Nb particles. An excess enthalpy ΔH^{xs} can be defined as[7] $\Delta H^{xs} = \Delta H - \Delta H^\sigma$.

With the same deduction the excess irreversible energy in Ni-Ti-Nb based alloys may be expressed by $\Delta H_{fr}^{xs} = \Delta H^{xs} - \Delta_{el}^{xs}$, where ΔH_{fr}^{xs} can be calculated according to Ref.[5]. So we can obtain the consumed energy for each alloy. The results are shown in Fig.1.

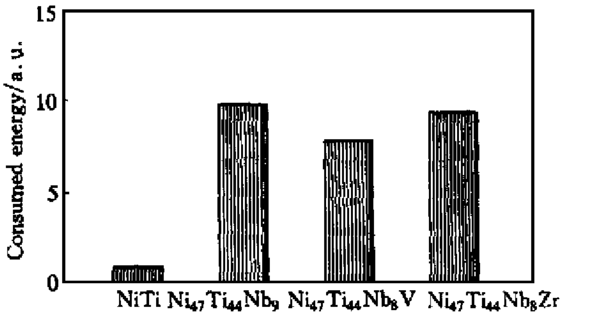

Fig.1 Consumed energy during martensitic transformation

It is clear that the irreversible energy values for Ni-Ti-Nb based alloys are much larger than that for Ni-Ti binary alloy during thermoelastic martensite transformation. According to Eq.(8), the increase in the irreversible energy and the decrease in the elastic energy play an important role on the increase in the inherent temperature hysteresis of the martensitic transformation. The calculated results are in good agreement with the measured ones, the inherent temperature hysteresis of the martensitic transformation for $Ni_{47}Ti_{44}Nb_9$, $Ni_{47}Ti_{44}Nb_8V$ and $Ni_{47}Ti_{44}Nb_8Zr$ alloys are 49, 44 and 43 K, respectively, while that for Ni-Ti alloy is only 20 ~ 30 K.

5 CONCLUSIONS

We proposed a thermodynamic method for expressing the inherent temperature hysteresis of thermoelastic martensite transformation, which provides a possibility to quantitatively calculate the inherent temperature hysteresis for Ni-Ti alloys. The results suggest that the irreversible energy and the elastic energy are the most important factors for the transformation temperature hysteresis. It was demonstrated that the consumed energy values during forward and reverse martensitic transformation of Ni-Ti-Nb based alloys are larger than those of Ni-Ti binary alloys, which can explain the reason why Ni-Ti-Nb alloys have wider inherent temperature hysteresis than Ni-Ti binary alloys.

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