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## Characteristic of specific heat capacity of NiTi alloy phases<sup>①</sup>

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**[Abstract]** The specific heat capacity of NiTi alloy at constant pressure using MDSC (Modulated differential scanning calorimeter) was determined. It was found that the variation tendencies of the specific heat capacity for different phases are different. The fitting equations of the specific heat capacity for martensite and austenite phases were presented. Then, a reason, based on thermodynamic point of view, was proposed to explain the difference of the specific heat capacity between martensitic and austenitic phases. Finally, compared with the specific heat capacity of pure Ni and Ti, it was found that the specific heat capacity of NiTi alloy is inherent to that of pure Ti. When the specific heat capacity of NiTi alloy is calculated by Neumann-Kopp, in the temperature region of phase transformation and the temperature higher than 400 K, the results are not desirable.

**[Key words]** specific heat capacity; NiTi; phase transformation; thermodynamic

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### 1 INTRODUCTION

NiTi is an important shape memory alloy (SMA). It has been confirmed that three phases appear during heating and cooling the material across phase transformation temperatures. At low temperature, a kind of monoclinic phase called martensite (M) exists, while austenite (A) exists at high temperature. When cooling the material from high temperature, an intermediate, rhombohedral (R) phase will appear. The shape memory effect of NiTi alloy is induced by such phase transformations.

As an important thermophysical property, the specific heat capacity has great influence on the behavior of the temperature field both in space and time. Therefore, it is meaningful to investigate the specific heat capacity especially when NiTi is used as actuator, and need to be manipulated by means of heating or cooling. Some author like Smith has done some work in this area<sup>[1~3]</sup>, but the investigation on the variation tendency of the specific heat capacity for NiTi alloy has not been reported up to now. So an experiment is performed in order to determine the exact variation trend of the specific heat capacity of NiTi alloy, and find out the tendency of different NiTi alloy phases being not the same, but different completely.

### 2 EXPERIMENTAL

#### 2.1 Specimen preparation

NiTi (Ni 50.6%, Ti 49.4%, mole fraction) wires of 0.5 mm in diameter were used in the present experiment. The NiTi wires were annealed at 700 °C for 1 h then aging at 450 °C for 1 h. Before experi-

ment, oxidized films on the surface of NiTi wires were removed by pickling using a solution of  $V(H_2O): V(HNO_3): V(HF) = 5: 4: 1$ <sup>[4]</sup>.

#### 2.2 MDSC measurement

The specific heat capacity has been measured with a MDSC (Modulated differential scanning calorimeter), TA instruments 2910 MDSC. The heating rate of the MDSC in the investigation was 5 K/min, at the set point temperatures, the isothermal equilibrating time were 10 min. To reduce the error due to different positions of the sample in the Aluminum pan, and to gain a more accurate result, experiments have been carried out two times. The first run of the measurement for specific heat capacity was in the temperature range from 223 K to 473 K (heating), isothermal, then back round (cooling). In the second run, the measurement being from 223 K to 573 K, isothermal, then back round as shown in Fig.1, is similar to Rohde's and Smith's measurements<sup>[1,2]</sup>. From Fig.1, it could be found, in the two process (heating and cooling), the specific heat capacity outside the phase transformation region roughly overlaps. However, in the second measurement, phase transformation occurs earlier than that of the first run. Thermal cycling may affect the temperature of phase transformation in certain degree<sup>[4,5]</sup>. In the condition without stress, thermal cycling affects austenitic transformation start temperature ( $A_s$ ) slightly, but increases the R phase and martensitic transformation start temperature much higher, this can be easily found from Fig.2.

### 3 RESULTS AND ANALYSES

#### 3.1 Heat capacity of M and A phase

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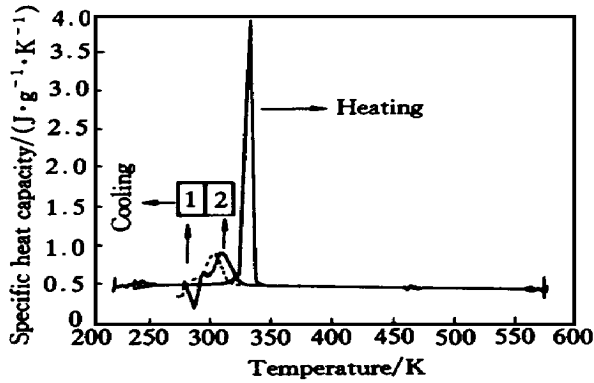


Fig.1 Specific heat capacity determined from two experiments  
1 — First experiment ; 2 — Second experiment

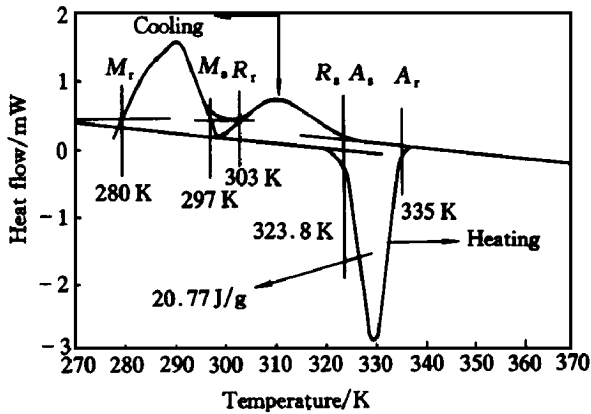


Fig.2 Characteristic temperatures determined from heat flow curve

The specific heat capacity in the PC output includes the latent heat produced during phase transformation. The relationship of true specific heat capacity variation versus temperature will be exposed if the up and down data caused by phase transformation were removed, as shown in Fig.3. The lower two fluctuant curves are the first run experimental result, the higher one belongs to the second run, the middle two smooth curves are the mean of the fitting results of the two experiments. The specific heat capacity vari-

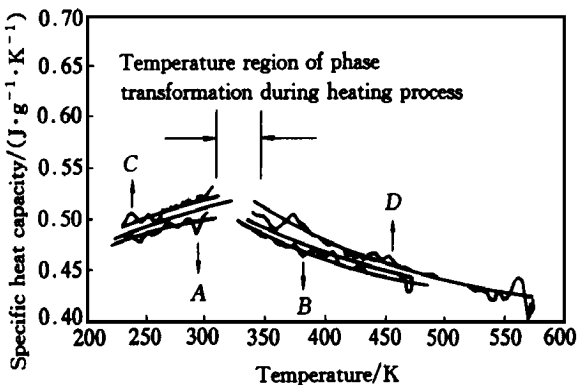


Fig.3 Fitting results of two experiments

ation tendency versus temperature is different outside the temperature region of phase transformation during the heating process. Before phase transformation ( $M \rightarrow A$ ), the specific heat capacity fluctuates to an ascending tendency, after phase transformation, however, fluctuates to decrease. This is different from Smith's result<sup>[2]</sup>.

Since the specific heat capacity is usually given by the equation:  $C_p = a + bT + cT^{-2}$ , which is adopted for fitting the data of specific heat capacity with the method of least square. The fitting results are shown in Fig.3 (the smooth curves).

On the left side of temperature region of phase transformation, the data of specific heat capacity of martensite are fitted by

$$C_{pM} = 0.436 + 2.744 \times 10^{-4} T - 708.156 T^{-2} \quad (1)$$

On the right side of the temperature region of phase transformation, The fitting result of the austenite specific heat capacity as follows:

$$C_{pA} = 0.50 - 1.90 \times 10^{-4} T + 7128.5 T^{-2} \quad (2)$$

At low temperature, the specific heat at constant volume ( $C_V$ ) follows the usual relation  $C_V = \gamma T + \beta T^3$ , where  $\gamma$  is the electronic coefficient, and  $\beta$  the lattice coefficient related to the Debye temperature  $\theta_D$ . At the very low temperature, the electronic contribution to the specific heat predominates over that of the lattice, with increasing temperature, the specific heat is mainly up to lattice vibration ( $\beta T^3$ ).

According to Debye model, the specific heat capacity ( $C_V$ ) is given by  $C_V = 9 Nk \left[ \frac{T}{\theta_D} \right]^3 \int_0^{T/\theta_D} \frac{e^x x^4}{(e^x - 1)^2} dx$ , where  $N$  and  $k$  are Avogadro number and Boltzmann constant, respectively. When temperature is very low, i.e.  $T \ll \theta_D$ , then the Debye model can be simplified as follows:

$$C_V \approx 1.945 \left[ \frac{T}{\theta_D} \right]^3$$

$$\text{As for NiTi, } C_V \approx 36.7 \left[ \frac{T}{\theta_D} \right]^3.$$

Generally, the measured specific heat capacity is the capacity at constant pressure, but the volume of a solid state material does hardly change with pressure, so we postulate  $C_p$  approximately equal  $C_V$  ( $C_p \approx C_V$ ).

Since at low temperature, the specific heat capacity mainly comes from the lattice contribution, we can get the following equation

$$C_p \approx C_V \approx \beta T^3 \quad (3)$$

Suppose the two curves govern by Eqn.(1) and Eqn.(3) smoothly meet at the point of inflection  $T_m$ <sup>[6]</sup>. So

$$\beta T_m^3 = 0.436 + 2.744 \times 10^{-4} T_m - 708.156 T_m^{-2} \quad (4)$$

$$3\beta T_m^2 = 2.744 \times 10^{-4} + 1416.312 T_m^{-3} \quad (5)$$

According to Eqn.(4) and Eqn.(5),  $\beta$  and  $T_m$  can be solved:

$$\beta = 1.27 \times 10^{-6}$$

$$T_m = 52 \text{ K}$$

Therefore, at low temperature,

$$C_p \approx 1.27 \times 10^{-6} T^3 \quad (6)$$

$$\text{Because, } C_V \approx 36.7 \left[ \frac{T}{\theta_D} \right]^3 = \beta T^3$$

So

$$\theta_D = 3.32 \beta^{-1/3}$$

In this way, the Debye temperature of NiTi can be obtained as  $\theta_D = 306 \text{ K}$ , which is in agreement well with Kuentzler's results<sup>[3]</sup>.

### 3.2 Calculation of Gibbs free energy

As we know, heat capacity reflects the crystal lattice vibration. The lattice will not be stable any more during phase transformation, the crystal structure will change, and the free energy of the whole system will tend to be on the lowest level.

The absolute enthalpy, entropy and Gibbs free energy are calculated by following equations:

$$H(T) = \int_0^T C_p dT$$

$$S(T) = \int_0^T \frac{C_p}{T} dT$$

$$G(T) = H(T) - TS(T) \\ = \int_0^T C_p dT - T \int_0^T \frac{C_p}{T} dT$$

where  $C_p$  takes value from Eqns.(1), (2) and (6) respectively when temperature varies from 0 to  $T \text{ K}$ .

However, in the temperature region of phase transformation, the equations above mentioned must be corrected due to the consideration on the effect of endothermic energy during the heating process. In order to simplify the computation procedure, suppose  $C_p$  is an average of the value at  $A_s$  and  $A_f$ , the absolute enthalpy, entropy, and Gibbs free energy are linear function dependent on temperature. Then at  $A_f$ , they follow

$$H(A_f) = H(A_s) + C_p(A_f - A_s) + \Delta Q$$

$$S(A_f) = S(A_s) + C_p(\ln A_f - \ln A_s) + \frac{\Delta Q}{T_{A_s}}$$

$$G(A_f) = H(A_f) - A_f S(A_f)$$

$\Delta Q$  is the latent heat, which can be measured from Fig.3 by using a PC during the MDSC measurement. In the heating process, the endothermic energy  $\Delta Q$  equals to  $20.77 \text{ J/g}$ . the results are shown in Fig.4. From the computation procedure, the enthalpy and the entropy are calculated from the specific heat capacity, thus it is a direct reflection of  $C_p$ . The Gibbs free energy is calculated from the enthalpy and entropy, so it reflects the variation tendency of  $C_p$ . As shown in Fig.4, the Gibbs free energy of  $M$

phase is higher than the extrapolated value of  $A$  phase, this means  $A$  phase is stable at high temperature. That is to say, the Gibbs free energy of the system should maintain the lowest level when NiTi alloy experience temperature changes, which directly results in the different variation tendency of  $C_p$ .

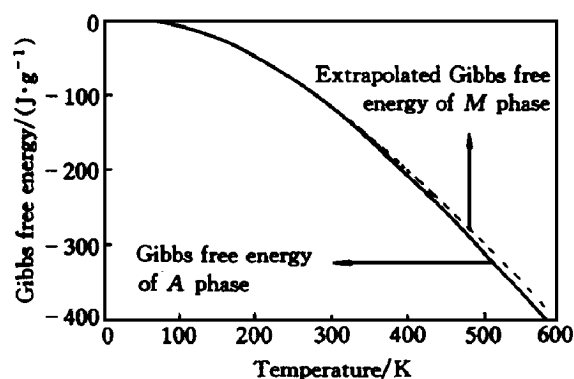


Fig.4 Gibbs free energy of NiTi alloy

### 3.3 Discussion

When allotropic transformation happens among metals, a regularly phenomena may be observed near the temperature of phase equilibrium, the following inequality is tenable:  $C_p(\text{HCP}) > C_p(\text{BCC}) > C_p(\text{FCC})$ <sup>[7]</sup>.

Fig.5 shows the discrepancies of the  $C_p$  between Ni, Ti, and NiTi. The peak value of  $C_p$  for Ti appears when  $\alpha(\text{Ti})(\text{HCP})$  transformed into  $\beta(\text{Ti})(\text{BCC})$ , the value outside the temperature range of phase transformation has different variation tendency, which is similar to that of NiTi. So we can safely say, the  $C_p$  of NiTi is inherent to the characteristics displayed by Ti. The  $C_p$  of martensite is higher than that of austenite near the transformation temperature:  $C_p(\text{monoclinic}) > C_p(\text{BCC})$ . The inference may be somewhat explained by the two-sets-of-atoms model proposed by Kafka<sup>[10]</sup>.

A quantitative calculation can be given according

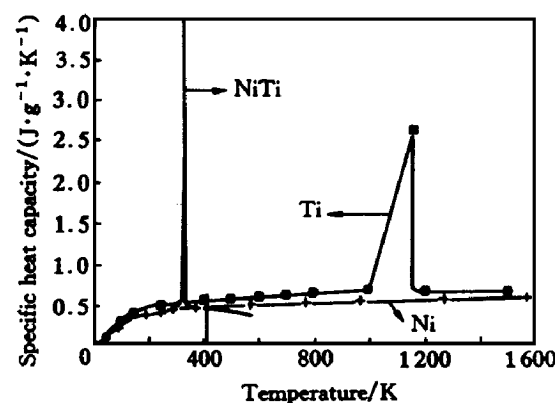


Fig.5 Specific heat capacity of Ni, Ti and NiTi

to Neuman-Kopp rule: for binary alloy,  $C_p = x C_1 + (1 - x) C_2$ , where  $x$  is the atomic composition of component  $C_1$ . As for NiTi alloy,  $C_p = 0.5(C_1 + C_2)$ , therefore, if the specific heat capacity of NiTi alloy was calculated from the  $C_p$  of Ni and Ti by employing the Neuman-Kopp rule, the value should lie between the  $C_p$  curves of Ni and Ti. However, as shown in Fig. 5, both in the temperature range of phase transformation and in the temperature higher than 400 K, the gap between calculation and determination will be too wide, and the rule will be invalid.

#### 4 CONCLUSIONS

1) The specific heat capacity of different phases of NiTi alloy has different variation tendency. As to martensitic phase, it follows the function:

$$C_{pM} = 0.436 + 2.744 \times 10^{-4} T - 708.156 T^{-2}$$

To austenitic phase:

$$C_{pA} = 0.50 - 1.90 \times 10^{-4} T + 7128.5 T^{-2}$$

2) The different variation tendency of  $C_p$  results from the Gibbs free energy of the system which should maintain the lowest level when NiTi alloy experience temperature changes.

3) The  $C_p$  of NiTi is inherent to the characteristics displayed by Ti.

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