A Thermal Perspective of NiTi Alloy under Non-Isothermal Conditions

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Changes of phase transformation temperatures of a NiTi alloy have been investigated under non-isothermal conditions by using a differential scanning calorimeter (DSC). It has been found that the duration for phase transformation declines exponentially with increasing the heating rate. The specific heat capacity of the NiTi alloy at a constant pressure (Cp) was also determined in the experiment. Differences in the variation tendency of the Cp for the martensite and austenite phases have been observed. The temperature distribution of NiTi wire, when heated by electric current, was calculated based on Cp measured, discussions addressing the calculation results are given.

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1. Introduction

NiTi is an important alloy that exhibits shape memory effect. It has been confirmed that three phases exist, and can transform from one to another in a certain sequence, i.e., from the high temperature austenite (A), through an intermediate rhombohedral (R) phase, to the low temperature martensite (M) at certain conditions. The shape memory effect of NiTi alloy is induced by such phase transformations.

It is known that the transformation temperatures change with increasing the heating rate. In the experiments, the changes of the transformation temperatures were investigated, and it was found that the duration for phase transformation is different under different heating rates, then, the thermodynamic characteristics under non-isothermal conditions are discussed.

As an important thermophysical property, the specific heat capacity (Cp) has a great influence on the behavior of the temperature field both in space and time. Therefore, it is meaningful to investigate Cp. Researchers such as Smith have done some work in this area,1 3) but the investigation on the variation tendency of the specific heat capacity for NiTi alloy has not been reported up to now. So experiments were performed in order to determine the variation trend of the specific heat capacity of NiTi alloy. It has been found that the variation tendencies of Cp for different NiTi phases are different.

Due to its high strength and high recoverable transformation strain, shape memory alloys (SMAs) are usually used as structural control components,4 6) and can be heated by electric current. Heat produced by electric current in the SMA wire transfers to air by means of natural convection, and the temperature of the wire can be determined from the electric current history, heat transfer process and phase transformation process. Latent heat would deliver in the latter process, so causes the calculation of the wire temperature nonlinear. For easy calculation, methods like Equivalent Heat Capacity, Equivalent Heat and Specific Enthalpy were developed in the computation of the temperature distribution.7) However, all of these methods can not well reflect the real process of phase transformation. However, if the Cp determined from experiments were adopted in the calculation, this problem would be solved. The computation results may provide helpful information to calculate the temperature field of heated NiTi wires rationally and efficiently.

2. Experimental

2.1 Specimen preparation

NiTi (Ni 50.6 at%, Ti 49.4 at%) wires of 0.5 mm in diameter were used in the present experiments. The NiTi wires were annealed at 973 K for one hour then aged at 723 K for one hour. Before measurements, oxidized surface of NiTi wires were removed by pickling using a solution of H2O : HNO3 : HF = 5 : 4 : 1.

2.2 MDSC measurement

The experiments were carried out with a TA instruments 2910MDSC (Modulated differential scanning calorimeter), which can give the heat flow curves and the specific heat capacity curves simultaneously. The specimens were put into aluminum pan, and were protected under nitrogen atmosphere. The modulation amplitude and frequency are 0.5°C and 1min−1, respectively. The transformation temperature of In, the standard material, was measured under different heating rates in order to eliminate the effect of the apparatus itself. The Cp of sapphire was determined under the same scheduled procedure for measuring the Cp of NiTi. The experimental value was compared with the standard one from the manual, and then a correction factor can be obtained accordingly. Therefore, all the results given in this paper are the values with correction.

Experiments have been performed for two times. The first experiment was aimed to find the changes of the transformation temperatures under non-isothermal conditions. The specimen weighs 15.2 milligrams, experimental procedure has been taken as follows: Isothermal at 253 K, heating to 373 K, isothermal, cooling to 253 K. The isothermal time was one minute. The experiment was carried out under different heating rates, i.e., 1 K/min, 5 K/min, 8 K/min and 10 K/min, respectively.

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The second experiment was carried out to determine the $C_p$ of NiTi wire for the calculation of the temperature field when NiTi was used as a control component. Thermal cycling before measurement stabilized the specimen. In the experiment, a heating rate of 5 K/min was adopted, and the weight of specimens were 11.9 mg. In the first run of the measurement, $C_p$ was determined in the temperature range from 223 to 473 K. At the set temperatures, the specimens were kept in the isothermal condition for five minutes. In the second run, the measurements were taken from 223 to 573 K.

3. Results and Discussion

3.1 Thermodynamics under isothermal condition

The heat flow curves were similar in the experiments, so only one is presented in this paper (Fig. 1(a)). The transformation temperatures determined from the experiments are presented in Table 1, where the subscription “s” means the phase transformation start temperature, and “f” the finish temperature.

Figure 1(b) presents the variation tendency of the transformation temperatures determined from experiments. The
start and finish temperatures of austenite transformation increase with the increase of the heating rate, which is in agreement with Kvarciak’s result. While the transformation temperatures of both R phase and martensite decrease with the increase of the cooling rate. The results are in accordance with that of conventional materials under the similar non-isothermal conditions that is caused by the thermal inertia of the materials. As discussed below, the changed transformation temperatures gradually deviate from the equilibrium temperature with increasing the heating/cooling rate, then the driving force of phase transformation increases accordingly.

Supposing the process of phase transformation proceeds completely, the duration for phase transformation \( \tau \), which is called transformation time in this paper, can be obtained. Taking the heating process as an example, \( \tau = (A_f - A_s)/v \), where \( v \) is the heating rate. As for the martensite and R phases, the transformation time can be obtained by the same method. The results are shown in Fig. 1(c), where the points were calculated from the experiment results, and the curves are the fitting results using the method of least square.

As for austenite:
\[
\tau_A = 2.17 + 7.51e^{-\frac{t}{39}}
\]
(1)

For martensite:
\[
\tau_M = 1.48 + 9.48e^{-\frac{t}{56}}
\]
(2)

For R phase:
\[
\tau_R = 3.05 + 30.32e^{-\frac{t}{59}}
\]
(3)

The above fitting results follow the same equation: \( \tau = t_0 + Ce^{-\frac{t}{t_0}} \), where \( t_0 \), \( C \) and \( t_0 \) are constants. It can be observed from Fig. 1(c) that the transformation time arrived at a limit when the heating rate was high enough. The minimum value can be read conveniently from the fitting result, of which the constant term \( t_0 \). This means that there exists a minimum value of transformation time for the whole process of phase transformation.

It is known that the system energy change \( \Delta G \) only includes the chemical energy change \( \Delta G_c \) before martensitic phase transformation, so \( \Delta G^{A\rightarrow M} = \Delta G^{A\rightarrow N} = 0 \) when \( T = T_0(T_0 = \frac{1}{2}(M_f + A_s)) \). However, the non-chemical energy \( \Delta G^{A\rightarrow R} \) increases along with the process of phase transformation, and arrives at the highest value at \( M_f \). Therefore, there exists another equilibrium temperature \( T_0'(T_0' = \frac{1}{2}(M_f + A_s)) \). Both the non-chemical and chemical energy \( \Delta G^{M\rightarrow A} \) must be considered in the reverse martensitic transformation, thus \( T_0' \) follows the equation \( \Delta G^{M\rightarrow A} = \Delta G^{M\rightarrow A} + \Delta G^{N\rightarrow R} = 0 \). \( T_0 \) and \( T_0' \) can be determined from the experiment, as also shown in Fig. 2(b).

The difference of the transformation start temperature and the equilibrium temperature \( \Delta T_1 = T_0 - M_s \) or \( \Delta T_2 = A_s - T_0' \) is proportional to the driving force of phase transformation. Figure 1(d) shows the difference verse the heating rate, indicating that the driving force increases with increasing the heating rate.

The non-chemical energy term is a main term in thermoeelastic martensitic transformation. The difference of the two equilibrium temperature \( \Delta T_3 = T_0 - T_0' \) reflects the change of the elastic strain energy. Owing to the thermal cycling of the alloy before the experiment, the increase of the elastic energy caused by thermal cycling is negligible. Figure 1(e) shows the dependence of temperature difference on the heating rate, it can be seen that the elastic strain energy increases with increasing the heating rate.

Taking the heating process as an example, the transformation time includes duration for nucleation and duration for growth. Shorter transformation time stands for higher rate for nucleation and growth. The transformation temperatures are pushed to higher level with increasing heating rate. On the one hand, the diffusion proceeds more easily at higher temperatures, that promotes the growth of new phase grains. Meanwhile, the phase transformation takes place in a shorter time because of the increase of the driving force. On the other hand, transformation time cannot decrease without limit because of the resistance for phase transformation, i.e., interface energy, strain energy, etc. Moreover, the elastic strain energy increases with increasing the heating rate. A minimum \( t_0 \) exists when the heating rate is infinite, and the increase in driving force and in the strain energy arrives at equilibrium. Then the resistance for phase transformation from other terms is negligible. These terms are mainly due to the materials factors, for an example, interface energy is high if the crystal grain in all is small. Therefore, transformation time is materials dependent.

From above analyses, the transformation time reflects the rate for nucleation and growth, reflects both driving force and resistance force for phase transformation, and is materials dependent under non-isothermal conditions.

3.2 Heat capacity of NiTi alloy
3.2.1 Experiment results
From Fig. 2(a), it could be found that in the two processes (heating and cooling), the \( C_P \) outside of the phase transformation region roughly overlaps. However, in the measurement of the second run, phase transformation occurs earlier than that of the first run. Thermal cycling may affect the temperature of phase transformation to a certain degree. Thermal cycling affects austenitic transformation start temperature \( (A_s) \) slightly, but it has a significant influence on the R phase and martensitic transformation start temperatures.

The \( C_P \) in the PC output includes the latent heat produced during phase transformation. The true \( C_P \) versus temperature relationship will be exposed if the up and down data caused by phase transformation are removed, as shown in Fig. 2(b). The \( C_P \) variation tendency versus temperature is different outside the temperature region of phase transformation during the heating process. Before phase transformation, \( C_P \) fluctuates to ascend. After phase transformation, however, \( C_P \) fluctuates to decrease. Then two different equations are needed
for the description of $C_p$ for austenite and martensite. Since the specific heat capacity is usually given by the function:

$$C_p = a + bT + cT^{-2},$$

this formula is adopted in the present paper for fitting the data of specific heat capacity with the method of least square.

The data of specific heat capacity of martensite are fitted by

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

(4)

The fitting result of the austenite specific heat capacity as follows:

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

(5)

This is different from Smith’s result. He showed a linear fitting function of the parent phase (austenite) based on their experiment ($C_p = 0.439 + 7.279 \times 10^{-5}T$), then extrapolated to the low temperature phase (martensite).

### 3.2.2 Calculation of debye temperature

At low temperature, the specific heat at constant volume ($C_v$) follows the 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 the lattice’s, 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

$$C_v = 9Nk \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D} \frac{x^4 e^x}{(e^x - 1)^2} dx,$$

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: $C_v \approx 1945 \left( \frac{T}{\theta_D} \right)^3 (J \text{ mol}^{-1} \text{K}^{-1})$, as for NiTi, $C_v \approx 36.7 \left( \frac{T}{\theta_D} \right)^3 (J \text{ g}^{-1} \text{K}^{-1})$.

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 to $C_v$ ($C_v \approx C_p$).

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

$$C_p \approx C_v \approx \beta T^3$$

(6)

Suppose the two curves govern by eq. (1) and eq. (3) smoothly meet at the point of inflection: $T_{m}$. So

$$\beta T_{m}^3 = 0.436 + 2.744 \times 10^{-4}T_{m} - 708.156T_{m}^{-2}$$

(7)

$$3\beta T_{m}^2 = 2.744 \times 10^{-4} + 1416.312T_{m}^{-3}$$

(8)

According to eq. (7) and eq. (8), $\beta$ and $T_{m}$ can be solved:

$$\beta = 1.27 \times 10^{-6}, \ T_{m} = 52 \text{ K}.$$ Therefore, at low temperature,

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

(9)
Because, \( C_V \cong 36.7 \left( \frac{T^3}{T_0^3} \right) \), so \( \theta_D = 3.32\beta^{-\frac{1}{2}} \).
In this way, the Debye temperature of NiTi can be obtained:
\( \theta_D = 306 \text{ K}, \) which is in agreement well with Kuentzler’s results.\(^{13}\)

### 3.2.3 Characteristics of \( C_P \)

In general, \( C_P \) of a material monotonously increases with increasing temperature. While \( C_P \) of the studied alloy having austenite phase decreases with increasing temperature, as shown in Fig. 2(b).

It is known that when allotropic transformation happens among metals, a certain regular change of \( C_P \) may be observed, for an example, the \( C_P \) of the high temperature phase (fcc) of Co increases with increasing temperature, as that of the low temperature phase (hcp) does.\(^{14}\) However, the \( C_P \) variations of Ti before and after transformation are different. Figure 2(c) shows the \( C_P \) curves of Ti and Ni (data from\(^{15} \) and\(^{16} \)). It can be seen that the peak value of \( C_P \) for Ti appears when \( \alpha \)-Ti (hcp) transforms into \( \beta \)-Ti (bcc) with increasing temperature, the values outside the temperature range of phase transformation show different variation tendency, which is similar to that of NiTi. So we can safely say, the \( C_P \) of NiTi is inherent to the characteristic displayed by Ti.

The inference may be somewhat explained by a two-sets-of-atoms model:\(^{17} \) one substructure is described as elastic, the other elastic in some limits, like an elastic sponge filled with paraffine.

As discussed above, the \( C_P \) of different phases of a metal or an alloy may exhibit same or different variation tendency, why? As we know, heat capacity reflects the crystal lattice vibration. The lattice will be unstable during phase transformation, the crystal structure will change, and the free energy of the whole system will tend to be on the lowest level. That is to say, when phases transform from one lattice type into another, the free energy of the system should be the lowest. Different lattice shows different vibration mode, which affects the free energy of the system, as well as the \( C_P \). Therefore, both the lattice type and the requirements of the lowest free energy may attribute to the same or different \( C_P \) variations of different phases.

\[
\begin{align*}
T^{i+1} &= AT^i + B, \\
A &= C_{\rho_0}\pi r^2 \rho_1/\Delta t/(2\pi r\alpha_0 + C_{\rho_1}\pi r^2\rho_1/\Delta t) \\
&= 1/(2\pi r\alpha_0 \Delta t/C_{\rho_1}\pi r^2 \rho_1 + 1) \\
B &= (I^2R + 2\pi r\alpha_0 T_0)/(2\pi r\alpha_0 + C_{\rho_1}\pi r^2\rho_1/\Delta t) \quad (10)
\end{align*}
\]

### 4. Application

Assuming the same thermal effect would be produced in the whole section of the wire owing to the electric resistance while the structural system were electrified, the wire can be considered as a heat source, and the temperature does not alter across the section of the wire. Now, two kinds of wires are considered, i.e., bare wires and wires with oxide film on their surface.

X-ray diffraction indicates,\(^{18} \) the oxide film on the NiTi wire surface is mainly TiO\(_2\), of which the mass density \( \rho_2 \) is equal to 4270 Mg/m\(^3\), the specific heat \( C_P \) is 7.14 J/g-K, and the conduction coefficient \( k \) is 8.16 W/m-K. The mass density \( \rho_1 \) of NiTi alloy is 6.5 Mg/m\(^3\), convective coefficient \( \alpha \) 20 W/m\(^2\)-K, SMA resistivity \( \rho_s \) = 1.02 × 10\(^{-6}\) Ωm, the diameter 0.5 mm, the thickness of the oxide film 0.05 mm, and the circumstance temperature \( T_s = 293 \text{ K} \). The above data are used for the following calculations.

As for the heating process, a simple deduction result is given as follows:

#### 4.1 Bare wire

The heat produced by electric current is equal to the heat absorbed by the wire plus the heat transferred with air. Thus, the following equations are obtained:

\[
\begin{align*}
T^{i+1} &= AT^i + B, \\
A &= C_{\rho_1}\pi r^2 \rho_1/\Delta t/(2\pi r\alpha_0 + C_{\rho_1}\pi r^2\rho_1/\Delta t) \\
&= 1/(2\pi r\alpha_0 \Delta t/C_{\rho_1}\pi r^2 \rho_1 + 1) \\
B &= (I^2R + 2\pi r\alpha_0 T_0)/(2\pi r\alpha_0 + C_{\rho_1}\pi r^2\rho_1/\Delta t) \\
&= (I^2R + 2\pi r\alpha_0 T_0)/(2\pi r\alpha_0 + C_{\rho_1}\pi r^2\rho_1/\Delta t) \quad (11)
\end{align*}
\]

As for the cooling process, the heat source term should be removed from the above equations.

In the calculation, the current values are taken to be 0.4 A, 0.6 A and 0.8 A. In the heating process, the time step is 1.0 s, while in the cooling process the value is −1.0 s. Thus time counts down after the wire is heated for 300 s, in this way, the curves comes back to its start point. The results are shown in Figs. 3(a) and (b).

Because the reverse martensite transformation is an endothermic process, there will be a step (shown an arrow A in Fig. 3(a)) in the heating process. After the phase transformation finishes, the temperature of NiTi wire arrives at a platform (Fig. 3(a)), which was caused by equilibrium between heating by electric and cooling by air convection. As shown

in Fig. 3(a), there exists an apparent step when the current value is 0.6 A. If the heating current is low of 0.4 A, the phase transformation will not occur in the alloy, consequently, there will be no step. However, if the current is intense (0.8 A), and the heating rate is high, the step will not be evident.

Figure 3(b) shows the temperatures of the wire with oxide film. Because the oxide film is thin, the temperature of the oxide is close to that of NiTi wire, so only the temperature of the wire is given. In this figure, it can be seen that the steps are less obvious than those in Fig. 3(a). The heating curves climb up steadily, and the temperature reaches a much higher level compared with that of the bare wire. The reason lies in that the oxide film impedes heat exchange of wire with air.

While in the cooling process, the fluctuation caused by
Fig. 3  Heating and cooling curves of two kinds of NiTi wires: (a) Bare wire and (b) Wire with oxide film.

phase transformation did not appear in the curves because the wire is too fine and the cooling rate is fast. The bare wire can efficiently transfer the heat to air, so the descending temperature curves are steeper than that of wire with oxide film.

Heat \( (Q) \) produced by electric current obeys the following relationship: \( Q = I^2 R t \), where \( I \), \( R \) and \( t \) is electric current, electric resistance and time, respectively. Different currents corresponding to the different heating rates. Calculation results indicate that phase transformation will be observed from the heating curve so long as the temperature reaches the phase transformation point. Higher heating rate or isothermal effect caused by oxide film will result in less prominent steps. Calculation errors would be small if an average value of heat capacity is adopted to calculate the temperature distribution of the NiTi wire at this time. On the contrary, the phase transformation can proceed sufficiently and the latent heat can deliver adequately if appropriate current (say 0.6 A) heated the wire. As a result, the temperature region of phase transformation will exhibit clearly in the heating curves, obvious error will occur in the calculation of the temperature distribution.

5. Conclusions

(1) The start and finish temperatures of austenite transformation increase with increasing heating rates. While the transformation temperatures of R phase and martensite decrease with the increase of the cooling rates. The transformation time follows the equation: \( \tau = \tau_0 + Ae^{-\frac{Q}{T}} \), i.e., the transformation time declines exponentially upon the heating rates. The existence of a minimum \( \tau_0 \) is the result of the equilibrium of the increase in driving force and in the strain energy.

(2) The curves of the specific heat capacity in the heating process roughly overlaps with that of in the cooling outside of the temperature region of phase transformation, but the variation tendency versus temperature for austenite and martensite are different. Before phase transformation, the specific heat capacity fluctuates to ascend, after phase transformation, however, fluctuates to decrease. The specific heat capacity of martensite and austenite follow the equation \( C_P = 0.436 + 2.744 \times 10^{-4}T - 708.156T^{-2} \) and \( C_P = 0.50 - 1.90 \times 10^{-4}T + 712.85T^{-2} \), respectively.

(3) Owing to the latent heat, there will be a step in the heating curve if the specific heat capacity was used in the calculation of the wire temperature. The step will be not obvious even if the wire was enclosed by a thin oxide film. In the cooling process, the fluctuation disappears. Errors would be small if an average value of the heat capacity were adopted to calculate the temperature field of the NiTi wire under conditions of higher heating rate or isothermal effect caused by oxide film. On the contrary, obvious error will occur if phase transformation can proceed sufficiently and the latent heat can deliver adequately if the wire were heated by an appropriate current.

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REFERENCES