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Multiple steady state phenomenon in martensitic transformation①

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[Abstract] Based on the basic facts that the martensitic transformation is a physical phenomenon which occurs in non-equilibrium conditions and there exists the feedback mechanism in the martensitic transformation, the dynamical processes of the isothermal and athermal martensitic transformations were analyzed by using nonlinear theory and a bifurcation theory model was established. It is shown that a multiple steady state phenomenon can take place as austenite is cooled, and the transitions of the steady state temperature between the branches of stable steady states can be considered the transformation from austenite to martensite. This model can estimate the starting temperature of the martensitic transformation and explain some experimental features of the martensitic transformation such as the effects of cooling rate, fluctuation and austenitic grain size on the martensitic transformation.

[Key words] martensitic transformation; multiple steady states; steady state transition
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1 INTRODUCTION

The martensitic transformation has been one of the most active fields in condensed matter physics for many years. A number of theoretical models have been proposed to understand the physical nature of the martensitic transformation[1~6]. However, as yet there is not a general satisfying theoretical description for the martensitic transformation.

Pati and Cohen[1] once pointed out that there existed important nonlinear changes in the martensitic transformation. Since it is usually difficult to study a nonlinear physical phenomenon, the studies of the martensitic transformation by using nonlinear theory have been hardly reported. In fact, non-equilibrium thermodynamics and nonlinear theories developed by Prigogine et al have provided very useful tools for describing nonlinear phenomena. In the last decades of the 20th century, many progresses in describing various nonlinear phenomena in physics, chemistry, biology, and even sociology by using nonlinear theory have been made[7, 8]. In these works, it has been confirmed that at a point far from the equilibrium conditions, the feedback mechanism such as autocatalytic process may cause a multiple steady state phenomenon in a system, which makes the transition between the branches of stable steady states possible. This transition can be understood as the occurrence og a transformation. Recently, Chao and Chen successfully set up a bifurcation theory model for the glass transition by using nonlinear dynamics and explained the features of the glass transition well[9, 10, 24]. Inspired by these works and based on the basic facts that there exists strongly autocatalytic process in the transformation from austenite to martensite and the austenite-to-martensite reaction is usually far from the equilibrium conditions between austenite and martensite, in present paper, we are to set up a new physical picture for the martensitic transformation by using nonlinear theory.

2 THEORETICAL MODEL

The martensitic transformations are well known to be classified into two distinct classes: athermal and isothermal. In the general experiments of the isothermal martensitic transformation, austenite is firstly quickly cooled from an austenitizing temperature, the cooling rate being fast enough to maintain the fully austenitic state at low temperature, and then austenite is kept isothermally at different temperatures. The initiation and the progress of the transformation are followed by the changes in some physical parameters such as electrical resistance. Indeed, such an experimental procedure includes the process of temperature change. In order to set up a unified bifurcation theory model for describing two kinds of the martensitic transformations by using nonlinear theory, we assume that in the isothermal martensitic transformation, austenite is slowly continuously cooled from the austenitizing temperature, the cooling rate being slow enough to make the austenite-to-martensite reaction start on cooling. The time of austenite being kept in each temperature interval is inversely proportional to cooling rate.

For obtaining the steady state equation for de-

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scribing the process of the martensitic transformation, it is necessary to determine some state parameters which can describe the transformation from austenite to martensite. The martensitic transformation during cooling includes two physical processes; one is nucleation and growth which results in the increase of the martensite volume fraction x, the other is heat transfer which results in the change of austenitic temperature T. So, the state of the transformation system may be defined by x and T. However, x is related to T. So, in fact, we can determine the state of the system by only using the austenitic temperature T.

In the transformation, two factors resulting in the change of austenitic temperature are the latent heat released by the martensitic formation and the heat transferring from matrix to circumstance. So the temperature change rate equation of austenite can be written as[10, 11]

$$\mathrm{d}T/\mathrm{d}t = (L/c_p)(\mathrm{d}x/\mathrm{d}t) - h(T - T_e) \qquad (1)$$

where c_p is the heat capacity, L is the heat of transformation, $\mathrm{d}x/\mathrm{d}t$ is the martensitic transformation rate, T_e is the circumstance temperature and h is the cooling ability coefficient which is proportional to the cooling rate. Since the martensitic formation kinetics in the isothermal and athermal martensitic transformations are different, we will analyze their steady state solutions, respectively.

2.1 Steady state analysis of isothermal martensitic transformation

In the isothermal martensitic transformation, nucleation rate n is expressed by[1]

$$n = n_i \gamma \exp(-\Delta W/RT) \qquad (2)$$

where n_i is the number of embryos initially present per unit volume, γ is the lattice vibration frequency and ΔW is the activation energy for the nucleation of martensite. According to the works of Cohen et al[1, 2, 12], the activation energy ΔW for the isothermal nucleation is linearly related to the chemical driving force ΔG:

$$\Delta W = B + C\cdot\Delta G \qquad (3)$$

with B and C being constants. $B = 7.2\times10^{22}\times((\delta r_e)^{3/2}/A^{1/2}))\,\mathrm{mol}^{-1}$ and $C = 2.4\times10^{22}(\delta/A)\cdot r_e^2\,\mathrm{mol}^{-1}$, δ is the interfacial energy, A is the strain energy factor, and r_e is the embryo radius.

The transformation rate $\mathrm{d}x/\mathrm{d}t$ is given by

$$\frac{\mathrm{d}x}{\mathrm{d}t} = n\cdot\bar{V} \qquad (4)$$

where $\bar{V}$ is mean volume per martensitic plate. Combing Eqns. (1) ~ (4), we have

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{L n_i \bar{V}\gamma}{c_p}\cdot\exp\left[-\frac{B + C\cdot\Delta G}{RT}\right] - h(T - T_e) \qquad (5)$$

Letting $\frac{\mathrm{d}T}{\mathrm{d}t} = 0$ and $\alpha_t = c_p\cdot h$, we can obtain a steady state equation met by austenitic temperature in the isothermal martensitic transformation:

$$\frac{L n_i \bar{V}\gamma}{\alpha_t}\cdot\exp\left[-\frac{B + C\cdot\Delta G}{RT_s}\right] - T_s + T_e = 0 \qquad (6)$$

where T_s is the steady state temperature. The solution of Eq. (6) depends on the values of the parameters in Eq. (6). However, it is not easy to know the values of the parameters exactly for an alloy with data now available. According to Refs. [1, 12, 13], some approximate data are adopted for calculation in order to show the new physical implications in the transformation from austenite to martensite. Taking Fe-23%-Ni-3.1%Mn (mole fraction) as an example, we use a set of data as follows: $L = 2.5\,\mathrm{kJ/mol}$, $n_i = 10^7\,\mathrm{cm}^{-3}$, $\gamma = 10^{13}\,\mathrm{s}^{-1}$, $\bar{V} = 10^{-9}\,\mathrm{cm}^3$, $r_e = 190\,\mathrm{Å}$, $\delta = 120\times10^{-7}\,\mathrm{J/cm^2}$, $A = 2.1\times10^3\,\mathrm{J/cm^3}$; ΔG is known as a function of temperature and composition from the work of Imai and Izumiyama[13]. The numerical solutions of Eq. (6) are shown in Fig. 1. It is shown that for a given cooling ability α_t, three steady state temperatures may appear in the transformation system corresponding to each circumstance temperature in some range of T_e, i.e. a multiple steady state phenomenon occurs[14]. Among three steady states, two are stable and one is unstable.

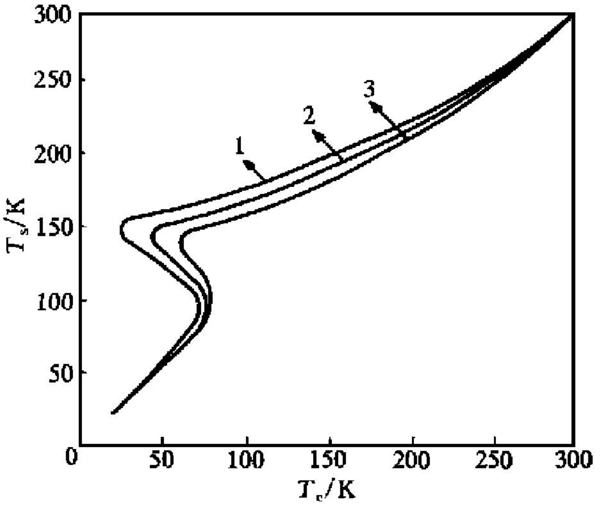

Fig. 1 Numerical solution of Eq. (6) for Fe-23%Ni-3.1%Mn (mole fraction)

1 — $\alpha_t = 6.6\times10^{-3}$ J/(mol·K·s);

2 — $\alpha_t = 8.2\times10^{-3}$ J/(mol·K·s);

3 — $\alpha_t = 10.0\times10^{-3}$ J/(mol·K·s)

2.2 Steady state analysis of athermal martensitic transformation

The kinetics of the athermal martensitic transformation is different from that of the isothermal martensitic transformation. In the athermal martensitic transformation, the transformation rate $\mathrm{d}x/\mathrm{d}t$ in the initial stage may be expressed by[16]

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \bar{V}\varphi\cdot\frac{\mathrm{d}\Delta G}{\mathrm{d}T}\cdot\dot{T} \qquad (7)$$

where φ is a constant and $\dot{T}$ is the cooling rate. Combining Eqns. (1) and (7), we have

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{L\bar{V}\varphi}{c_p} \cdot \frac{\mathrm{d}\Delta G}{\mathrm{d}T} \cdot \dot{T} - h(T - T_e) \qquad (8)$$

Since h is proportional to the cooling rate $\dot{T}$, $h = \rho \cdot \dot{T}$, in which ρ is a constant. Letting $\mathrm{d}T/\mathrm{d}t = 0$ and $\beta = c_p \cdot \rho$, we can obtain a steady state equation met by austenitic temperature in the athermal martensitic transformation:

$$\frac{L\bar{V}\varphi}{\beta} \cdot \frac{\mathrm{d}\Delta G}{\mathrm{d}T_s} - T_s + T_e = 0 \qquad (9)$$

Since Eq. (9) includes the temperature derivation of chemical driving force, it is necessary to know the exact dependence of chemical driving force on temperature, especially in the range of low temperature. According the third law of thermodynamics effect, $\mathrm{d}\Delta G/\mathrm{d}T_s$ tends to be zero at 0 K. Taking Fe-30. 8% Ni(mole fraction) alloy as an example because of the availability of the exact dependence of chemical driving force on temperature below 300 K in this alloy. We combine the works of Refs. (17) and (18), and use a set of approximate data as follows[4, 10, 18]: $L = 2.4$ kJ/mol, $\bar{V}\varphi \sim 0.0045$ and $\beta \sim 0.2$. The numerical solutions of Eq. (9) are shown in Fig. 2. The multiple steady state phenomenon also appears during cooling.

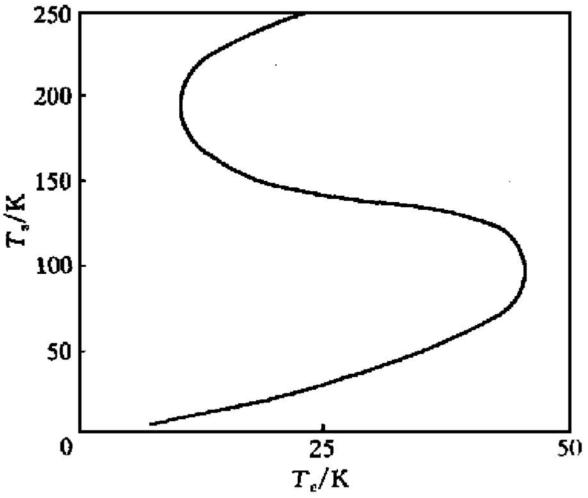

Fig. 2 Numerical solution of Eqn. (9) for Fe-30. 8% Ni(mole fraction)

2. 3 Physical implications of multiple steady state phenomenon

In order to discuss the physical implications of Figs. 1 and 2 more clearly, we take one of the curves of Figs. 1 and 2 as an example and slightly deform it, as schematically shown in Fig. 3. According to linear stability theory[8], the portions of curve labeled *ABCD* and *EFG* are the branches of stable steady states, whereas the portion of curve labeled *DE* is the branch of unstable steady states. When austenite is cooled from an austenitizing temperature by a cooling circumstance with the temperature being T_e, the steady state temperature T_s of austenite continuously changes along the curve *ABCD*. At the beginning, the steady state temperature T_s is able to follow the change of T_e, and the transformation system is in stable state. When T_e decreases to T_e^D, the steady state temperature of austenite is T_s^D. At this point, the transformation system is in a critical state, $(\mathrm{d}T_s/\mathrm{d}T_e) \rightarrow \infty$ at this time, any slight decrease of T_e will cause the transformation system to jump from *D* to *F*, i. e. a steady state temperature transition occurs. According to the work of Glansdorff and Prigogine[8], this behavior of the steady state temperature transition will correspond to the appearance of a new phase. To the authors' knowledge for the martensitic transformation, we suggest that this phenomenon of the steady state temperature transition can be considered the transformation from austenite to martensite. So, the temperature T_s^D at which the steady state temperature transition occurs can be understood as the starting temperature of the austenite-to-martensite reaction T_s^M. From Figs. 1 and 2, we know that this temperature is about 140 K or 200 K, respectively, which is very close to the nose temperature of the isothermal martensitic transformation in Fe-23% Ni-3. 1% Mn (148 K)[1] and the starting temperature of the athermal martensitic transformation in Fe-30. 8% Ni (196 K)[18].

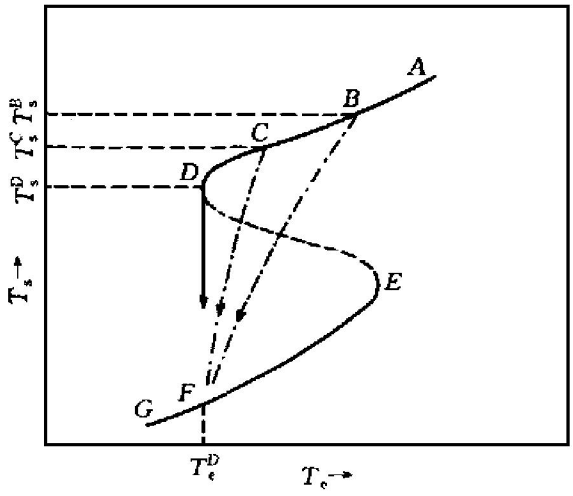

Fig. 3 Schematic curve of steady state solution

In the process of solving Eqns. (6) and (9), all the data and equations are derived from the experimental and theoretical results of the transformation from austenite to martensite. So, the steady state curves in Figs. 1 and 2 only represent the transformation process from austenite to martensite.

3 DISCUSSION

3. 1 Effects of cooling rate and fluctuation on martensitic transformation

In the isothermal martensitic transformation, it can be seen from Fig. 1 that the measured T_s^D increases with decreasing cooling rate. However, this effect is very small. If further considering the effect of fluctuation on the isothermal martensitic transformation, the effect that the starting temperature of the martensitic transformation increases with decreasing cooling rate will increase. Many scientists have pointed out that fluctuation plays an important role in the isothermal martensitic transformation[13, 22]. If considering the effect of fluctuation, the transition path of the steady state temperature will change, as indicated by the dash and dot lines in Fig. 3[15]. A large fluctuation may induce a transition between the branches of the stable steady states to occur at points considerable away from the critical stability point (D), which results in the elevation of the temperature of the steady state transition, i. e. the increase of the starting temperature of the martensitic transformation. The transition between the branches of the stable steady states is more prior to the critical stability point, the larger the fluctuation. When austenite is cooled from an austenitizing temperature, the slower the cooling rate, the longer the time of the austenite being kept in each temperature interval, and the larger the possibility of the large fluctuations appearing in each temperature interval. Due to the cooling ability α_t being proportional to cooling rate, the change of the real transition paths of the steady state temperatures with cooling rate in the isothermal martensitic transformation is indicated by the dotted lines in Fig. 4 ($H \rightarrow I$ and $J \rightarrow K$). With increasing cooling rate, the effect of fluctuation becomes smaller and smaller, and the transformation system comes closer to the critical stability point before making the transition. The change of the starting temperature of the austenite-to-martensite reaction with cooling rate is schematically shown in Fig. 5. This corresponds to, above the nose temperature, the increase of the incubation period of nucleation with increasing experimental temperature. If further increasing the cooling rate, when the cooling rates $\dot{T}$ exceed a critical value $\dot{T}_c$, the transformation system has only steady state temperature corresponding to each circumstance temperature, i. e. the multiple steady state phenomenon disappears, as schematically shown in Fig. 4. So, the transformation from austenite to martensite can not occur on cooling. These results are consistent with the experimental observations.

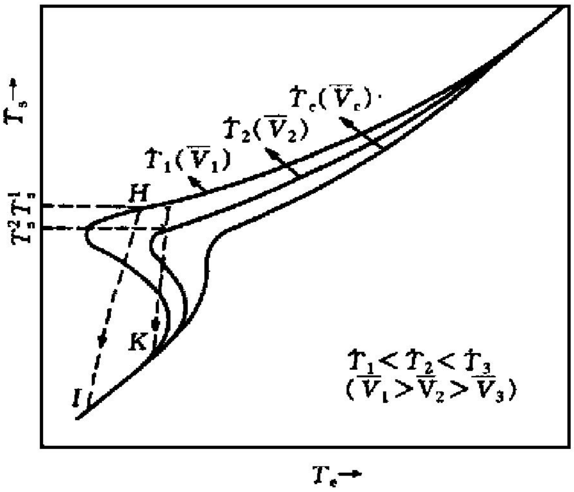

Fig. 4 Schematic change of numerical solution of steady state equations with cooling rate $\dot{T}$ or martensitic plate volume $\overline{V}$

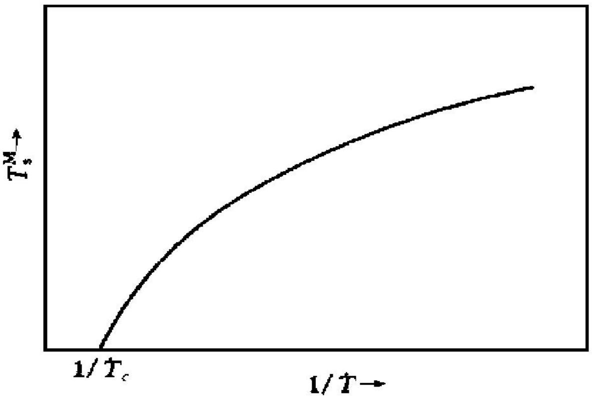

Fig. 5 Schematic change of starting temperature of isothermal martensitic transformation T_s^M with cooling rate $\dot{T}$

In the athermal martensitic transformation, the starting temperature of the martensitic transformation is not sensitive to cooling rate, especially when the cooling rate is not too rapid[3, 19]. In general, the dependence of chemical driving force on temperature is not closely related with the cooling rate, moreover, Eqn. (9) does not include the term of cooling rate. So, the temperature of steady state transition calculated from Eqn. (9) is independent of cooling rate. However, when the cooling rate is extremely rapid, it is observed that the starting temperature of the martensitic transformation slightly changes with increasing cooling rate in the experiments of the athermal martensitic transformation[19]. The reason for this experimental phenomenon would be that the dependence of chemical driving force on temperature will change with cooling rate when the cooling rate is extremely rapid, which has been confirmed by the work of Sakamoto[23]. So, the starting temperature of the athermal martensitic transformation calculated from Eqn. (9) will change with the cooling rate.

3.2 Effect of austenitic grain size on martensitic transformation

Experimental results show that the decrease of austenitic grain size can repress the transformation from austenite to martensite[20, 21]. In present model, Eqns. (6) and (9) include the mean volume of martensitic plate $\overline{V}$ which is dependent on austenitic grain size. The finer the austenitic grain size, the smaller the mean volume of martensitic plate[1, 17]. In fact, the effect of austenitic grain size on the martensitic transformation has been considered in this model. For a given cooling rate, if the nucleation rates of the isothermal and athermal martensitic transformations are not affected by austenitic grain size, the schematic change of the numerical solutions of Eqns. (6) and (9) with the martensitic plate volume is shown in Fig. 4. When the martensitic plate volume $\bar{V}$ is smaller than $\bar{V}_c$, the multiple steady state phenomenon disappears, and the martensitic transformation can not occur on cooling. Indeed, when the austenitic grain size is very small, the reduction of the austenitic grain size will result in less autocatalytic effect in the nucleation. The nucleation rate of martensite will change with the austenitic grain size. This will accelerate the disappearance of the multiple steady state phenomenon and result in the change of the steady state transition temperatures calculated from steady state equations.

It has been confirmed that the incubation time of the isothermal martensitic transformation is proportional to $1/d^3$ when the change of austenitic grain size does not affect the nucleation rate of martensite in some range of austenitic grain size, in which d is austenitic grain size[19]. Such experimental observations can be interpreted well by using the present model. The mean volume per martensitic plate $\bar{V}$ in Eqn. (6) is controlled by the austenitic grain size d. In a given range of austenitic grain size, $\bar{V} \propto d^3$[1]. The α_t in Eqn. (6) is proportional to the cooling rate $\dot{T}$. When $\bar{V}/\alpha_t$ is equal to a constant in Eqn. (6), i. e. $d^3 \cdot (\dot{T}^{-1})$ is equal to a constant, the solutions of steady Eqn. (6) will be independent of the austenitic grain size d and cooling rate $\dot{T}$. This indicates that if the austenitic grain size is decreased, only when the cooling rate is simultaneously decreased, the multiple steady state phenomenon can appear in the numerical solutions of Eqn. (6) and the martensitic transformation can take place on cooling. However, $1/\dot{T}$ corresponds to the incubation time of the isothermal martensitic transformation, as indicated in Fig. 5. So, the incubation time of the isothermal martensitic transformation is proportional to $1/d^3$.

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