

## Phenomenological description of thermal and isothermal martensite formation in alloys

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A THERMAL and isothermal martensite formation in alloys is described at the subzero temperature range from the phenomenological point of view. Transformation kinetics for the athermal and isothermal martensitic transformation are presented. Numerical simulation is carried out for such a process of the athermal martensite formation, followed by the isothermal run in order to explain the effect of the holding temperature and the initial athermal martensite on the subsequent isothermal martensitic formation. The results explain qualitatively the experimental observations.

W ujęciu fenomenologicznym omówiono procesy atermicznego i izotermicznego powstawania martenzytu w stopach utrzymywanych w zakresie temperatur ujemnych. Przedstawiono kinetykę przemiany martenzytycznej w warunkach atermicznych i izotermicznych. Wykonano symulację numeryczną takiego procesu, w którym po przemianie atermicznej następuje faza izotermiczna, dla wyjaśnienia wpływu temperatury i początkowej fazy atermicznej na następującą po niej przemianę izotermiczną. Uzyskane wyniki pozwalają wyjaśnić w sposób jakościowy rezultaty eksperymentalne.

В феноменологическом подходе обсуждены процессы атермического и изотермического возникновения мартенсита в сплавах, получаемых в области отрицательных температур. Представлена кинетика мартенситного превращения в атермических и изотермических условиях. Проведена численная имитация такого процесса, в котором после атермического превращения наступает изотермическая фаза, для выяснения влияния температуры и начальной атермической фазы на следующее после ней изотермическое превращение. Полученные результаты позволяют выяснит ь качественным образом экспериментальные результаты.

### 1. Introduction

THE RETAINED austenite in the metals, which gradually transforms to the martensite even at the room or higher temperature and, as a result, often has a negative effect on their thermomechanical behavior, can be reduced by promoting the isothermal martensitic transformation at the temperature range below zero [1]. The process is called the subzero treatment, and is often used in the metal industries to achieve the stabilization of the micro-structures in the hardened steels or the high speed steels [2,3]. The study on the thermomechanical transformation behaviors of metals in the process is, therefore, one of the themes to be intensively investigated in the "Metallo-Thermomechanics [4]".

The isothermal martensitic transformation in certain metals also attracts attention since it induces a non-negligible superplastic deformation under the condition of small applied load, even in the presence of residual stresses [5].

The kinetics of isothermal martensitic transformation was examined experimentally in such metals as Fe-Ni-Cr, Fe-Ni-Mn and Fe-Ni-C alloys [6-11]. Formation of the isothermal martensite is reported, as in the case of the usual diffusion-type transformation, to be well pictured in the temperature (linear scale) — time (logarithmic scale) plane with the fraction of martensite as a parameter, which is called the time-temperature-transformation (T-T-T) diagram or simply the C-curve. The martensite formed diffusionlessly, or athermally in the terminology of metallurgy, has a strong influence on the subsequent isothermal run. Some researchers reported that the applied tensile stress promoted the isothermal transformation [1].

The present author has proposed kinetics of the athermal martensitic transformation to describe phenomenologically the transformation-induced plasticity (TRIP) [13], and of the isothermal transformation of metals, in order to investigate the thermomechanical aspects of the transformation superplasticity [13—15]. In this study the kinetics is applied to the martensitic transformation under the general temperature history by decomposing the total fraction of martensite into the athermal and the isothermal parts. The interaction between the isothermal and athermal martensite formations is discussed.

## 2. Phenomenological model of martensitic transformation

We assume that the volume fraction of martensite  $0 \leq \xi \leq 1$  can be decomposed into the athermal part  $\xi_a$  and the isothermal part  $\xi_i$ , and that the relation

$$(2.1) \quad \xi = \xi_a + \xi_i$$

holds during the whole process. Kinetics of each component may be first expressed generally as [13]

$$(2.2) \quad \begin{aligned} \dot{\xi}_a &= \tilde{\Xi}_a(\xi_a, \xi_i, \theta, \dot{\theta}), \\ \dot{\xi}_i &= \tilde{\Xi}_i(\xi_a, \xi_i, \theta, \dot{\theta}), \end{aligned}$$

where  $\theta$  and  $\dot{\theta}$  stand for the temperature and its time rate, respectively. The argument  $\xi_i$  in the kinetics of athermal transformation (2.2)<sub>1</sub> and  $\xi_a$  in the kinetics of isothermal transformation (2.2)<sub>2</sub> represent the fact that the athermal and isothermal martensite formation may have influence on each other. The effect of the stress or strain induced in the martensite [1, 16, 17] is not considered here.

Experiments reveal that the athermal martensitic transformation is diffusionless in nature [1]. Kinetics (2.2)<sub>1</sub> should, therefore, be reduced for a temperature history  $\theta(t)$  to the form

$$(2.3) \quad \xi_a = \Xi_a(\theta),$$

if the dependence of  $\xi_i$  is disregarded for simplicity. In this study we examine a simple case in which Eq. (2.3) reads as [17 – 19]

$$(2.4) \quad \xi_a = C_a[1 - \exp\{a(M_s - \theta)\}],$$

where the material parameter  $a$  is assumed to be constant throughout the process, while  $M_s$  denotes the temperature at which the formation of athermal martensite starts. The material parameter  $0 < C_a \leq 1$  is introduced to embody the experimental fact that the martensitic transformation is not always complete in the athermal process. It should be noted that kinetics (2.4) holds under the condition

$$(2.5) \quad \begin{aligned} a(M_s - \theta) &\leq 0, \\ \dot{\xi}_a &= (C_a - \xi_a)a\dot{\theta} \geq 0. \end{aligned}$$

If we, as usual in metallurgy, understand that the transformation is almost completed when  $\xi_a$  reaches  $0.99C_a$ , we have a relation

$$0.99 = 1 - \exp\{a(M_s - M_f)\},$$

where  $M_f$  denotes the temperature at which the athermal martensite formation is practically completed. The relation yields

$$(2.6) \quad a = -2(\ln 10)/(M_s - M_f).$$

Since  $M_s > M_f$  for the actual alloys, Eq. (2.6) means  $a < 0$ . This, together with Eq. (2.5), shows that kinetics (2.4) holds only for the temperature history below  $M_s$  with  $\dot{\theta} \leq 0$ .

Contrary to the athermal process, the kinetics of isothermal martensitic transformation (2.2)<sub>2</sub> remains to be governed by diffusion-type equation. Recently the present authors proposed a transformation kinetics in the isothermal process [13, 19], which is written in the present context as

$$(2.7) \quad \begin{aligned} \dot{\xi}_i &= n\{D\Pi(\theta)\}^{1/n} \left(\ln \frac{C_i}{C_i - \xi_i}\right)^{(n-1)/n} (C_i - \xi_i), \\ \Pi(\theta) &= V \left(\frac{T^u - \theta}{W^u}\right)^{\lambda^l} \left(\frac{\theta - T^l}{W^l}\right)^{\lambda^l}, \end{aligned}$$

for  $T^l \ll T^u$ , where  $n$ ,  $T^u$ ,  $T^l$ ,  $W^u$ ,  $W^l$ ,  $\lambda^u$  and  $\lambda^l$  are the material parameters. The material parameter  $V = 1 \text{ [s}^{-n}\text{]}$  is introduced to convert the unit. The upper and the lower bound temperatures  $T^u$  and  $T^l$  determine the temperature range where the isothermal martensitic transformation takes place. The temperature ranges of isothermal and athermal transformations vary from the alloy to the alloy. The contents of alloy is one of the important factors to be considered. In fact, experiments [9] revealed that  $T^u$  is lower than  $M_s$  in Fe-Ni-Cr alloys, when the content of Ni is small. The order is, however, reversed when the Ni content becomes large. The material parameter  $D$ , which has been introduced to evaluate the effect of applied stress, may be taken as a unit in this study. The material parameter  $0 < C_i \leq 1$  represents, as  $C_a$  in the athermal process, the maximum value of the fraction attainable in the isothermal process. According to the experimental results [6], the formation of isothermal martensite is evidently influenced by the athermal martensite formed so far. The material parameter  $C_i$  may, therefore, be a function of the fraction of athermal martensite,  $\xi_a$ . We note that the parameters  $C_a$  and  $C_i$  must always be chosen such that  $0 < C_a + C_i \leq 1$  holds. The parameter  $n$  represents the mechanism of nucleation [20]. In the isothermal martensitic transformation its value is reported to be smaller than the values taken in the Johnson-Mehl transformation kinetics [8, 15]. Small value of  $n$ , together with the introduction of the material parameter  $C_i$ , enables us to describe the slow rate of actual isothermal martensite formation. Validity of kinetics (2.7) has successfully been shown by the same author for the  $A_3$ -transformation in pure iron [14, 15], as well as for the isothermal martensitic transformation in Fe-Ni-Mn and Fe-Ni-Cr alloys [19].

It should be noted that for a constant temperature history  $\theta(t) = T$ , Eq. (2.7) with  $D = 1$  can be solved to yield

$$(2.8) \quad \xi_i(t) = C_i \left( \left[ 1 - \exp \left[ - \{ \Pi(\theta) \}^{1/n} t + \left( \ln \frac{C_i}{C_i - {}_0\xi_i} \right)^{1/n} \right]^n \right) \right),$$

where  ${}_0\xi_i$  denotes the initial value of  $\xi_i$ .

### 3. Numerical illustration

In order to demonstrate the applicability of the theory developed in the previous section, some numerical illustrations are shown below.

The first example: The specimen is uniformly cooled from a temperature above the values  $M_s$  and  $T^u$  to another temperature  $T$  below them, and then is

**Table 1. Material parameters.**

[243]

${}_a C$	$\alpha$	$\beta$	$^{\circ}\text{C}$		$^{\circ}\text{C}$		$\lambda^I$	$\lambda^u$	$n$	$^{\circ}\text{C}$		$^{\circ}\text{C}^{-1}$
			$T^I$	$T^u$	$W^I$	$W^u$				$M_f$	$M_s$	$a$
0.21	0.25	-0.8	-250	0	310	350	10	2	1.2	-194.5	-30	-0.028

exposed to the temperature. The cooling rate is chosen large enough to make the amount of isothermal martensite formed in the cooling process negligibly small. In other words, the isothermal process practically starts when the holding temperature is reached.

The amount of fraction obtained in the cooling process is determined as a function of the holding temperature by means of Eq. (2.4) with  $\theta = T$ . And Eq. (2.7) governs the isothermal martensitic transformation at  $\theta = T$ . We examine the case in which the material parameter  $C_i$  is simply expressed as

$$(3.1) \quad C_i = \alpha + \beta \xi_a$$

For the material parameters tabulated in Table 1, which are chosen to simulate qualitatively the experimental observations in Fe-Cr-Ni alloy by Kulin and Speich [6], the progress of martensitic transformation is calculated as shown in Fig. 1. The curve at  $t = 0$  s is just a distribution of the athermal martensite determined from Eq. (2.4). The fraction approaches its maximum values  $C_i + C_a$  at  $t = 7200$  s, and the transformation almost stops. At the temperature levels above  $M_s$ , only the isothermal martensite is produced.

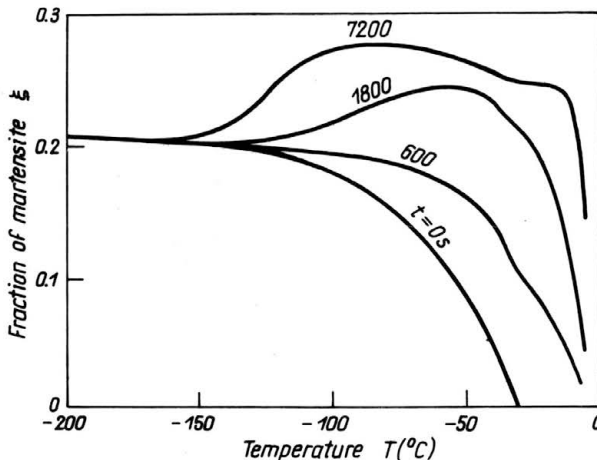


FIG. 1. Effect of holding temperature on formation of martensite.

Progress of the isothermal run is sketched in Fig. 2. The temperature level around  $-35^{\circ}\text{C}$ , at which the highest fraction is observed at all times, corresponds to the nose of the C-curve.

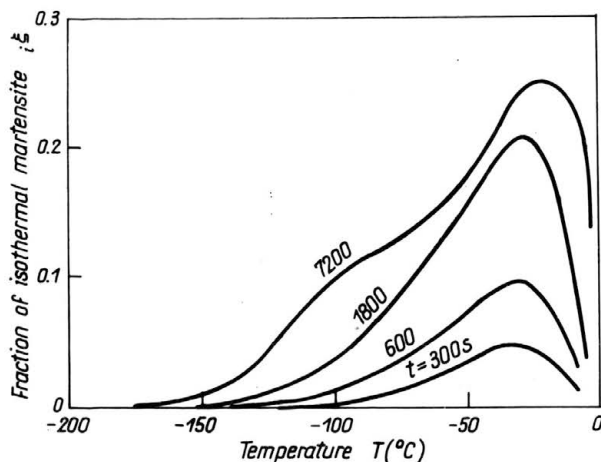


FIG. 2. Effect of holding temperature on formation of isothermal martensite.

Figure 3 shows the total amount of martensite and its components as a function of the holding temperature. The maximum amount of the isothermal martensite, 0.25 in this case, is attained above  $M_s$ , which, together with the whole profile of the curves, agrees with the experimental result.

Figure 4 illustrates the result of Fig. 1 in the T-T-T diagram. The horizontal lines on the shorter time side represent the formation of the athermal martensite below  $M_s$ . As the time progresses, the isothermal part  $\xi_i$  increases, and the lines gradually rise up to join the isothermal C-curves above  $M_s$ .

The amount of athermal martensite present at the start of isothermal transformation varies from 0 (at  $M_s$  point) to 0.208 (at  $-196^\circ\text{C}$ ), as illustrated by the  $\xi_a$ -curve in Fig. 3. The effect of this amount on the subsequent isothermal transformation is estimated as the second example of the numerical calculation. The specimen is first cooled to  $-196^\circ\text{C}$  to produce 0.208 of initial athermal martensite, and then up-quenched to a holding temperature  $T$  to run the isothermal test. It should be noted that the amount of initial athermal martensite is larger than that in the first example at all levels holding temperature. The fraction obtained after 7200 s of isothermal run is plotted as a function of  $T$  in Fig. 5. The maximum amount of  $\xi_i$  is 0.083 in this case. Comparison of Figs. 3 and 5 tells us that the theory confirms the experimental observation that the initial athermal martensite restrains the subsequent isothermal martensitic transformation.

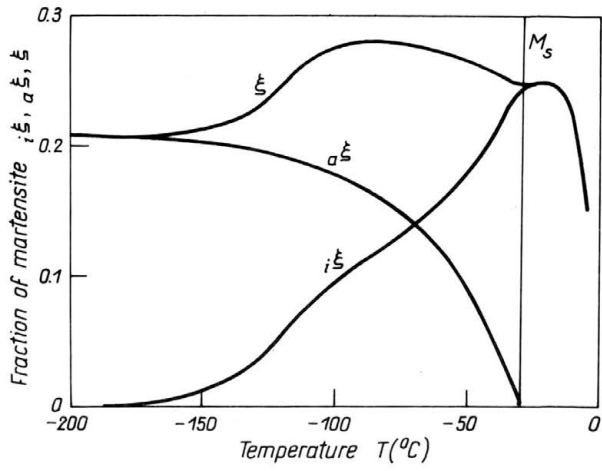


FIG. 3. Final amount of total, athermal and isothermal martensites.

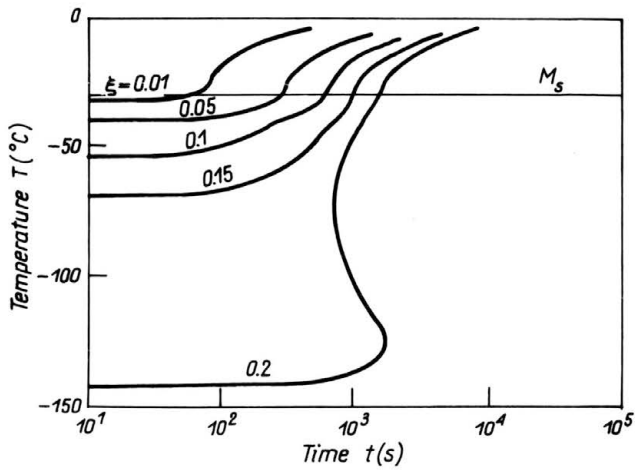


FIG. 4. T-T-T diagram.



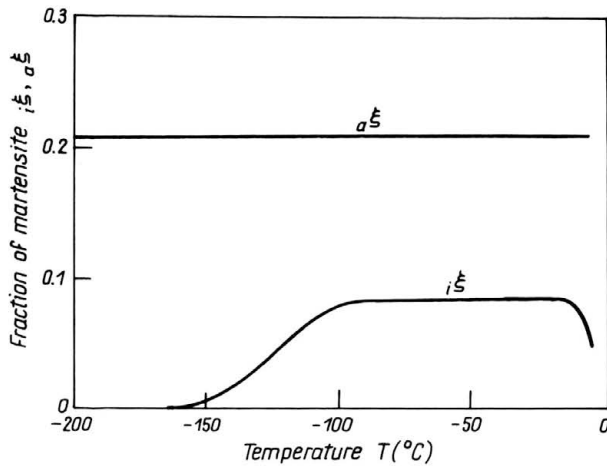


FIG. 5. Effect of initial athermal martensite on subsequent isothermal run.

Estimation of the thermomechanical variables: stress, strain and deformation, induced in the alloys in the subzero process (during the thermal and isothermal martensitic transformation) is a subject of further study.

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