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SELECTING A PHASE-DIAGRAM APPROXIMATION AND A MODEL OF THE DISAPPEARANCE OF MARTENSITE CRYSTALS FOR SHAPE MEMORY ALLOYS*

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A micromechanical model is used here to construct constitutive relations for the phase diagram of shape memory alloys. We propose an approximation of the phase diagram that, within the framework of the model, improves on known approximations in its description of forward and orientational transformations. We also propose another model to account for the disappearance of martensite crystals. These models can be used to describe normal and reverse manifestations of shape memory.

1. Shape memory alloys (SMA) have mechanical properties that differ sharply from those of ordinary metallic materials [1, 2]. These differences are related to thermoelastic martensitic (phase) transformations that occur in the alloys with a change in temperature and (or) stress [3]. The transformations involve the nucleation (disappearance) and growth (contraction) of martensite crystals in an austenite phase. In light of this, a key element in describing the behavior of SMAs is approximation of the phase diagram, i.e. the dependence of the volume fraction of martensite on temperature and stress in the forward and reverse transformations. For constant stresses, the phase diagram has the form shown in Fig. 1. Here, M_1 and M_2 are the temperatures at which the forward reaction begins and ends, while A_1 and A_2 are the same for the reverse reaction.

Functions approximating the sides of the phase diagram can be represented in the form

$$q = f_1(T, M_1, M_2), \qquad q = f_2(T, A_1, A_2), \tag{1.1}$$

where the characteristic temperatures M_1, M_2, A_1, and A_2 generally depend on the acting stresses [1].

The following linear relations were used in [1]

$$f_1(T, M_1, M_2) = \frac{M_1 - T}{M_1 - M_2}, \qquad f_2(T, A_1, A_2) = \frac{A_2 - T}{A_2 - A_1}. \tag{1.2}$$

In [4], preference was given to the exponential functions

$$f_1(T, M_1, M_2) = 1 - 10^{2\frac{M_1 - T}{M_2 - M_1}}, \qquad f_2(T, A_1, A_2) = 10^{2\frac{A_1 - T}{A_2 - A_1}}. \tag{1.3}$$

The authors of [5] used an approximation of the form

$$\begin{aligned} f_1(T, M_1, M_2) &= 0.5\left[\cos\left(\pi \frac{T - M_2}{M_1 - M_2}\right) + 1\right], \\ f_2(T, A_1, A_2) &= 0.5\left[\cos\left(\pi \frac{T - A_1}{A_2 - A_1}\right) + 1\right]. \end{aligned} \tag{1.4}$$

Here, we propose to use the following approximation:

$$\begin{aligned} f_1(T, M_1, M_2) &= \cos\left[\frac{\pi}{2}\left(\frac{T - M_2}{M_1 - M_2}\right)\right], \\ f_2(T, A_1, A_2) &= \cos\left[\frac{\pi}{2}\left(\frac{T - A_1}{A_2 - A_1}\right)\right]. \end{aligned} \tag{1.5}$$

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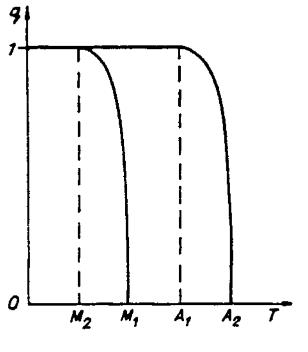

Fig. 1

Approximation (1.2) does not describe the saturation process that occurs during the forward transformation as q approaches unity. This process is accounted for in the other approximations. The graphs of the dependence of q on T for the forward and reverse transformations cannot be made to coincide by parallel displacement along the T axis if Eqs. (1.3) are used, although the experimental data in [1] indicates that this can be done. Equations (1.2), (1.4), and (1.5) are free of this problem. The dependence of q on T has a point of inflection according to (1.4) but not according to (1.5). The advantages of this or that approximation can ultimately be determined only by comparing it with empirical data.

2. Constitutive equations for the phase transformations of SMAs are constructed in accordance with a micromechanical scheme [6-8] that entails modeling the simultaneous nucleation and growth of martensite crystals in an austenite matrix. We will assume that the macroscopic phase distortion is equal to the sum of the microscopic distortions ρ_{ij} connected with the nucleation and growth of all martensite crystals present in a representative volume of the material at a given moment.

The growth of a martensite crystal is governed by the following equation in the forward and reverse transformation [8]

$$\frac{d\rho_{ij}}{dq} = a\rho_{ij}. \tag{2.1}$$

It can be shown [6-8] that, in this case, the determining equation for the deviator of phase distortion ε_{ij} should have the form

$$\frac{d\varepsilon_{ij}}{dq} = B_{ij} + a\varepsilon_{ij}. \tag{2.2}$$

Here, $a\varepsilon_{ij}$ is the strain rate associated with the growth of martensite crystals, while $B_{ij} = v\rho_{ij}^0$ is the strain rate associated with their nucleation; v is the nucleation rate, calculated from the parameter q; ρ_{ij}^0 is the microscopic strain, connected with the nucleation of a single crystal. For the forward transformation, in the simplest case we can take [8]

$$B_{ij} = c\sigma'_{ij} \tag{2.3}$$

(σ'_{ij} is the deviator of the acting stresses). Most of the well-known constitutive equations for the rate of change in phase distortion in SMAs do not contain a term of the type $a\varepsilon_{ij}$ [1, 9-11], although the possibility of including it in the equation for the rate of microscopic phase distortion was discussed in [12].

The rate of nucleation and growth of martensite crystals should decrease as q approaches unity. This effect is automatically accounted for by models (1.3-1.5) for the phase diagram. In the present case, the parameters a and c can be assumed to be constant: $a = a_0$ = const, c = c_0 = const. The model obtained for the forward transformation as a result of this assumption contains two parameters: a_0 and c_0. If we use linear phase-diagram approximation (1.2), then allowance can be made for the decrease in crystal nucleation and growth rate by taking a and c to be functions of the parameter q and having them approach zero as q approaches unity. For example:

$$a = a_0(1-q)^n, \qquad c = c_0(1-q)^n.$$

TABLE 1

Material	(1.2)	(1.3)	(1.4)	(1.5)
	S			
TN-1	0,182	0,327	0,544	0,181
CuAlMnCo	0,0017	0,122	0,0673	0,0072

As a result, one more material parameter n is added. The equation for the deviator of phase distortion in the forward transformation has the form

$$\frac{d\varepsilon_{ij}}{dq} = (c_0\sigma'_{ij} + a_0\varepsilon_{ij})(1-q)^n. \tag{2.4}$$

Here and in all subsequent formulas for the two-parameter model, we need to set n = 0.

3. The most suitable of phase-diagram approximations (1.2-1.5) can be chosen on the basis of the best description, by Eq. (2.4), of experimental results on the development of strain in the forward and orientational transformations [12-15]. In the first case, we are talking about the increase in phase distortion in the SMA as it cools through the temperature interval (M_1, M_2) under a constant stress. Integrating (2.4), we obtain the following with zero initial conditions

$$\varepsilon_i = \frac{2}{3}\sigma_i \frac{c_0}{a_0}\left(\exp\left(\frac{a_0}{n+1}\left(1-(1-q)^{n+1}\right)\right)-1\right), \tag{3.1}$$

where ε_i and σ_i are the intensities of the stresses and strains. In order to obtain the dependence of the intensity of the phase distortion on temperature, we need to replace q with (1.1) in one of the approximations (1.2)-(1.5) being considered.

To find the parameters of the model, we used experimental data on the forward transformation for titanium nickelide TN-1 [15] and a CuAlMnCo alloy [13]. We chose a series of points T_j in the temperature interval (M_1, M_2) (j = 1, 2, ..., k, k = 12, M_1 = 325 K, M_2 = 175 K for TN-1 and k = 9, M_1 = 340 K, M_2 = 316 K for CuAlMnCo). The values of the parameters were sought by minimizing the standard deviation S of the intensity of phase distortion ε_i, calculated from (3.1), relative to the experimental data ε':

$$\min_{a_0,c_0,n} \sum_{j=1}^{k} \left[\frac{\varepsilon_i(T_j) - \varepsilon'(T_j)}{\varepsilon'(T_j)}\right]^2 = S.$$

We used the coordinate descent method to find the parameters. The quality of the approximation can be judged from the minimum value of S attained. Values of S for the different phase-diagram approximations are shown in Table 1.

In accordance with Table 1, in most cases the three-parameter model (the first column of the table) gives lower values of S than two-parameter models (1.3), (1.4), and (1.5). Surprisingly, the two-parameter models and proposed phase-diagram approximation (1.5) give the same value of S as the three-parameter model with the linear phase diagram in the case of alloy TN-1. It must be noted that the slope of the minimized function is very small when the three-parameter model is used (the small change being related to the substantial change in the sought parameters), which makes a stable determination very difficult. The two-parameter models do not have this problem. According to Table 1, proposed approximation (1.5) yields significantly smaller errors than the other curvilinear approximations (1.3) and (1.4).

4. The experimental data on the orientational transformation [1, 12-15] differs from the experimental results on the forward transformation for a constant stress in the fact that the applied stress is removed at a certain intermediate value of temperature $T = T_0$, $M_2 < T_0 < M_1$ and the SMA cools from $T = T_0$ to $T = M_2$ without stresses. Experiments [1, 9, 12-15] show that the phase diagram continues to develop after the stresses are removed, albeit at a lower rate than when the forward transformation is continued (and the applied stress remains). For many well-known models (see [1, 6], for example), the rate of phase distortion in the forward transformation is assumed to be proportional to the deviator of the applied stress. Such an assumption does not permit even a qualitatively correct description of orientational transformation (at $\sigma'_{ij} = 0$, $d\varepsilon_{ij}/dq = 0$). In proposed model (2.4), the value of σ'_{ij} is proportional only to the rate of change of that part of the phase distortion connected with the nucleation of martensite crystals. The growth of nucleated crystals can also occur by (2.1) at zero stresses. Thus, the proposed model offers a qualitatively correct description of the increase in strain in the direction of the previously applied stress

TABLE 2

Material	(1.2)	(1.3)	(1.5)
	S		
TN-1	0,3085	0,538	0,0888
CuAlMnCo	0,0300	0,437	0,0059

TABLE 3

Material	a_0	$c_0 \cdot 10^4$ 1/MPa
TN-1	0,718	2,43
CuAlMnCo	2,257	1,517

at a rate which is lower than if the stress were continue to act. The rate is lower because the component of strain rate associated with crystal nucleation disappears.

The quantitative agreement of these conclusions with experimental results was checked using curves describing the orientational transformation of alloy TN-1 [15] (five curves for five temperatures T_0) and the CuAlMnCo alloy [10] (three curves). The calculation was performed by means of the formula

$$\varepsilon_i = \frac{2}{3}\sigma_i \frac{c_0}{a_0}\Big(\exp\Big(\frac{a_0}{n+1}(1-(1-q)^{n+1})\Big) - \exp\Big(\frac{a_0}{n+1}(1-q_0)^{n+1} - (1-q)^{n+1}\Big)\Big), \tag{4.1}$$

which was obtained by integrating Eq. (2.4) under the appropriate conditions. The value of q_0 is calculated through T_0 with the use of the corresponding phase-diagram approximation. We used all of the approximations employed earlier except for (1.4) to obtain curves of the orientational transformation. Approximation (1.4) was not used because a value less than zero was found for the parameter a when this model was used to construct the curve for the forward transformation, and a negative value would have resulted in a qualitatively incorrect description of the orientational transformation.

When calculations were performed with Eq. (4.1), we used values obtained from the curve for the forward transformation as c_0 and a_0 for each material. In other words, we used values obtained in an independent experiment. To compare theoretical and experimental values of strain for each orientational transformation curve within the interval of temperatures T_0-T_2 corresponding to the beginning and end of the transformation, we chose several (from three to seven, depending on the size of the interval) points T_i at which to determine experimental and theoretical values of strain. We then calculated the sum of the squares of their differences for all points on all of the curves for the given material. The resulting values of standard deviation S are shown in Table 2.

According to Table 2, the two-parameter model with phase-diagram approximation (1.5) is considerably more accurate than not only the two-parameter model with exponential approximation (1.3), but also the three-parameter model with linear approximation (1.2).

These results illustrate the advantages of proposed approximation (1.5) over the other approximations. Table 3 shows values of the parameters of a two-parameter model employing Eq. (1.5) for the materials discussed here.

The lines in Fig. 2 show the dependence of strain on temperature for titanium nickelide in the forward transformation (curve 1, σ = 110 MPa) and the orientational transformation with the same stress in the first stage of the cooling process (curves 2-6, corresponding to different temperatures T_0 at which the stresses were relieved). The curves were calculated from the proposed model with parameters (Table 3) obtained on the basis just of experimental data for the forward transformation. The points represent experimental results obtained for the same material [15] in tests involving the orientational transformation. Similar data is shown in Fig. 3 for the CuAlMnCo alloy [10] (curve 1 is for the forward transformation with a shear stress τ = 10.8 MPa, while curves 2-4 are for the orientational transformation with the same τ in the first stage and different values of T_0). The results demonstrate the possibility of describing empirical data with the model identified in independent experiments. We will henceforth examine only this model.

5. If the heating of a material is continued through the temperature interval (A_1, A_2) after the forward transformation at a constant stress, the reverse transformation of martensite into austenite will take place and the strain acquired in the forward transformation will be removed (shape memory effect [1]). The martensite crystals nucleated previously will be reduced to mini-

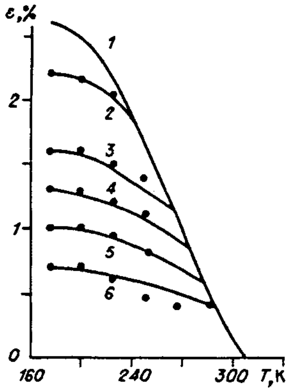

Fig. 2

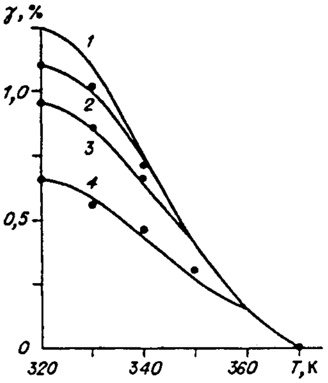

Fig. 3

mal dimensions and eventually disappear during the reverse transformation. If the reduction in the size of each crystal obeys the same law (2.1) as governs crystal growth, then the model that describes the disappearance of the crystal should be different from the model that describes its growth. There should be a difference because the orientation of the nucleated crystals is determined by the acting stress in the forward transformation, while the relatively small stress in the reverse transformation does not significantly affect the process. We further propose that the rate of disappearance of martensite crystals during the reverse transformation is determined only by the history of their nucleation and growth.

This relationship can be viewed from one of two extremes. From one viewpoint, the rate of disappearance of martensite crystals during the given stage of the forward transformation is constant. The value of this constant tensor can be found on the basis of the fact that the initial phase diagram vanishes after completion of the reverse transformation; integrating Eq. (2.4) for the reverse transformation, we find from the condition $\varepsilon_{ij}(0) = 0$ that

$$B_{ij} = \frac{a_0 \varepsilon^1_{ij}}{1 - \exp(-a_0 q_1)}. \tag{5.1}$$

Here, ε^1_{ij} and q_1 are values of the deviator of phase distortion and the parameter of the process q at the point where the given stage of the reverse transformation begins.

The alternative point of view is that

$$B_{ij}(q)|_{\dot q<0} = B_{ij}(q)|_{\dot q>0}, \tag{5.2}$$

i.e., the rate of disappearance of crystals during the reverse transformation is equal to the rate of their nucleation during the previous stage of the forward transformation at the point corresponding to the given value of q. These hypotheses give the same

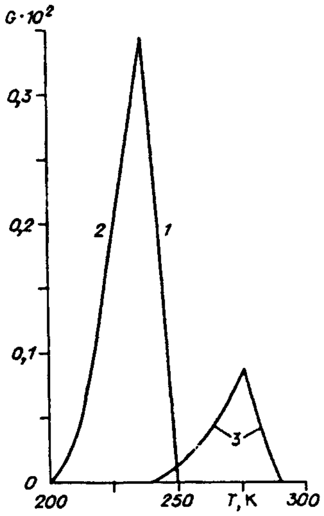

Fig. 4

result and correctly describe the experimental data in the simplest case of a reverse transformation after a forward transformation under a constant stress.

Let us now examine a more complicated case — reverse shape memory [1, 16-18]. One variant of this phenomenon consists of the following [1]. A specimen undergoes the forward transformation under the influence of a shear stress τ as it cools from M_1 to the temperature T_0 ($M_2 < T_0 < M_1$). This leads to the phase distortion γ_1. The specimen then cools further under the influence of the shear stress $-\tau$ from $T = T_0$ to $T = T_1 > M_2$. The phase distortion disappears as a result. The stress τ and temperatures T_0 and T_1 are chosen so that the phase distortion is zero at the end of the second stage of the forward transformation. Deformation changes nonmonotonically with further monotonic heating of the unstressed specimen. The material can behave in one of two ways [1], but we will examine the variant that corresponds to the principle of space–time heterogeneity [16, 17]. In this case, monotonic heating from the temperature A_1 is initially accompanied by an increase in strain γ to the maximum value γ_2 at $T = T_1$ (the signs of γ_2 and γ_1 coincide); with further heating, γ decreases to a value close to zero at $T = A_2$. Although the dependence of γ on T on the heating section is qualitatively the same as on the cooling section, the maximum strain in the reverse shape memory γ_2 is substantially smaller than the maximum strain during the forward transformation ($\gamma \sim 0.25\gamma_1$ for titanium nickelide, according to [1, 16]).

It is easy to see that when model (5.1) is used in experiments set up to test reverse shape memory, the rate of disappearance of martensite crystals during the reverse transformation will be zero; thus, the strain γ will also be identically zero, i.e. this model does not describe reverse shape memory.

Thus, the proposition that the rate of disappearance of martensite crystals is constant does not conform to the character of the recovery which occurs after the reverse transformation. At the same time, it is readily seen that, in accordance with Eq. (5.2), the graph of the dependence of γ on T during heating exactly (qualitatively and quantitatively) repeats the graph of the dependence of γ on T during the forward transformation (albeit in a different temperature interval); here, $\gamma_2 = \gamma_1$, which does not agree with the experimental data. Thus, adopting Proposition (5.2) causes shape memory to become of an "excessively reverse" nature. Adopting the proposition that B_{ij} is constant generally precludes reversal during monotonic heating. It is clear that reverse shape memory can be described by formulating a compromise between these two hypotheses. For example, we could adopt the following as our model to describe the disappearance of martensite crystals during heating:

$$B_{ij}\big|_{\dot q<0} = \lambda B_{ij}\big|_{\dot q>0} + (1-\lambda)\frac{a_0\varepsilon^1_{ij}}{1-\exp(-a_0 q_1)}\,. \tag{5.3}$$

It is easily seen that the value of B_{ij} obtained from (5.3) in the case of heating after occurrence of the forward transformation under a constant stress is independent of λ and is equal to the rate of disappearance of martensite crystals in each of the constituent models. Thus, the combination model correctly describes a simple experiment involving the reverse transformation — as does each of the simple models comprising it.

In an experiment studying reverse shape memory, $\varepsilon_{ij}^{1} = 0$ in (5.3) and the rate of disappearance of martensite crystals will be determined solely by the first term in the right side of (5.3). As a result, the dependence of γ on T for the reverse transformation qualitatively repeats the analogous graph for the forward transformation on a smaller scale (as seen in experiments) determined by the coefficient λ. The value of this material parameter can be found from the formula $\lambda = \gamma_2/\gamma_1$.

Figure 4 shows graphs of the temperature dependence of $\Gamma = a_0\gamma/(2c_0\tau)$ calculated by means of Eqs. (1.5), (2.2)-(2.3), and (5.3) in a reverse shape memory experiment for an SMA with $a_0 = 0.718$ (as for the above-examined titanium nickelide), $M_1 = 250$ K, $M_2 = 200$ K, $A_1 = 240$ K, and $A_2 = 290$ K. Curve 1 corresponds to the forward transformation with a constant shear stress τ, curve 2 corresponds to the same transformation with a shear stress $-\tau$, and curve 3 corresponds to the reverse transformation in the unstressed state.

The proposed model makes it possible to describe an alternative form of behavior of a material exhibiting reverse shape memory [1]. Here, martensite crystals nucleated at the beginning (as opposed to the end) of the forward transformation disappear first during the reverse transformation. The quantities γ_1 and γ_2 thus have opposite signs. For the situation just described to be realized, it is sufficient that α be negative. The change seen in the behavior of the material with a change in T_1 at the end of the forward transformation [1] and the reduction in γ_2/γ_1 seen experimentally with a decrease in T_0 [19] can be described by taking λ to be a decreasing function of q.

Here, we have used a simple variant of an approach that accounts for the simultaneous nucleation and growth of martensite crystals. The scheme can be generalized to allow for several structural levels of deformation [20-22].

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