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Theory of Martensitic Unelasticity of Crystals

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Abstract. It has been formulated a rather simple model of martensitic unelasticity due to martensitic transformations of the first order. It is based on the idea that a martensitic reaction comes out as a mechanism of unelastic micro-strain. An equation describing the variation of the size of martensite crystals in the direct and reverse reactions has been proposed. Kinetics of these reactions is determined by two external factors: temperature and stress. Macroscopic strain is calculated by orientation averaging of micro-strains. There are given examples of simulation of mechanical characteristics of a model material. A satisfactory correspondence has been established between the calculated and actually observed effects.

1. INTRODUCTION.

It is well known that some crystals can be unelastically deformed due to martensitic reactions. These reactions can be viewed as a specific mechanisms of mass transfer alternative to such processes as dislocation slip, diffusion and mechanical twinning. Functional-mechanical response of the material to martensitic reactions can vary greatly. Thus it can be the shape memory effect, superelasticity, reversing shape memory, etc. The experimental observations [1] show that martensitic unelasticity is very complex. It is difficult to describe it basing on classic methods of physics and mechanics of materials. Relatively successful attempts of mathematical modelling of martensitic unelasticity are made by many investigators but firstly they are based on rather complicated calculations, and secondly give only a qualitative prognosis of a limited number of phenomena. Nevertheless in [2] it has been proposed a new methodology which within the unified approach, provides a rather precise modelling of practically all known mechanical phenomena of martensitic unelasticity not only qualitatively but quantitatively as well. More specifically the ideas presented in [2] allow to model the following phenomena.

1. Calculation of isothermal deformation diagrams for all temperatures from austenitic to martensitic states and for arbitrary variations of the stress tensor when applying and removing the stress.

2. Calculation of transformation plasticity for an arbitrary temperature regime (including thermal cycles in a narrow temperature interval) and varying mechanical load.

3. Calculation of shape memory phenomena in both stressed and unstressed states for various regimes of preliminary deformation.

4. Calculation of the stress recovery for various regimes of preliminary deformation and subsequent heating and for system with various compliances.
5. Calculation of the two-way shape memory and reversing strain recovery initiated by various ways of preliminary thermo-mechanical loading.
6. Calculation of shape memory materials heat-into-work conversion characteristics for various thermo-mechanical working cycles.

Besides the mentioned above phenomena a qualitatively valid prognosis can be made for other physical phenomena, for example baromechanical shape memory effect [2].

In the work the simplest model of martensitic unelasticity is presented. It enables qualitative prediction of a large number of phenomena for alloys undergoing martensitic reactions of the first order. In this variant of the theory the interaction between the martensitic and dislocation mechanisms of mass transfer as well as the crystallographic texture are not taken into account. That is why some of the effects are not adequately described. This, first of all, concerns the two-way shape memory effect in unloaded objects. Besides the mechanical twinning and dislocation plasticity are neglected. However, this fact does not prevent to consider the unelastic deformation of martensite due to its reorientation.

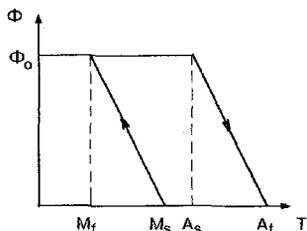
2. DESCRIPTION OF THE MODEL

We shall start from the assumption that the mass transfer (micro-deformation) is accomplished only by a martensitic reaction of the first order. We shall characterize it by the transformation distortion tensor D_{ik} referred to the orthogonal crystallographic basis u,v,w , by the enthalpy q_0 of the reaction, thermodynamical equilibrium temperature T_0 , start and finish temperatures M_s, M_f of the direct and A_s, A_f of the reverse transformations. By Φ we shall denote the normalized volume of a martensite crystal, the rate of its growth is $\dot{\Phi} = d\Phi / dt$, where t is the time, and the dot means the time derivative. Both Φ and $\dot{\Phi}$ must be functions of temperature T , stress tensor σ_{ik} (which we shall refer to an orthogonal laboratory basis x,y,z) and the history of the thermo-mechanical loading. This last fact is due to the hysteresis character of the martensitic crystal growth kinetics.

First we calculate the unelastic microstrain β_{ik}^{Φ} in the volume where a martensite crystal appears. We shall refer it to the crystallographic basis u,v,w . It is evident that if $\Phi=0$ only austenite exists in this part of the crystal and $\beta_{ik}^{\Phi} \equiv 0$. If then $\Phi = \Phi_0 > 0$ and only martensite exists then $\beta_{ik}^{\Phi} = D_{ik} \Phi_0$, where Φ_0 is the martensite crystal volume related to the volume of the region which it would occupy if it grew in an unstressed material. In other words, we shall require that an unstressed totally martensitic crystal be characterized by a normalization condition $\Phi_0 \equiv 1$. Following these considerations we write

$$\dot{\beta}_{ik}^{\Phi} = D_{ik} \dot{\Phi} . \quad (1)$$

Now we shall write down a constitutive equation for $\dot{\Phi}$. To do this we assume that the phase composition of an unstressed crystal is characterized by the simplest diagram shown in the following Scheme 1:



Scheme 1: Supposed kinetics of martensitic transformation on the microlevel

At the same time in the presence of the stress we must account for its effect on the characteristic temperatures M_S , M_f , T_0 , A_S and A_f . This can be done by using of the Clausius -Clapeyron type of equation in the form

$$\hat{T}^* = \hat{T} - \frac{T_0}{q_0} \alpha_{ip} \alpha_{kq} \hat{\sigma}_{ik} D_{pq} , \quad (2)$$

where T^* - is the effective temperature which controls the transformation, α_{ip} are the directing cosines characterizing the orientation of the crystallographic basis in relation to the laboratory one. The orientation we shall describe by using the Euler angles φ, θ, ψ , varying in the ranges $0 \leq \varphi \leq 2\pi$, $0 \leq \theta \leq \pi$, $0 \leq \psi \leq 2\pi$.

The relation between Φ and T^* is the same as between Φ and T for stress-free crystal. This simple method allows to express the dependence of $\dot{\Phi}$ on \hat{T} and $\hat{\sigma}_{ik}$ in an analytical form. To do this we shall describe the fact that the crystal is in the martensitic state when $T^* < M_S - \Phi(M_S - M_f)$ and in the austenitic state when $T^* > A_f - \Phi(A_f - A_S)$. The rate of a martensitic crystal growth in the direct transformation is determined by the factor $-\hat{T}^* / (M_S - M_f)$ and its reduction in the reverse transformation - by the factor $-\hat{T}^* / (A_f - A_S)$. If the point (T^*, Φ) is inside the hysteresis figure shown in scheme 1 then the martensitic reaction will not proceed. In the other words Φ does not change when $M_S - \Phi(M_S - M_f) < T^* < A_f - \Phi(A_f - A_S)$.

If we do not limit the volume of growing martensite crystals, that is, admit any values of Φ_0 then the direct transformation will stop only when there is no austenite in the volume under consideration. This means that the decisive role is played by the quantity Φ_M , which characterizes the total concentration of martensite in the volume with the specific set of characteristic temperatures M_f, M_S, A_S, A_f :

$$\Phi_M = \frac{1}{8\pi^2} \int_0^{2\pi} d\varphi \int_0^{2\pi} d\psi \int_0^{\pi} f(\varphi, \psi, \theta) \Phi(\varphi, \psi, \theta) \sin \theta d\theta, \quad (3)$$

where $f(\varphi, \psi, \theta)$ is the orientation distribution function. If we postulate that $\Phi_M=1$ when all the considered volume is in the martensite state and $\Phi_M=0$ when there are no martensite at all, then the direct austenite-to-martensite reaction will be allowed only under the condition $\Phi_M < 1$. As a rule the form of the function f is unknown but for macroscopically isotropic crystals it of course does not depend on the Euler angles and we arrive to an expression:

$$\Phi_M = \frac{1}{8\pi^2} \int_0^{2\pi} d\varphi \int_0^{2\pi} d\psi \int_0^\pi \Phi(\varphi, \psi, \theta) \sin \theta d\theta . \tag{4}$$

Here Φ is the function of φ, θ, ψ because of the direction cosines α_{ip} in (2).

We must also note that in many cases there is a limitation on the maximum size of martensite crystals. Because of this the growth of a crystal is possible only when the requirement $\Phi < \Phi_0$ is satisfied, Φ_0 being a material constant.

To write down the final expression for $\Phi(T^*)$ we suppose that each martensite crystal which appeared in "cooling" (in the terms of T^*) can shrink in "heating" only when $\Phi > 0$, that is, until it does not transform entirely into austenite. Of course one can find examples when this requirement does not correspond to the really observed regularities. Thus, the transformations in FeMn alloys can follow more complicated laws. In the frames of this report we shall not concern this point. All the aforesaid allow to write down the following equation:

$$\Phi = -T^* \left\{ H(-T^*) H(1 - \Phi_M) H[M_S - \Phi(M_S - M_f) - T^*] (M_S - M_f)^{-1} + H(T^*) H(\Phi) H[T^* + \Phi(A_f - A_s) - A_f] (A_f - A_s)^{-1} \right\}. \tag{5}$$

Here H is the Heaviside's function. The first term in braces refers to "cooling" when $H(-T^*)=1$ and $H(T^*)=0$ and the second term - to "heating" when $H(T^*)=1$ and $H(-T^*)=0$.

Besides we assume that $M_S - M_f$ does not much differ from $A_f - A_s$. In the opposite case there can appear physically unrealizable areas on the (Φ, T^*) plane and then it would be necessary to significantly alter the equation (5) [5,6].

Thus, if we know the characteristics of the martensitic transformation $M_f, M_s, A_s, A_f, T_0, q_0, D_{pq}$ and the structure of the body as a whole (that is the function $f(\varphi, \psi, \theta)$), equations (1), (2), (4), and (5) allow to calculate the size Φ of separate martensite crystals, the total concentration of martensite Φ_M as well as the micro-

distortion β_{ik}^Φ due to the transformation in the considered volume of the crystal. Eqs.(1)--

(5) do not restrict the admissible variations of the temperature T and the stress σ_{ik} . We note that T_0 and q_0 enter eq.(2) only in the combination T_0/q_0 and this gives the possibility to specify $T_0 = (M_f + M_s + A_s + A_f)/4$ and thus to reduce the number of the constants.

Now it is easy to calculate the macroscopic strain tensor ε_{ik}^{Φ} which we shall refer to the laboratory basis and which includes contributions of all the crystals with specified M_f , M_s , A_s , A_f . Further we shall use only the symmetric part of distortion tensors, that is, we pass to the transformation strain and martensitically unelastic strain keeping the same notations D_{pq} and β_{pq}^{Φ} .

If all martensitic crystals had the same values of M_f , M_s , A_s , A_f and the material was macroscopically isotropic we should have the following relation between ε_{ik}^{Φ} and β_{pq}^{Φ} :

$$\varepsilon_{ik}^{\Phi} = \frac{1}{8\pi^2} \int_0^{2\pi} d\varphi \int_0^{2\pi} d\psi \int_0^{\pi} \alpha_{ip} \alpha_{kq} \beta_{pq}^{\Phi} \sin\theta d\theta. \quad (6)$$

Here α_{ip} and β_{pq}^{Φ} are functions of φ , θ , ψ .

In reality statistical aspect affects martensitic transformations. By this reason hysteresis figures in scheme 1 for some regions are more narrow and more wide for others. Besides, their location relative to the temperature axis, that is, the temperature T_0 can also be different. If we introduce the mean hysteresis width $\Gamma_m = (A_f - M_s + A_s - M_f)/2$ then leaving the slopes (that is $A_f - A_s$ and $M_s - M_f$) constant we can speak of a distribution function the argument of which varies from $\Gamma_{\min} = \Gamma_m - \Delta > 0$ to $\Gamma_{\max} = \Gamma_m + \Delta$, where $\Delta < \Gamma_m$. We assume that if A_f is shifted due to the statistical scatter by s that is becomes $A_f + s$ then A_s will be $A_s + s$ and the temperatures M_s and M_f become $M_s - s$ and $M_f - s$.

Therefore, we can account for the statistic scatter of hysteresis width introducing the distribution function $\varphi(s)$, $-\Delta < s < \Delta$.

Similar considerations allow to account for the temperature T_0 scatter. Let T_0 vary from $T_0 - D$ to $T_0 + D$. Then to keep the width and the slopes of the hysteresis figure constant we must assume that the temperatures M_f , M_s , A_s , A_f vary respectively from $M_f - D$, $M_s - D$, $A_s - D$, $A_f - D$ to $M_f + D$, $M_s + D$, $A_s + D$, $A_f + D$. We introduce the center temperature T_0 distribution function $\psi(p)$, $-D \leq p \leq D$. By physical considerations we limit D by the value $0.5\Gamma_m$. From the aforesaid it follows that eq.(5) should be transformed into

$$\Phi = -T^*(p) \left[-T^*(p) \right] H[1 - \Phi_M(s, p)] H[\Phi_0 - \Phi(s, p)] H[M_s + p - s - (M_s - M_f)\Phi(s, p) - T^*(p)] \cdot \\ \cdot (M_s - M_f)^{-1} + H[T^*(p)] H[\Phi(s, p)] \cdot H \left[T^*(p) + (A_f - A_s) \Phi(s, p) - A_f - p - s \right] (A_f - A_s)^{-1} \quad (7)$$

Here $\Phi_M(p, s)$ can be calculated by means of (4), (7) and $T^*(p)$ by means of (4) where T_0 is substituted by $T_0 + p$. We shall make an assumption that the distributions of hysteresis widths, temperatures T_0 and crystallographic orientations are independent. Then

considering functions $\varphi(s)$ and $\psi(p)$ normalized to a unity for a macroscopic strain tensor we have:

$$\varepsilon_{ik}^{\Phi} = \int_{-D}^D dp \int_{-\Delta}^{\Delta} ds \int_0^{2\pi} d\varphi \int_0^{2\pi} d\psi \int_0^{\pi} \psi(p)\varphi(s)f(\varphi, \psi, \theta) \cdot \alpha_{ip}\alpha_{kq}\beta_{pq}^{\Phi}(s, p, \varphi, \psi, \theta) \sin \theta d\theta \quad (8)$$

or for uniform distributions and isotropic material:

$$\varepsilon_{ik}^{\Phi} = \frac{1}{32\pi^2 D \Delta} \int_{-D}^D dp \int_{-\Delta}^{\Delta} ds \int_0^{2\pi} d\varphi \int_0^{2\pi} d\psi \int_0^{\pi} \alpha_{ip}\alpha_{kq} \beta^{\Phi}(s, p, \varphi, \psi, \theta) \sin \theta d\theta. \quad (9)$$

To eqs.(1), (2), (4), (7), (8) one must add equations for calculation of thermal expansion and elastic strains. To do this we shall use the considerations of [5,6] from where it follows that elastic and strains depend on the mean concentration of martensite of all orientations and all values of s and p . This sum concentration is equal to

$$\Phi_{\Sigma} = \frac{1}{32\pi^2 D \Delta} \int_{-D}^D dp \int_{-\Delta}^{\Delta} ds \int_0^{2\pi} d\varphi \int_0^{2\pi} d\psi \int_0^{\pi} \Phi(s, p, \varphi, \psi, \theta) \sin \theta d\theta \quad (10)$$

Uniform distributions are assumed. When martensite is absent $\Phi_{\Sigma}=0$ and $\Phi_{\Sigma}=1$ when it fills all the volume.

When elasticity and heat expansion are isotropic [5,6] give the following equations.

$$\dot{\varepsilon}_{ik}^T = \left\{ \gamma_A + (\gamma_M - \gamma_A)\Phi_{\Sigma} + \left[(\gamma_M - \gamma_A)T + \frac{1}{3} D_{\parallel} \right] \frac{d\Phi_{\Sigma}}{dT} \right\} T \delta_{ik}, \quad (11)$$

$$\varepsilon_{ik}^e = \frac{1}{9K_A} \sigma_{\parallel} \delta_{ik} + \frac{1}{2G_A} \left(\sigma_{ik} - \frac{1}{3} \sigma_{\parallel} \delta_{ik} \right) + \left[\frac{1}{9} \left(\frac{1}{K_M} - \frac{1}{K_A} \right) \sigma_{\parallel} \delta_{ik} + \frac{1}{2} \left(\frac{1}{G_M} - \frac{1}{G_A} \right) \left(\sigma_{ik} - \frac{1}{3} \sigma_{\parallel} \delta_{ik} \right) \right] \Phi_{\Sigma}. \quad (12)$$

Here γ_A, γ_M are heat expansion factors, K_A, K_M - bulk modulae, G_A, G_M - shear modulae of austenite and martensite, δ_{ik} is the unit tensor.

On the whole (1), (2), (4), (7), (8), (9), (11), (12), are sufficient for qualitative prediction of the relation between $\sum \varepsilon_{ik}^{\Phi}$, ε_{ik}^T , ε_{ik}^e and T , σ_{ik} for arbitrary variation of T and σ_{ik} . We remind only that this system of equations does not allow to calculate the two-way shape memory of an unstressed material as well as the mechanical behaviour of highly textured objects.

Analysis of some solutions of this system of equations shows that in some cases in (7) it is better to use quantity Φ_{Σ} from (10) instead of Φ_M from (4). This depends on specific features of the martensitic transformation. It is with this variant of equations that some typical examples presented further have been obtained.

3. EXAMPLES

Examples of mathematical modelling of specific functional-mechanical characteristics of materials.

For simulations there were used the following values of material constants: $M_f = 280$ K, $M_s = 300$ K, $A_s = 310$ K, $A_f = 330$ K, $\Delta = 28$ K, $D = 25$ K, $\Phi_0 \gg 1$, $q_0 = 150$ MJ/m³, $D_{31}=D_{13}=0.075$ (other $D_{ik} \equiv 0$), $E_m = 60$ GPa, $E_A = 74$ GPa, $\nu_M = 0.45$, $\nu_A = 0.33$, $\gamma_M = 6.8 \cdot 10^{-6}$ K⁻¹, $\gamma_A = 5 \cdot 10^{-6}$ K⁻¹.

In fig.1 there is presented a series of diagrams in coordinates "elongation strain ε_{11} - temperature T " of mathematical experiments in which cooling and subsequent heating were held under various tensile stresses $\sigma_{11} = 0, 100$ and 200 MPa. On the same diagram as everywhere further the dashed lines demonstrate the variation of the total martensite concentration Φ_{Σ} . One can see a good agreement with the known experiments [1] though very roughly is modeled the finish of the direct reaction. This kinetics can be better described if Φ_M and not Φ_{Σ} is put in (7).

We note that fig.1a shows the kinetics of heat expansion. It depends on the relation between γ_A and γ_M . Besides there is a linear dependence between ε_{11} and σ_{11} for not very large values of σ_{11} just as in real experiments [1].

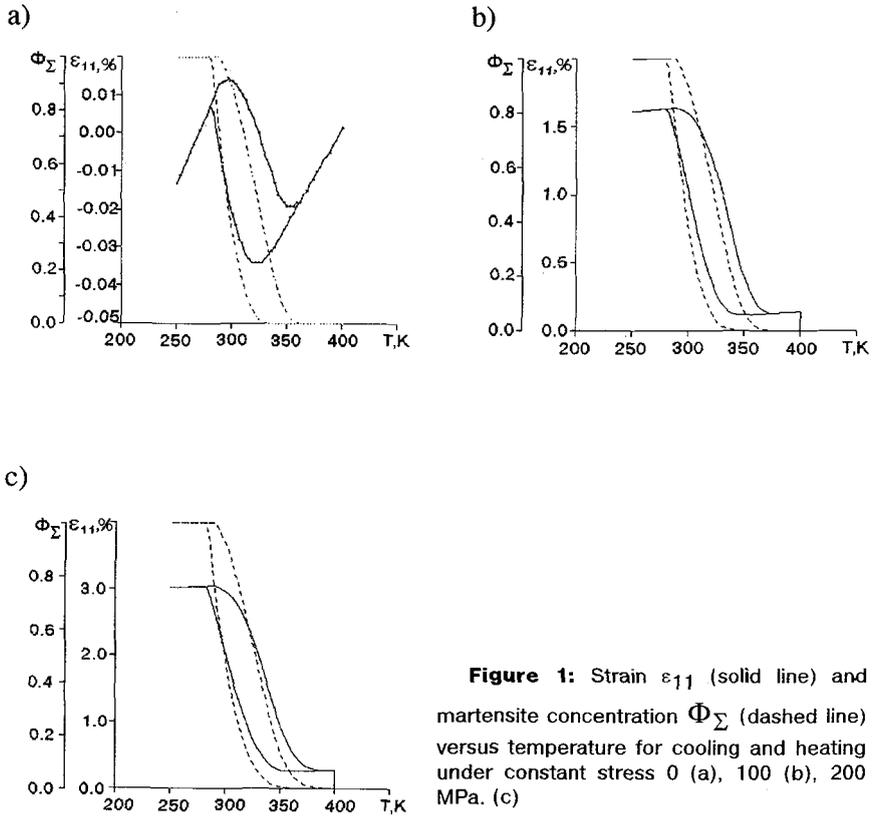


Figure 1: Strain ε_{11} (solid line) and martensite concentration Φ_{Σ} (dashed line) versus temperature for cooling and heating under constant stress 0 (a), 100 (b), 200 MPa. (c)

In fig.2 there are plotted diagrams of isothermal tension and unloading for three temperatures of testing. When $T < M_f - \Delta - D$ (fig.2a) residual strain is produced. It is not recovered in unloading but only in the subsequent heating (fig.2b). The loading does not cause a variation of martensite concentration. There occurs only its reorientation which is reversed in the stage of heating. At the same time at $M_f - \Delta - D < T < A_f + \Delta + D$ (fig.2c) there takes place more complicated evolution of martensite concentration. In this case the strain is partially recovered in the stage of the removing of the force and the rest part of it - in heating. When austenite is loaded at $T > A_f + \Delta + D$ martensite is induced which in the unloading again transforms into austenite with strain recovery, in other words there is typical pseudoelasticity.

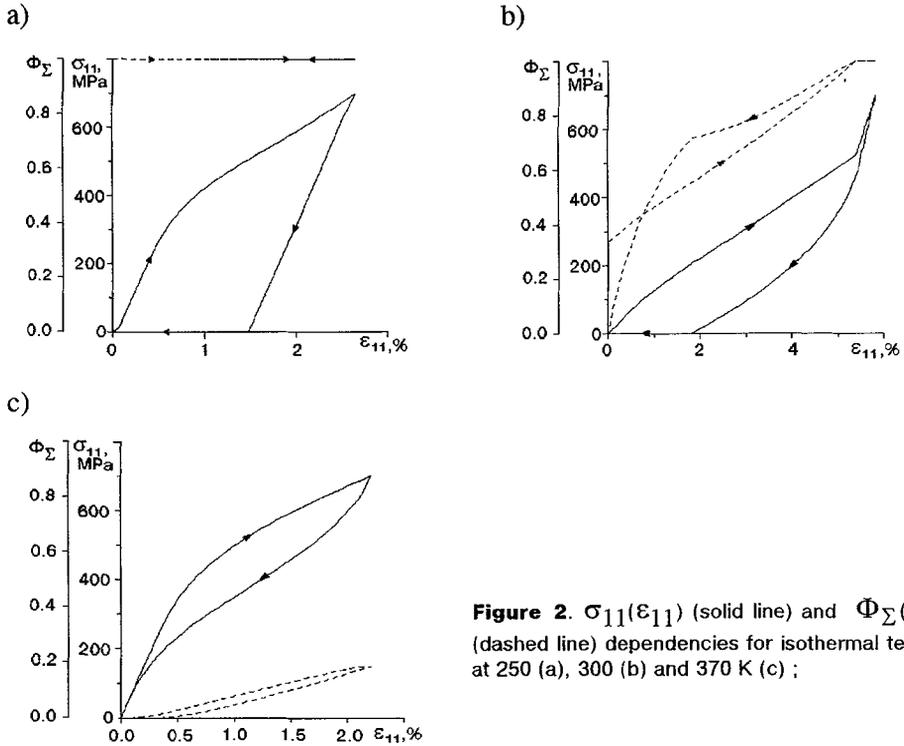


Figure 2. $\sigma_{11}(\epsilon_{11})$ (solid line) and $\Phi_{\Sigma}(\epsilon_{11})$ (dashed line) dependencies for isothermal tension at 250 (a), 300 (b) and 370 K (c) ;

Fig.3 shows the possibility of strain calculation for thermocycling in the incomplete interval of the transformation. The passage from cooling to heating when the direct transformation is not finished (curve 1) and from heating to cooling before the finish of the inverse transformation (curve 2) is accompanied by a specific change of the transformation kinetics well-known from experiments.

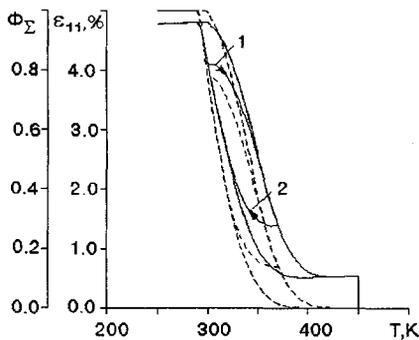
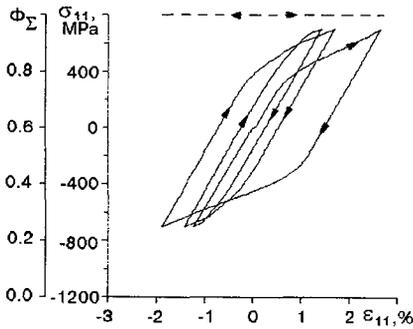


Figure 3. Dependencies of ϵ_{11} strain (solid line) and martensite concentration Φ_{Σ} (dashed line) on temperature in heatings and coolings under constant stress 400 MPa.

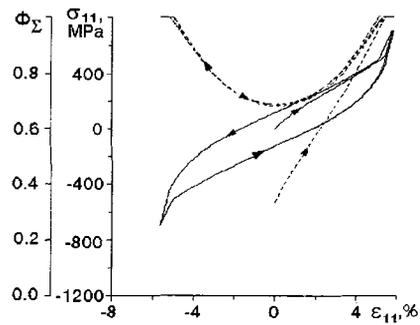
In fig.4 there are plotted diagrams of cyclic loading in the stress range $-700 \leq \sigma \leq 700$ MPa for three temperatures $T < M_f - \Delta - D$, $M_f - \Delta - D < T < A_f + \Delta + D$ and $T > A_f + \Delta + D$. It is remarkable that in fig.4a one can observe the deformation cyclic hardening which is due only to martensite reorientation. At the same time at $M_f - \Delta - D < T < A_f + \Delta + D$ (fig.4c) there is no such hardening but there is a very complicated picture of martensite concentration evolution. Its amount at first increases from $\Phi_\Sigma > 0$ to $\Phi_\Sigma = 1$. Then in unloading the reverse transformation takes place and this reduces Φ_Σ down to a level $\Phi_\Sigma = \Phi_{\min}$ at $\epsilon_{11} = 0$. The new loading again initiates the direct transformation so that Φ_Σ having passed through a minimum becomes equal to unity. A similar picture is for the upper semi-loop of the $\sigma_{11}(\epsilon_{11})$ dependence.

At $T > A_f + \Delta + D$ there is a typical cyclic pseudoelasticity due to reversible austenite - martensite austenite transformation.

a)



b)



c)

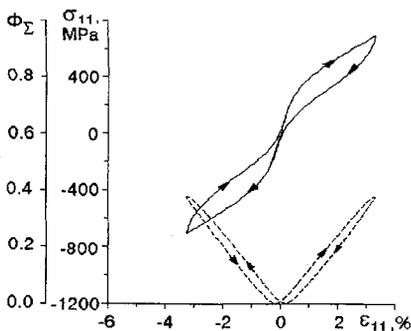


Figure 4. Stress - strain (solid lines) and martensite concentration - strain (dashed lines) tensile diagrams for mechanocycling with the stress amplitude 700 MPa at temperatures 250 (a), 300 (b) and 350 K (c).

Fig.5 shows the possibility of calculation of stress recovery. From this illustration it follows that application of the stress at $T < M_f - \Delta - D$ practically does not effect the level of the maximum recovered: on the first stage of heating the stress relax and it is only with the further development of the inverse transformation that it begins to grow. This first drop of the stress is connected with the reorientation of martensite and the second with the martensite - austenite reaction. Naturally cooling also causes the relaxation of the stress.

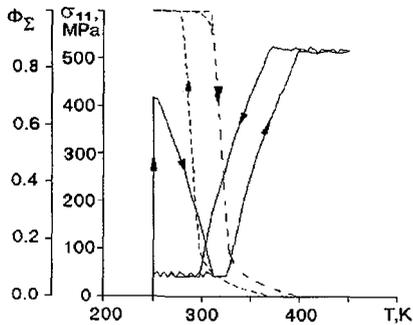


Figure 5: Diagram of variation of axial stress and martensite concentration in constrained (with zero compliance) heating and cooling. Initially stress had been applied at 250 K and then the strain was fixed (thermal expansion strain was compensated).

This phenomenon can be seen also in fig.6 which shows the kinetics of the strain variation in heating of the stressed object which has been preliminarily stressed by a tensile force at 250 K (fig.6a) and 300 K (fig.6b). Fig.6a shows that subsequent coolings and heatings give the same results as in fig.1.

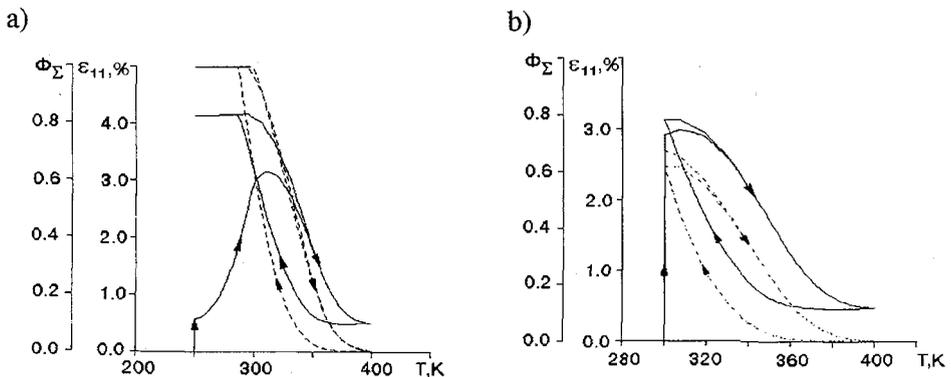


Figure 6: Strain ε_{11} and martensite concentration Φ_{Σ} versus temperature at a constant stress σ_{11} , applied at 250 (a) and 300 K (b).

One more phenomenon is illustrated in fig.7. Here first was the cooling down to $T = 250$ K under constant tensile stress $\sigma_{11} = 700$ MPa. Then the produced strain was removed by isothermal compressing of martensite and then the model object was heated. In heating the so-called reversing shape memory effect took place [1].

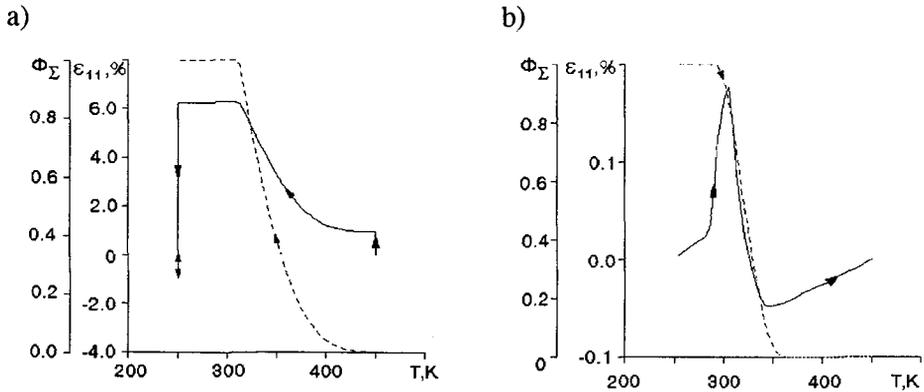


Figure 7: Dependence of the strain ϵ_{11} and martensite concentration Φ_Σ on temperature in conditions of initiation of the reversing shape memory effect; a - preliminary straining: cooling from 450 K to 250 K under stress 700 MPa, then compression at 250 K until complete removal of the strain; b - reversing shape memory effect in subsequent heating of a stress-free object.

The last illustration in fig.8 concerns combined loading. (This calculation has been fulfilled for $\Delta = D = 0$). Here martensite was isothermally tensioned by σ_{11} . Then this stress was removed and σ_{12} was applied. Then there was heating into austenite. Naturally it caused the full recovery of all the components of the strain tensor. However the kinetics of this recovery was rather complex. Fig.8a shows that for a small preliminary strain of the martensite the shear does not effect the strain having been produced in tension. Besides the stored components ϵ_{11} and ϵ_{12} of the strain recover practically synchronically. But if the deformation by σ_{12} had been very intensive the picture was quite different (fig.8b). In this case the unelastic ϵ_{11} strain is recovered already in the stage of loading by σ_{12} and the recovery of ϵ_{11} and ϵ_{12} is no more synchronic.

Comparison of these illustrations with phenomena observed in a direct experiment [1] allows to make a conclusion that the described model is in a not bad agreement with experiments.

Its more complicated variants [2-6] give better results. In [2] one can find many

illustrations of this kind as well as the perspective of the developing of the theory.

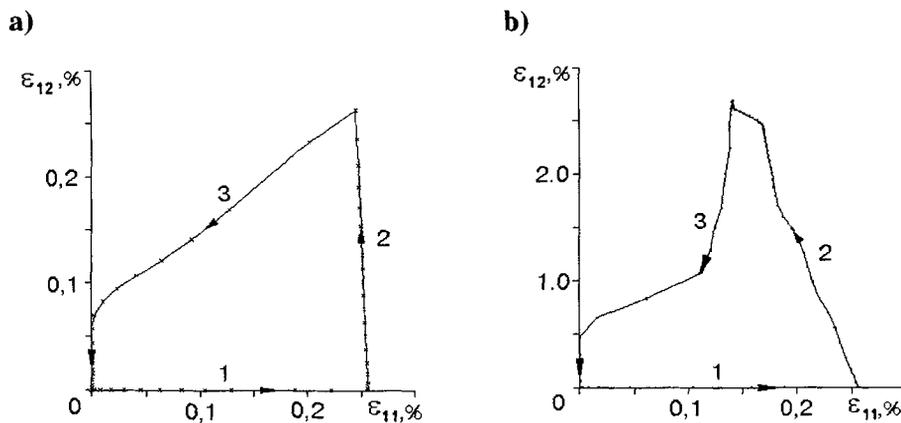


Figure 8: Two phase diagrams plotted on $\varepsilon_{11} - \varepsilon_{12}$ plane. Preliminary deformation was at 250 K first by tension up to ε_{11} (1) and then by shear up to ε_{12} (2). Subsequent heating in a stress-free state (3). Elastic and heat expansion strains are not taken into account; a - $\varepsilon_{11}=0.257\%$, $\varepsilon_{12}= 0.264\%$; b - $\varepsilon_{11}= 0.257\%$, $\varepsilon_{12}= 2.7\%$.

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