



Shape memory strain glasses can be frozen in post-critical states

D.L. Beke^{a,*}, A.A. Azim^{a,b}, L.Z. Tóth^a, L. Daróczy^a

^a Department of Solid State Physics, Doctoral School of Physics, University of Debrecen, P.O. Box 2, Debrecen H-4010, Hungary

^b Physics Department, Faculty of Science Ain Shams University, Abbassia, Cairo 11566, Egypt

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ABSTRACT

It is shown that the presence of defects, causing destabilization of martensite in shape memory alloys, can lead not only to suppression of martensitic transformation, but also to a dramatic decrease in the critical temperature, above which only a continuous change in the physical parameters is expected, similarly to liquid-gas systems. This can lead to post-critical (anhysteretic) stress-strain curves of strain glasses above the glass transition temperature. The arguments are based on the possible internal pressure or internal axial stress caused by different types of defects, assuming that these are proportional to defect concentration. Thus, it is expected that the stress-strain curves of such strain glasses can have near zero hysteresis at high temperatures, while below the glass transition temperature either a shape memory effect, corresponding to the rearrangement of martensite nanodomains, or a reversible superelasticity (stress induced strain-glass to martensite transition) can be observed, in accordance with experiments. Furthermore, stress-strain curves taken above the critical temperature can be related to the crossing of the Widom line emanating from the critical point.

1. Introduction

In the last two decades, series of papers were published on special superelasticity with close to zero hysteresis in certain shape memory alloys, SMAs, which did not show a first order martensitic transformation, MT, behaviour. These are the so-called strain-glass SMAs [1–4] as well as SMAs in which, with increasing test temperature the stress-strain loops (or in tests under fixed stress, the strain-temperature loops) gradually closed up [5–13] and a transition to a non-hysteretic behaviour was observed. This latter behaviour is called post-critical superelasticity, or weak first-order (nearly second order) transformation [5–13]. In both groups, the recoverable strain can be comparable or even higher than those provided by conventional superelastic SMAs with first order MTs. For instance, in nanocrystalline NiTiPt strain glass it was about 11% [4] and in single crystalline $\text{Ni}_{55-x}\text{Co}_x\text{Fe}_{18}\text{Ga}_{27}$ fibres it was about 15% [13].

The search for SMAs with nearly zero hysteresis and large recoverable strain forms one of the most important research areas of advanced materials: lowering the hysteresis of the thermomechanical actuators with large superelastic properties is the key issue to attain high cyclic deformation of SMAs with reduced fatigue and energy losses [14].

Strain-glass state is characterized by nanoscale martensitic domains in the austenite, formed during freezing transition [2]. Strain glass

describes a structural state with static (dynamically frozen) nanodomains of transformation strains (i.e. martensitic variants) below the glass transition temperature, T_g , and the strain-glass transition during cooling is broadly smeared, higher-order-like and takes place in a wide range of temperature [2]. In the strain-glass SMAs the basic mechanism, in contrast to the classical superelastic deformation during the stress induced MT, is the reversible rearrangement of martensitic strain nanodomains by the applied stress [1–4] above T_g .

In the second group two approaches were used: a) based on the orthodox Landau theory of first order transformations [5,9,10] or b) based on a modified Landau description as a transition between the first and second order phase transformation (see e.g. [13]). It was shown from the 2–3–4 type orthodox Landau theory (containing the strain order parameters on 2nd 3rd and 4th power) that in stress induced first order MTs a critical point (with T^* and σ^* critical temperature and stress) in the temperature-stress phase diagram can be reached [5,9–11]. Thus, in the stress-strain curves, taken above T^* , the typical (for first order transitions) plateau-like segments disappear (i.e. stress induced first order transformation does not exist) and only a gradual strain is expected with close to zero hysteresis: this is the so-called post-critical behaviour. It was argued [5,9–11] that the critical point is in fact the end point of the phase transition line (similarly to the well-known critical point in the liquid-gas system). The calculated stress-strain loops for $T >$

* Corresponding author.

E-mail address: dbeke@science.unideb.hu (D.L. Beke).

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T^* were obtained taking also into account the interaction with crystal defects [11], which led to a small finite hysteresis: without this, the hysteresis would be zero in the post-critical region [10]. It was emphasized that it is difficult to make a clear distinction experimentally between first-order transformation and post-critical deformation: the application of the two-tangent method can easily lead to “reading out” of start and finish stresses, although these do not exist if there is only a gradual deformation without strain jump. There is still a dispute in the literature whether approach a) or b) provides the correct description (see e.g. [10,12,13]). We will turn back to this in the next chapters.

Regarding the atomic scale picture of the above processes the strain-glass behaviour is better understood [1–3]: the superelastic stress-strain behaviour can be understood by the reversible rearrangement of martensite nanodomains under the applied stress. On the other hand, for the post-critical or nearly-second order behaviour the situation is less clear at present (see e.g. [6,12,13]). Nevertheless, experimental investigation of $\text{Ni}_{55-x}\text{Co}_x\text{Fe}_{18}\text{Ga}_{27}$ single crystals in [13] revealed, that the austenite finish and martensite start stresses versus the Co concentration showed that their difference disappeared at a critical value $x_0 = 10.5\text{at}\%$. It was suggested that this also represents a critical point above which a post-critical (in [13] called as supercritical) state may exist. TEM pictures of $\text{Ni}_{35}\text{Co}_{20}\text{Fe}_{18}\text{Ga}_{27}$ single crystals provided a similar atomic scale picture as those offered for strain-glass alloys: atomically entangled layered nano-structure was observed. One of the most interesting conclusion of [13], based on a 2–4 type Landau-model at around the critical point (predicting a transition from first to second order at x_c) that for $x > x_c$ no first order transformation is predicted and still there is a continuous superelastic regime down to 0 K. For post-critical systems the first order transition exists at low temperatures and for strain glass there is a shape memory effect (i.e. a below the glass transition temperature, T_g , there can be a residual strain, which recovers by heating up [15]) too. This is why the authors of [13] concluded: the observed effect is different from both the post-critical and strain-glass behaviour. It has to be noted however, that such a simple Landau model used in [13] can not take into account the effects of random local and average stress fields of the dopant elements (like sophisticated phase field theories do: see e.g. [2,16]) and can not describe freezing effects either.

From a thermodynamic point of view, the common feature of the strain glass and post-critical systems is the non-hysteretic, continuous superelastic stress-strain curves. Attempts to explain the latter behaviour were based on orthodox Landau expansion of the free energy of the system and the importance of the transition beyond the critical point was emphasized. Thus, the elastic behaviour of ferroelastic systems is the central question around and beyond the critical point. Regarding the post-critical state above the critical point, according to textbooks, at the end of the line separating the two phases transforming by first order transition (e.g. solid/liquid or austenite/martensite), no measurable physical quantity exists on the basis of which one can make a distinction between the two phases [16]. However, as it was demonstrated in a liquid/gas system [16], there are some thermodynamic quantities (velocity of acoustic waves, inelastic X-ray scattering) having maxima along a line emanating from the critical point (Widom line) and a sharp transition on crossing the Widom line was observed above T^* . Thus, the Widom line divides the supercritical region into two regions: gas-like and liquid-like regions. According to these results, it is expected that for ferroelastic first order martensitic transformations above the critical point a Widom line separates the austenite-like and martensite-like regions and a relatively sharp transition should exist on crossing the Widom line.

In this communication we argue, on the basis of the orthodox Landau theory, that the dynamic (high temperature) strain glass can also be considered as a post-critical state, since the critical point can also be reached by increasing defect concentrations [2,4]. The freezing of a post-critical strain glass is just a dynamic effect when the temperature decreases below the glass transition temperature. Thus, it is expected that the stress-strain curves in post-critical states - achieved by simply

increasing the temperature (or pressure) above the critical value or by increasing the defect (dopant) concentration above its critical value - are similar and exhibit nearly zero hysteresis. It will be illustrated that the value of the effective transformation strain, belonging to the austenite-like/martensite-like transition is also determined (besides the Hook regimes of the austenite and martensite) by the width of the transition during crossing the Widom line. It should obviously be orientation-dependent: it can be a fingerprint of the maximum transformation strain, observable during first order ferroelastic phase transformations. Our treatment is based on the orthodox Landau theory of cubic to tetragonal transformation, and on the use of the results that both the equilibrium transformation temperature, T_0 , and T^* decrease by increasing the content of defects (dopants, dislocations, grain boundaries). Thus, increasing the dopant concentration or the amount of plastic deformation (i.e. increasing the number of dislocations and grain boundaries), parallel with the decrease of T_0 , the critical temperature can also be decreased and the post critical behaviour can be observed even below room temperature. In contrast to this behaviour the glass transition temperature can be dependent not only on the decrease of the global transformation temperature, but can be sensitive to effects of changes of local transformation temperature or local elastic fields, caused by local spatial distribution and local lattice distortions of defects [15,17] too.

2. Orthodox Landau theory in the presence of defects

The results of the description of the first order ferroelastic (martensitic) transformations in the framework of the orthodox Landau theory is summarized for cubic austenite to tetragonal martensite transformations.

2.1. Thermally induced first order ferroelastic MT

It can be shown that, the expansion of Gibbs free energy per unit volume by the strain parameter $u = 2\left(\frac{c}{a} - 1\right)$ (a and c are the corresponding lattice parameters: $\left(\frac{c}{a} - 1\right)$ is called “tetragonality” parameter) can be expressed in the following form (assuming small transformation volume change, $u_1 = \frac{1}{3} \frac{\Delta V}{V}$) [5,10,11,18,19]

$$\Delta g = \frac{1}{2}c_2(T)u^2 + \frac{1}{3}au^3 + \frac{1}{4}bu^4 - \frac{1}{6}\sigma u. \quad (1)$$

Here

$$c_2\left(T, \underline{p}\right) = c_2(T) - 3\frac{a_2}{c_1}\underline{p} = c_2(T, 0) - \lambda_{pa}\underline{p} \quad (2)$$

$$\underline{a}\left(\underline{p}\right) = a - 9\frac{b_7}{2c_1}\underline{p} = a - \lambda_{pa}\underline{p} \quad (3)$$

$$\underline{b} = b - \frac{a_2^2}{2c_1} \quad (4)$$

as well as

$$\underline{\sigma} = 2\left[\sigma_{zz} + \sigma_{zz}^{in}\right] \quad (5)$$

and

$$\underline{p} = p + p^{in}. \quad (6)$$

Here c_1 , a_i and b are positive constants, while b_7 is a negative constant [11] and $c_2 = c_{20}(T - T_2)$. These are the input parameters. T_0 T_2 is some temperature at which $A(T) = c_2(T)$ changes sign and below which the high temperature phase (austenite) is unstable ($c_{20} > 0$), due to the well-known phonon softening in shape memory alloys, if both $\underline{a}$ and $\underline{p}$ are zero. c_{20} has entropy per volume dimension,. In Eq. (5) $\sigma_{zz} =$

$\frac{\sigma}{2}$ is the external compressive axial stress, i.e. $\sigma_{zz} < 0$, (shear compressive strain on one (110) plane in one [110] direction for cubic/tetragonal transformation is considered) and p is the external pressure. σ^{in} and p^{in} stem from the perturbations caused by the presence of defects (see also below). In Eqs. (2) and (3) the c_1 , a_2 and b_7 coefficients are the second, third and four order elastic constants (present in the u_1^2 , $u_1 u^2$ and $u_1 u^3$ terms in the original expansion of Δg) and $c_1 = 9B$, where B is the bulk modulus. In addition, it can be shown [20] that $\frac{a_2}{c_1} = -\frac{2u_1}{u_0^2}$ where u_0 is the equilibrium value of u (see also below). Furthermore, $c_2 = \frac{c'}{3} \cong \frac{E}{9}$ ($C' = \frac{c_{11}-c_{12}}{2}$ is the shear modulus and E is the Young modulus). The form of Eq. (1) is also called as 2–3–4 Landau potential, proven to be the most correct version for the description of first order phase transformations in shape memory alloys [10].

If σ is equal to zero, the equilibrium condition is given as

$$\frac{\partial \Delta g}{\partial u} = c_2(T)u + \underline{a}u^2 + \underline{b}u^3 = 0, \quad (7)$$

and one gets

$$\text{for } T > \underline{T}_1 \quad (8)$$

and (from the second order equation for u)

$$u_0(T) = -\frac{\underline{a}}{2\underline{b}} \left[1 + \sqrt{1 - \frac{c_2(T)}{c_t}} \right], \text{ for } \underline{T}_2 < T < \underline{T}_1. \quad (9)$$

Thus, $u_0(T)$ is the equilibrium value and $\underline{T}_1$ is the temperature above which the non-zero solution is unstable (i.e. above which $1 - \frac{4c_2(T)\underline{b}}{a^2} = 1 - \frac{c_2(T)}{c_t} < 0$). It is easy to show (see e.g. [21]), using the definition of $\underline{T}_2$ ($c_2(\underline{T}_2) = 0$), and

$$c_2(\underline{T}_1) = \frac{\underline{a}^2}{4\underline{b}} = c_t, \quad (10)$$

that

$$c_2(T) = c_{20} \left(T - \underline{T}_2 \right) = c_t \frac{T - \underline{T}_2}{\underline{T}_1 - \underline{T}_2}, \text{ for } \underline{T}_2 < T < \underline{T}_1. \quad (11)$$

Thus

$$\underline{T}_1 = \underline{T}_2 + \frac{c_t}{c_{20}} = \underline{T}_2 + \frac{\underline{a}^2}{4\underline{b}c_{20}}. \quad (12)$$

The austenite phase is stable if $T > \underline{T}_2$, and the martensite phase is stable if $T < \underline{T}_1$. Thus, conditions $c_2(\underline{T}_2) = 0$ and $c_2(\underline{T}_1) = \frac{\underline{a}^2}{4\underline{b}} = c_t$ prescribe the liability temperatures of the austenite and martensitic phases and $\underline{T}_1 - \underline{T}_2$ is the measure of the possible maximum width of the hysteresis. Note that this version of the theory gives an instantaneous transition and $A_s = A_f = \underline{T}_1$ as well as $M_s = M_f = \underline{T}_2$. Thus, the difference of $\underline{T}_1 = A_s (= A_f)$ and $\underline{T}_2 = M_s (= M_f)$ is the measure of the maximum width of hysteresis (M_s , M_f , A_s and A_f have their usual meaning as start and finish temperatures of martensite and austenite). The relation between u_0 and the transformation strain, ε^T , measurable during MT, is $u_0(\underline{T}_2) = -\frac{\underline{a}}{\underline{b}} \cong 3\varepsilon^T$ [9–11]. Furthermore, it is easy to show (replacing Eq. (9) into (1) for $\sigma = 0$) that the equilibrium transformation temperature, $\underline{T}_0$, at which $\Delta g(u_0(T))$ is zero, can be given as

$$c_2(\underline{T}_0) = \frac{8}{9}c_t \quad (13)$$

i.e.

$$\underline{T}_0 = \underline{T}_2 + \frac{8}{9} \frac{c_t}{c_{20}} = \underline{T}_2 + \frac{2}{9} \frac{\underline{a}^2}{\underline{b}c_{20}}, \quad (14)$$

from which $\underline{T}_2 < \underline{T}_0 < \underline{T}_1$ and $\underline{T}_0$ is closer to $\underline{T}_1$. Thus, e.g. during heating

or cooling the foremost temperature at which the phase transition occurs is at $\underline{T}_0$ [19]. (The driving force for the transformation is $\Delta g(T) - \Delta g(\underline{T}_0)$.) In the presence of energy losses due to nucleation and frictional growth of the nuclei of martensite and accumulation of elastic energy due to the size difference of the martensite and austenite [22] the transformation can start only below $\underline{T}_0$, i.e. $M_f < M_s < \underline{T}_0$ (undercooling). For heating, by similar reasons, there exists overheating, i.e. $\underline{T}_0 < A_s < A_f$ (see also Fig. 1 below).

By definition the elastic modulus is given by $\frac{\partial^2 \Delta g}{\partial u^2}$. Thus, from Eq. (1)

$$c_2 = 3C' = c_{2A}(T) + 2\underline{a}u + 3\underline{b}u^2. \quad (15)$$

Here $c_{2A}(T) = c_{20}(T - \underline{T}_2)$ stands for the austenite; in the austenite (at $T > \underline{T}_1$ where $u_0 = 0$) c_2 coincides with it. $c_{2A}(T)$ has a linear dependence for $T > \underline{T}_2$ (where $u_0 = 0$) and c_2 is zero at $T = \underline{T}_2$ and the slope $\frac{\partial c_2}{\partial T}$ is $\frac{\partial c_2}{\partial T} = \frac{1}{3}c_{20}$. c_2 denotes the shear modulus for the martensite within the interval $[\underline{T}_2, \underline{T}_1]$. It has to be calculated with u given by Eq. (9). For the martensite, the $u_0(T)$ function, as given by Eq. (9), has to be inserted into Eq. (14) and it is a decreasing function in the $[\underline{T}_2, \underline{T}_1]$ interval and becomes zero at $T = \underline{T}_1$ (see Fig. 1).

2.2. Stress induced MT

We have to make an important comment first: in the presence of external stress, the elastically deformed austenite is no longer cubic, it has a small tetragonal distortion. Thus, the first order phase transformation will have an isomorphic character. One can expect that at increasing stress the temperature induced jump in u_0 should decrease and gradually goes to zero, i.e. the nature of the phase transformation changes.

From the extremum condition of Eq. (1) it is possible to construct the stress-temperature diagram taking $\frac{\partial \Delta g}{\partial u} = 0$ and $\frac{\partial^2 \Delta g}{\partial u^2} = 0$. From the latter one, which determines liability lines for an axially stressed alloy [5, 9–11, 18, 19, 23],

$$\sigma_A = -\frac{16c_t^2}{9\underline{a}}(1 - R(T))^2(1 + 2R(T)) \quad (16)$$

and

$$\sigma_M = -\frac{16c_t^2}{9\underline{a}}(1 + R(T))^2(1 - 2R(T)) \quad (17)$$

follow, where

$$R(T) = \sqrt{1 - \frac{3}{4} \frac{c_2(T)}{c_t}} = \sqrt{1 - \frac{3}{4} \frac{T - \underline{T}_2}{\underline{T}_1 - \underline{T}_2}}, \quad (18)$$

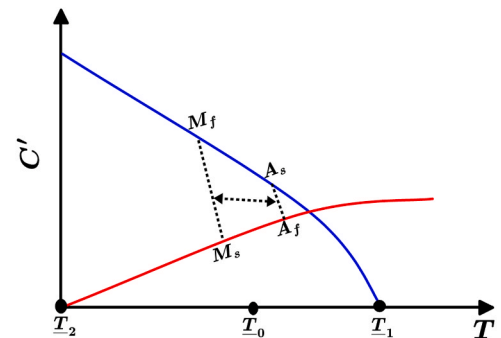


Fig. 1. Shear modulus ($C' = 3c_2$) versus temperature, schematically. Blue and red lines belong to martensite and austenite. The inclined vertical lines indicate the cooling and heating transition. If the transition would exactly happen at $\underline{T}_0$ then vertical jump between the blue and red curves would give the jump in C' . The dashed horizontal arrow shows the actual hysteresis width (which is less than $\underline{T}_1 - \underline{T}_2$).

and $\sigma_{zz} = \sigma_{zz} + \sigma_{zz}^{in}$ (for compressive stress $\sigma_{zz} < 0$).

Thus, the austenite is stable if $|\sigma_{zz}| < |\sigma_A|$ and the martensitic phase is stable if $|\sigma_{zz}| > |\sigma_M|$ and a two-phase region exists if $|\sigma_M| < |\sigma_{zz}| < |\sigma_A|$. Fig. 2 shows schematically the σ_A and $\sigma_M(T)$ functions. The liability lines cross each other at $R(T^*) = 0$, which gives the parameters of the critical point as

$$\sigma_{zz}^* = -\frac{16c_t^2}{9\alpha} = -\frac{1}{9} \frac{\alpha^3}{b^2} \quad (19)$$

and

$$3c_2(T^*) = 4c_t, \text{ i.e.} \quad (20)$$

$$T^* = T_2 + \frac{4c_t}{3c_{20}} = T_2 + \frac{1}{c_{20}} \sqrt{-\sigma_{zz}^* \alpha} = T_2 + \frac{1}{3} \frac{\alpha^2}{bc_{20}}. \quad (21)$$

Furthermore,

$$T^* = T_0 + \frac{1}{9} \frac{\alpha^2}{bc_{20}} = T_0 + \frac{1}{3c_{20}} \sqrt{-\sigma_{zz}^* \alpha}. \quad (22)$$

It can be noted that, while b is always positive, the sign of α is related to the sign of $u_0 \cong 3\epsilon^r$ [10] (see also Eq. (9)): for alloys with $\epsilon^r < 0$, $\alpha > 0$, which is used here. Approximating the equilibrium transformation stress by $\sigma_o(T) = \frac{\sigma_A(T) + \sigma_M(T)}{2}$ we get, using Eq. (20) as well, that

$$\begin{aligned} \sigma_o(T) &= -\frac{16c_t^2}{9\alpha} [1 - 3R^2] = -\frac{16c_t^2}{9\alpha} \left[\frac{9}{4} \frac{c_2(T)}{c_t} - 2 \right] \\ &= \sigma^* \left[\frac{9}{4} \frac{T - T_2}{T_1 - T_2} - 2 \right], \end{aligned} \quad (23)$$

which shows that, as expected, it has a linear dependence on the temperature. Obviously, the self-consistency also dictates that $\frac{\partial \sigma_o}{\partial T} = -4 \frac{c_t}{\alpha c_{20}} = -\frac{\alpha c_{20}}{b}$ should coincide with the expression for the well-known Clausius-Clapeyron relation $\frac{\partial \sigma_o}{\partial T} = -\frac{\Delta s}{\epsilon^r}$ (which can be checked by calculating the transformation entropy, from the general definition, as $\Delta s = -\frac{\partial \Delta g}{\partial T}$).

2.3. Effect of defects (disorder)

The presence of different types of disorder in the orthodox Landau

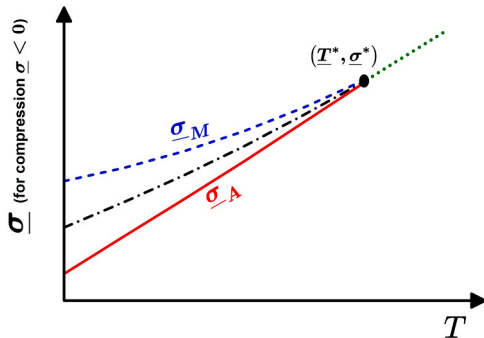


Fig. 2. Schematic stress temperature phase diagram ($\sigma_{zz} \equiv \sigma$ here) with the critical point (see also [23]). Dashed, blue line: $\sigma_M(T)$; continuous red line: $\sigma_A(T)$; dash-dotted black line: σ_o ; dotted green line is the Widom line (see also the text). As an example, typical experimental values for σ^* and T^* are $\sigma^* = -284 \text{ MPa}$, $T^* = 434 \text{ K}$ and $T_0 = 246 \text{ K}$ [24] as well as $\sigma^* = -(340 \pm 50) \text{ MPa}$ and $T^* = (327 \pm 40) \text{ K}$ [6] in $\text{Ni}_{55-x}\text{Co}_x\text{Fe}_{18}\text{Ga}_{27}$ single crystals with $x = 4.5\%$ as well as $x = 5.0 \text{ at\%}$, respectively. Thus, as an approximate average values $\sigma^* = 310 \text{ MPa}$ and $T^* = 380 \text{ K}$ at about $4.75 \text{ at\%}$ can be considered (see also below).

theory can be taken into account by adding terms to the Gibbs free energy difference of the defect-less system (with u and u_1 order parameters), containing η_i so called configurational parameters, related to perturbations caused by defects [25–28]. In fact, it is a delicate task to find the minimal set the necessary η_i parameters [27]. It was shown [11, 18, 25–28] that, for cubic to tetragonal transformation only two variables, η and η_1 are enough, which describe that defects can cause isotropic strain (volume change), η_1 , as well as axial strain, η . Thus, internal stresses, conjugated to the above strains, can be given [11, 25, 26] as

$$\sigma^{in} = 6d\eta, \quad (24)$$

as well as

$$\sigma_1^{in} (= -p^{in}) = \frac{1}{3} d_1 \eta_1, \quad (25)$$

with $\eta \propto u$ and $\eta_1 \propto u_1$. It was pointed out that if the sign of the proportionality constants, d and d_1 , in the above relations are such that the internal stresses, σ^{in} and $\sigma_1^{in} = -p^{in}$, have the same sign as u as well as u_1 , then σ^{in} and σ_1^{in} can be referred to as stabilizing stresses [25–29]. Indeed, during martensite aging under external axial stress (during symmetry conforming short range ordering [30], which can be called stress induced stabilization, SIM, aging) the short-range order defects, created by the symmetry change during austenite to martensite transition, can be annealed out resulting in stabilization of martensite. This also means that, in the austenite after SIM aging, creation of symmetry conforming defects (produced by the SIM aging itself), during martensite to austenite transformation, results in the stabilization of martensite.

Thus, the effect of defects can be formally described by effective stresses: $\sigma = \sigma_{ext} + \sigma_i(\eta_i)$, where the σ_{ext} is the external (applied) stress. Perturbations caused by defects can be even time (and temperature) dependent: e.g. during symmetry conforming short-range ordering [30]. Here we concentrate on static (equilibrium) perturbations caused by defects and the time dependence during annealing out will not be considered.

There are experimental evidences when defect induced stresses destabilize the martensite i.e. their presence in the austenite leads to decrease of the equilibrium transformation temperature [2, 15, 27]. For these cases the proportionality factors in Eqs. (24) and (25) should be negative. From the point of view of production of strain glasses or low temperature post-critical systems, defects causing destabilization of martensite are important and we will consider these. Beside of point defects, such effects can also be caused by increasing number of dislocations or grain boundaries or precipitates. For the sake of simplicity, and because we concentrate on the main trends, we will simply assume that T_0 linearly decrease with the defect composition, x . This means, in the terms of internal pressure and or stress, that we assume that they are linear functions of composition (see Fig. 3), i.e. $\eta_i \propto x$, similarly as e.g. was done in [11, 25] or [28].

It is also worth to make a comment on the composition dependence in ferromagnetic shape memory alloys. It was nicely demonstrated in [28] that in these alloys the magnetostriction energy contribution to Δg can be treated as it would lead to an internal magnetic pressure in accordance with formulae given by Eqs. (1)–(6). Thus, in ferromagnetic SMAs the composition dependence of the characteristic temperatures can dominantly originate from the composition dependence of the magnetic properties (see e.g. Fig. 1 in [31], which illustrate that the Curie temperature has, similarly as T_0 , a strong composition dependence). This also means that our description can be quite general and can account for composition dependences of different origin.

3. Composition dependence of the characteristic temperatures

Adequate theoretical description of destabilizing effect of defects is a challenging task [2, 15]. Indeed, various possible effects of random point

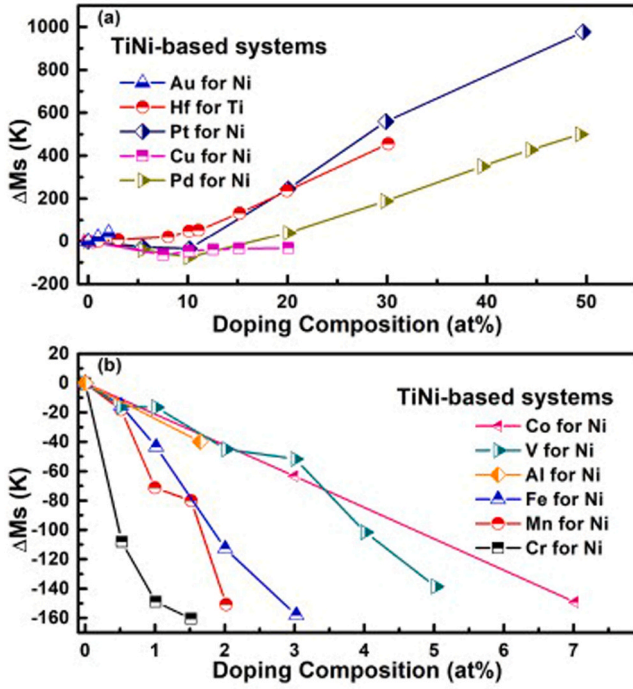


Fig. 3. Effect of increasing defect concentration, x , on the martensite start temperature in NiTi alloys. [15] (Reprinted from “Doping effects of point defects in shape memory alloys” *Acta Materialia*, 176, (2019) 177–188, Yang, Y., et al. Copyright No; 6271880376558 (Sep 1, 2019), with permission from Elsevier). It can be seen that numerous defects decrease it (see Figure b): these are strain-glass forming systems and here the linear approximation seems to be good.

defects can be considered: i) lowering of the global transformation temperature; ii) local transition temperature effect caused by random spatial distribution of defects; iii) local elastic field effects associated with local lattice distortions which can also influence the martensite variant selection [2]. These effects can be treated in the framework of well-sophisticated phase-field (using Landau-Ginzburg) theories [2,5,17].

It is well known that in general, the equilibrium transformation temperatures have strong composition dependence, and the effect of dopants can result in both positive or negative slope for a linear dependence [21]. In the following we will concentrate on those cases when T_o decreases with x , i.e. doping results in destabilization of martensite.

In the following, concentrating on the main trends, we consider only i) and take also, as usual, that in the orthodox Landau theory, summarized in Chapter 2, all the other input parameters, c_{20} , α_i and b_i are constants, i.e. their temperature and composition dependence is negligible. Expressions (12), (14), (21) and (22) show that, in the absence of external pressure, the characteristic temperatures can have a p^{in} dependence via the $\frac{\alpha^2}{4bc_{20}} = \frac{(\alpha - \lambda_{pa}p^{in})^2}{c_{20}4b}$ as well as $c_2 = c_2 - \lambda_{pc}p^{in}$ terms, if $\sigma = 0$. Seeking for linear composition dependence, i.e. using that $\sigma_1^{in} = -p^{in} = \delta_1 x$, in accordance with experimental results, we can write

$$\frac{\alpha^2}{b} = \frac{(\alpha - \lambda_{pa}p^{in})^2}{b} \cong \frac{\alpha^2}{b} \left[1 - \frac{2\lambda_{pa}}{\alpha} p^{in} \right], \quad (26)$$

where it was also used that $\frac{b}{b} = 1 - \frac{a_2^2}{b_2c_1} \cong 1$. This approximation is consistent with $\frac{a_2}{c_1} \ll 1$ [11] as well as $\frac{a_2}{b} < 1$ [11]. Furthermore, from the condition $c_{20}(T_2) = 0$

$$c_{20} \left(\frac{T_2}{T_2} - T_2 \right) - \lambda_{pc} p^{in} = 0, \quad (27)$$

i.e.

$$T_2 - T_2 \equiv T_2(x) - T_2(0) = \frac{\lambda_{pc}}{c_{20}} p^{in}, \quad (28)$$

where Eq. (2) was also used. Furthermore, from Eq. (14), writing it for x and $x = 0$ and using Eqs. (28) and (3) as well, we can write

$$\begin{aligned} \Delta T_o(x) &= T_o(x) - T_o(0) = T_2(x) - T_2(0) + \frac{2}{9} \frac{\alpha^2}{bc_{20}} \left[\frac{\alpha^2}{\alpha^2} - 1 \right] \\ &= \frac{\lambda_{pc}}{c_{20}} p^{in} - \frac{4}{9} \frac{\alpha \lambda_{pa}}{bc_{20}} p^{in} = -\frac{4}{9} \frac{\alpha \lambda_{pa}}{bc_{20}} \left[1 - \frac{9}{4} \frac{\lambda_{pc}}{\lambda_{pa}} \frac{b}{\alpha} \right] p^{in} \\ &= -\mu \left[1 - \frac{\varphi}{\mu} \right] \delta_1 x = -D_o x. \end{aligned} \quad (29)$$

where Eq. (26) with $\frac{b}{b} \cong 1$ and $\left(\frac{\alpha}{\alpha} \right)^2 - 1 = -\frac{2\lambda_{pa}}{\alpha} p^{in}$ as well as $p^{in} = -\delta_1 x$ were also used. Let us estimate the sign of μ and $\frac{\varphi}{\mu}$ and thus the sign of D_o . First, for the estimation of the $\frac{\varphi}{\mu} = \frac{3}{2} \frac{a_2}{b_7} \frac{b}{a}$ ratio, we can take $\varepsilon^r = -0.06$ [11] as a typical value. Furthermore, we can take $\frac{b_7}{c_1} = -0.343$ [11] as well as $\frac{a_2}{c_1} = 0.062$ [11], and using that $u_o(T_2) = -\frac{a}{b} \cong 3\varepsilon^r$ [9–11,27], we get $\frac{b}{a} = 5.6$ and $\frac{b_7}{a_2} = \frac{b_7}{c_1} \frac{c_1}{a_2} = -5.5$. This gives $\frac{\varphi}{\mu} \cong -\frac{3}{2}$, i.e. $D_o = \mu \left[1 - \frac{\varphi}{\mu} \right] \delta_1 \cong \frac{5}{2} \mu \delta_1$.

It can also be seen from the above data, that $\mu = -\frac{4}{9} \frac{\alpha \lambda_{pa}}{bc_{20}} = -2 \frac{ab_7}{bc_1 c_{20}}$ is positive and thus, $D_o > 0$, if $\delta_1 > 0$. This means that $T_o(x)$ decreases with increasing x only if $\delta_1 > 0$, i.e. for destabilizing defects the induced internal pressure $p^{in} = -\delta_1 x$ is negative (the volume expansion of austenite, caused by defects, is positive).

We can also estimate the change of the $T_1 - T_2$ difference (the maximum width of the hysteresis) from Eq. (12), writing it again for x and $x = 0$, and using the notations $T_1 - T_2 \equiv T_1(x) - T_2(x)$ and $\Delta_h(x) = T_1(x) - T_2(x) - [T_1(0) - T_2(0)]$, as

$$\Delta_h(x) = \frac{\alpha^2}{4bc_{20}} \left[\frac{\alpha^2}{\alpha^2} - 1 \right] = -\frac{\alpha \lambda_{pa}}{2bc_{20}} p^{in} = -\frac{9}{8} \mu \delta_1 x = -\frac{1}{10} D_o x, \quad (30)$$

which shows that Δ_h indeed decreases with increasing x for destabilizing defects. This is in accordance with experiments: see e.g. [21] and Figures 7 and 8a for $\text{Ni}_{50-x}\text{Ti}_{50+x}$ alloys in [32], where the slope of T_o versus x indeed larger than the slope of the experimental Δ_h versus x : $D_o \cong 100 \frac{\text{K}}{\text{at}\%}$ from T_o versus x , while the slope of $\Delta_h(x)$ versus x is $\cong -8$. This also agrees with theoretical calculations on the effect of destabilizing defects [33] too.

The values of $D_o \cong \frac{5}{2} \mu \delta_1$ can be approximately calculated from the slopes of the decreasing martensite start versus composition functions, shown in Fig. 3b [15], for different doping elements in NiTi alloys. Of course, D_o is different for different types of defects: D_o lies between 160 K/at% and 22 K/at%. We can use these data for the estimation of the composition dependence of the critical temperature or critical pressure. From Eq. (21), writing it again for x and $x = 0$, and we get

$$\begin{aligned} \Delta T^*(x) &= T^*(x) - T^*(0) = \frac{\lambda_{pc}}{c_{20}} p^{in} + \frac{1}{3} \frac{\alpha^2}{bc_{20}} \left[\frac{\alpha^2}{\alpha^2} - 1 \right] = -\frac{3}{2} \mu \left[1 - \frac{2}{3} \frac{\varphi}{\mu} \right] \delta_1 x \\ &\cong -\frac{6}{5} D_o x, \end{aligned} \quad (31)$$

where Eqs. (28), (29) and $\frac{\varphi}{\mu} \cong -\frac{3}{2}$ was also used. Thus, for the decrease of

T^* by changing x from zero to 1 at% we get $\Delta^*(x = 1\%) = T^*(x = 1\%) - T^*(0) = -(200 - 25) \text{ K}$, which shows that T^* can decrease significantly in the presence of destabilizing defects.

Finally, it is also worth estimating the x -dependence of the $T^* - T_0$ difference. From the difference of Eqs. (31) and (29), and introducing the notation: $\Delta_o^* = T^*(x) - T_0(x) - [T^*(0) - T_0(0)]$, we can get

$$\Delta_o^*(x) = -\frac{1}{5}D_{0\sigma}x. \quad (32)$$

If we define x_0 as the composition at which $T_0(x_0) = 0$, we get

$$\Delta_o^*(x_0) = -\frac{1}{5}D_{0\sigma}x_0. \quad (33)$$

Since the value of x_0 is typically larger than 1 at%, we can conclude that at x_0 the decrease of T^* can be several times larger than 100 K, i.e. T^* can be below the room temperature.

Fig. 4 illustrates as an example the $T^*(x)$ and T_0 functions in $\text{Ni}_{55-x}\text{Co}_x\text{Fe}_{18}\text{Ga}_{27}$ single crystals (experimental data for $T^*(4.75\text{at}\%)$ and $T_0(5\text{at}\%)$ were taken from [6] and [24] as well as $D_o \cong 15 \frac{\text{K}}{\text{at}\%}$ [5,24,29] was used. It can be seen that above 10 at% T^* is below room temperature which is in good agreement with the experimental results of [13], where $x_c \cong 10.5\text{at}\%$ was obtained above which superelastic (post-critical) behaviour was observed, if we take into account the error bars of the estimated input parameters ($\Delta D_o \cong \pm 5 \frac{\text{K}}{\text{at}\%}$, $\Delta T^* = \pm K$ and $\Delta T_0 \pm 50\text{K}$).

Effects of defects causing internal pressure were discussed above. We can also get approximate expressions for $T_0(x)$ and $T^*(x)$ if $p^{in} = 0$, but σ^{in} is not zero. In this case Eqs. (19)-(22) will be valid for the original input parameters α, b, c_{20} and T_2 . Seeking again for a linear x -dependence, from the difference of Eqs. (21) and (22), using that $\sigma_{zz}^* = \sigma_{zz} + \sigma^{in}$ as well as the proportionality $\sigma^{in} = \delta x$,

$$\begin{aligned} T_0(x) - T_2 &= \frac{2\sqrt{-\sigma_{zz}^*}\alpha}{3c_{20}} \sqrt{1 + \frac{\delta x}{-\sigma_{zz}^*}} \cong \frac{2\sqrt{-\sigma_{zz}^*}\alpha}{3c_{20}} + \frac{1}{3c_{20}} \sqrt{\frac{\alpha}{-\sigma_{zz}^*}} \delta x \\ &= T_0(0) - T_2 - D_{0\sigma}x \end{aligned} \quad (34)$$

can be obtained, where $\sqrt{1+x} \cong 1 + \frac{1}{2}x$ was also used and $D_{0\sigma} = -\frac{\delta}{3c_{20}} \sqrt{\frac{\alpha}{-\sigma_{zz}^*}}$. Similarly, from Eq. (21), one can get

$$\begin{aligned} T^*(x) - T_2 &= \frac{\sqrt{-\sigma_{zz}^*}\alpha}{c_{20}} \sqrt{1 + \frac{\delta x}{-\sigma_{zz}^*}} \cong \frac{\sqrt{-\sigma_{zz}^*}\alpha}{c_{20}} + \frac{1}{2c_{20}} \sqrt{\frac{\alpha}{-\sigma_{zz}^*}} \delta x \\ &= T^*(0) - T_2 - \frac{3}{2}D_{0\sigma}\delta x. \end{aligned} \quad (35)$$

Thus,

$$\Delta T_0 = T_0(x) - T_0(0) = -D_{0\sigma}x \quad (36)$$

and

$$\Delta T^*(x) = T^*(x) - T^*(0) = -\frac{3}{2}D_{0\sigma}x. \quad (37)$$

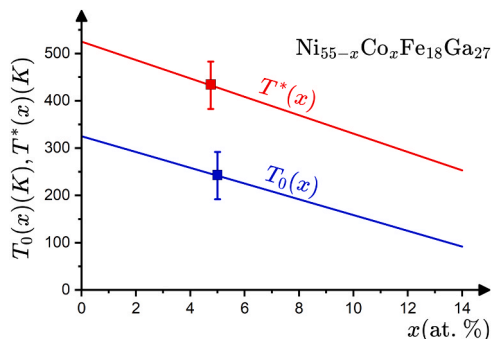


Fig. 4. Estimated $T^*(x)$ and T_0 functions for $\text{Ni}_{55-x}\text{Co}_x\text{Fe}_{18}\text{Ga}_{27}$ system.

Furthermore, from Eq. (22)

$$T^*(x) - T_0(x) = \frac{\sqrt{-\sigma_{zz}^*}\alpha}{3c_{20}} \sqrt{1 + \frac{\delta x}{-\sigma_{zz}^*}} = T^*(0) - T_0(0) - \frac{1}{2}D_{0\sigma}x. \quad (38)$$

We can see that i) $D_{0\sigma}$ is positive if δ in relation $\sigma^{in} = \delta x$ is negative, i. e. for destabilizing defects the created strain $\eta \propto \delta x$, as expected, has opposite sign as u_o (for stabilizing defects they have the same sign) and ii) relations (34)-(38) are similar to (29) and (33) and thus similar conclusion can be drawn, as done above. Finally, it can also be added that it was shown in [33] that T^* decreases with the defect composition for defects causing destabilization of martensite. In [33] the shear strain, and thus shear stress, of nanoparticles was also considered in detailed calculations, confirming that our arguments above qualitatively apply for these effects with axial internal stress too.

We have seen above that T^* can be significantly low or even can be below the room temperature where the stress-strain curves are usually measured and thus one can observe superelasticity in the post-critical state. It is also worth noting that the slopes of the $T_0(x)$, $T^*(x)$ or $\Delta_o^*(x)$ linearized functions are interrelated: all of them can be expressed via D_o .

It can be noted that if T_0 is not zero, i.e. $x < x_0$, it is still possible to reach a transition to the strain glass state, if the strain glass temperature, T_g , is still below T^* : $T_0 < T_g < T^*$. In this case a post-critical behaviour is expected above T_g , and by cooling the strain glass state forms and by further cooling a strain glass to martensite transition during stress induced transformation can take place. The Clausius-Clapeyron relation allows to reach the martensite start stress at temperatures above T_0 ($\sigma = 0$) but still below T_g , and by changing the magnitude of the stress a reversible strain-glass/martensite transformation can be observed as it was demonstrated in [34].

If x is well above x_0 it is expected that the stress-strain curves taken above T_g will show a superelastic behaviour in the post-critical state (see also Fig. 4). At temperatures below T_g also a shape memory effect is expected, but now this will be related to the stress induced alignment on frozen-in nanodomains of the strain glass state. This residual strain will be recovered by heating up above T_g : the magnitude of this can be determined by the maximum difference of the strain curves measured under field-cooled and zero-field-cooled condition (typically about 0.1–0.4% [2]).

4. Behaviour near and above the critical point

We have seen that the 2–3–4 type potential in the orthodox Landau theory provides a clear explanation for the existence of critical point in the stress-temperature phase diagram. In addition, experimental observations confirmed that above the critical point there is practically close to zero hysteresis (anhysteretic behaviour) [5]. Furthermore, it is expected that the stress-strain curves, measured above the glass transition temperature, typically can have a post-critical, trilinear character [13], consisting of the Hooke's laws of the austenite and martensite (the first and third parts) and of the recoverable non-hysteretic post-critical transformation part (central part in Fig. 5). The magnitude of this can be different in different systems. It is important to underline that the full superelastic regime (which e.g. extended up to 11% in [4] or up to about 15% in [13]) thus contains all the above contributions and the effective transformation strain (corresponding to the central part of the curve shown in Fig. 4) is about 5–7% e.g. in Fig. 1 of [13].

Understanding the stress-strain behaviour near the critical point and above it is a central problem in post-critical systems. It is well known that there exist scaling laws on both sides of the critical point [35,36], and scaling exponents above the critical point can be predicted only from sophisticated renormalization theories. It is also known that there can exist a Widom line [16], emanating from the critical point above it. It was shown in liquid-gas systems that some thermodynamic quantities (velocity of acoustic waves, inelastic X-ray scattering) have maxima

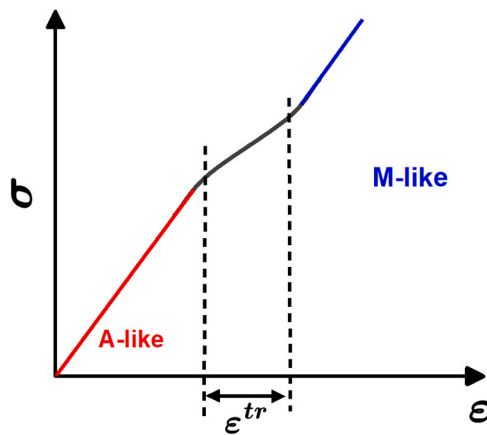


Fig. 5. Schematic, non-hysteretic stress-strain curve above the critical point. The central part is the transition region around the Widom line, the first and third parts are the Hook regimes for the austenite-like and martensite-like phases (see also the text).

along the Widom line) and a sharp transition on crossing the Widom line was observed. Thus, it is challenging to investigate the behaviour of post-critical ferroelastic systems as a function of the distance from the critical point ($T - T^*$). From this point of view, the temperature dependence of the effective transformation strain (as defined in Fig. 1) can be interesting and investigations of whether it indeed corresponds to an austenite-like/martensite-like transition, similarly to a transition between liquid-like to gas-like behaviour [16], are also challenging.

It is worth to summarize the trials provided in [13] for the explanation of superelastic behaviour of single crystalline $\text{Ni}_{55-x}\text{Co}_x\text{Fe}_{18}\text{Ga}_{27}$ fibres. It was concluded that neither the post-critical neither the strain glassy behaviour can explain the stress-strain curves observed. However, no experimental curves were provided below 123 K and the conclusion that the superelastic behaviour remained down to 0 K was obtained only from model calculation based on the used simplified Landau theory. In this, 2–4 Landau potential was used and the expansion was made around the critical point. This provides first order phase transformation (i.e. below x_c as observed) only if the elastic modulus of the 2nd order term, (corresponding to $c_2 \propto E$ using our notations above) is negative (which would mean that the austenite is unstable below x_c) and it becomes positive only above x_c . This version provides a second order transition above the critical point, and using the fits to the experimental stress-strain curves the authors obtained the calculated unchanged supercritical curve even at 0 K. Furthermore, from the obtained composition dependence of the critical stress it was concluded that it can be considered as Widom line: crossing this line by changing x there is a transition from softening to hardening behaviour of the stress induced Young modulus. Thus, there are still puzzling points, which call for further experimental investigations (stress-strain curves at lower temperatures) and for theoretical efforts, with more sophisticated theoretical models and more reliable predictions on the possible measurable parameters showing changes when crossing the Widom line.

Our arguments, based on the orthodox Landau theory provide a plausible explanation for the existence of a critical composition observed in [13] and explain the low temperature post-critical behaviour and a possible freezing of the nano-martensite domains below a certain glass transition temperature (see Fig. 4). On the other hand, we believe that predictions on the behaviour of the system above the critical temperature (i.e. on the existence of the Widom line and on the behaviour when the system crosses the Widom line) require more sophisticated experimental and theoretical approaches. For instance, ultrasonic velocity and attenuation measurements can provide important contribution to understanding of the details of martensitic transformations in SMAs [37,38] and such measurements during the

stress-strain curves taken at fixed temperatures above the critical temperature can be considered as analogue ones to the ultrasound velocity measurements made in liquid/gas system [16].

5. Additional remarks

5.1. Effects determining the value of T_g

While the composition dependence of T_0 and T^* can be satisfactorily described and interpreted by taking into account the lowering of the global transformation temperature, the glass transition temperature should certainly be sensitive to the local effects caused by defects. Indeed, it is expected that especially the local elastic field effects associated with local lattice distortions [2], can be important. Their density and distribution can determine how easily the dynamic high temperature state freezes in. The nature of these local elastic fields can also influence the martensite variant selection [2]. Indeed, it was shown in [17], from a 2D cubic to rectangular Landau-Ginzburg theory, that the elastic anisotropy of the disorder plays a crucial role in forming strain glass state. It was illustrated that strain glass transition can be observed at stresses proportional to the anisotropy: the higher the value of anisotropy the higher the required stress. Furthermore, no geometrical frustration, associated with glassy states was found. It was concluded that the glassy behaviour is primarily kinetic in origin due to the existence of local energy barriers caused by disorders (dynamic freezing; see also [1,2]).

5.2. On the easy way of transition to a critical behaviour

We used above the orthodox Landau theory for the cubic to tetragonal martensitic transformation. For this case the crystallographic aspects of approaching or going beyond the critical point is clear: the tetragonally deformed austenite has an isomorphic transition to the tetragonal martensite. However, for general cases the idea about “good fitting phases”, transforming into each other [39], should also be considered: the compatibility of the austenite and martensite phases requires i) zero transformation volume, u_1 , and ii) existence of crystallographic planes, common for both phases (called also as invariant, or undistorted planes [9,14,39]). The middle eigenvalue of the martensitic transformation matrix, λ_2 , was introduced for the characterization of this crystallographic requirement [36]: in case of ideal compatibility $\lambda_2 = 1$. These invariant planes are absent in many SMAs and search for their existence can be made by variations of concentration of dopants [9] too. Thus, it turned out that the existence of invariant interfaces is a key condition to obtain system with minimum hysteresis and has a primary importance, while the volume effect is less crucial [9]. Similarly, one can expect that the existence of a critical point should be closely related to the fulfilment of this condition for transformations other than cubic to tetragonal. Nevertheless, in these cases if addition of dopants, parallel with the decrease of T_0 , also leads to production of undistorted planes, T^* can exist and thus the strain glass as a frozen-in post-critical state can form.

From the above points of view, it is an interesting question that in strain glasses, where no such an invariant plane exists or can not be created by doping, what can explain the almost anhysteretic stress-strain curves above T_g . In this latter group of SMAs the formation of strain-glass can be interpreted as an interruption of the formation of long range ordered martensite by the presence of nanosized random stress-carrying defects. Their random stress field is incompatible with the long range ordered (macroscopic) martensite and the nanosized random stress fields also suppress the autocatalysis, by which the formation of macroscopic martensite takes place [2]. This smears the transition into strain glass state. Since the microstructure of the frozen in strain glass state also do not contain sharp interfaces, during stress-induced ordering (reorientation) of strain nanodomains there is no need for either i) nucleation of stable martensite nuclei and/or ii) intermittent motion of

sharp interfaces. Both of them can lead to energy loss during the stress induced transition in usual first order MTs [40]. Thus, in this case the width of the hysteresis should be minimal in accordance with the minimal cumulative energy of acoustic emission, similarly as it was detected during approach to the post critical state $\text{Ni}_{48}\text{Fe}_{20}\text{Co}_5\text{Ga}_{27}$ (at%) single crystal [6]. The remaining question for future investigations is: is there any difference in the temperature dependence of the stress-strain curves measured in post-critical strain glasses and in strain glasses produced by suppressing the MT by random stress fields of defects?

6. Conclusions

- it is shown, using the results of the orthodox Landau theory for cubic to tetragonal transformation, that defects causing destabilization of the martensite by induced internal pressure or axial stress, parallel with the decrease of the equilibrium transformation temperature, T_0 , can cause significant decrease of the critical temperature too.
- using the simple assumption that the destabilization effect is proportional to the defect composition, x , it was shown that at x_0 , where $T_0 = 0$, the critical temperature can be even below the room temperature.
- it is illustrated that in these shape memory alloys the strain glass state can be a frozen in post-critical state and at temperatures above the glass transition temperature, T_g , an hysteretic superelastic stress-strain curves are expected. Below T_g , depending on how strong the arrest of the martensitic transformation is, either a shape memory effect (reflecting the residual strain belonging field cooled and zero field cooled states) can be observed or a stress induced superelastic behaviour manifests between strain-glass and martensitic state.
- the importance of the investigations of stress-strain curves in wide temperature range is emphasized, in order to understand the behaviour above the critical point when crossing the Widom-line
- the role of existence/creation of undistorted interface (to enhance the compatibility of the martensite and austenite) when changing the composition of stabilizing defects can be an important factor in the above processes.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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