ANALI PAZU
Vol. 13, No. 1, pp. 51–63, June 2023

ANALI PAZU

IMPACT OF THE ORIGINATING MARTENSITIC PHASE ON THE CHARACTER OF MARTENSITIC PHASE TRANSFORMATION

Accepted
30. 10. 2022

Revised
14. 3. 2023

Published
9. 6. 2023

Keywords:
austenitic-martensitic phase transformation, landau mean field, ginzburg term, parameter, approximation

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In the article, we discuss the influence of the locally perturbed order parameter in austenitic-martensitic phase transformation on the character of the phase transformation. We choose Landau type mean field approximation which covers the most important features of the proposed theoretical description.

https://doi.org/10.18690/analipazu.13.1.51-63.2023
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Univerzitetna založba Univerze v Mariboru

ANALI PAZU
Vol. 13, Št. 1, pp. 51–63, junij 2023

VPLIV NASTAJAJOČE MARTENZITNE FAZE NA ZNAČAJ MARTENZITNEGA FAZNEGA PREHODA

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Sprejeto
30. 10. 2022

Recenzirano
14. 3. 2023

Izdano
9. 6. 2023

V članku obravnavamo vpliv lokalno spremenjenega ureditvenega parametra pri avstenitno-martenzitnem faznem prehodu na značaj takega faznega prehoda. Sistem modeliramo z metodo povprečnega polja Landau-ovega tipa, ki vsebuje najpomembnejše značilnosti tega teoretičnega opisa.

Ključne besede:
avstenitno-martenzitni fazni prehod, Landau-ovo povprečno polje, Ginzburgov člen, parameter, modeliranje

University of Maribor Press

https://doi.org/10.18690/analipazu.13.1.51-63.2023
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1 Introduction

Shape memory alloys (SMA) are due to its superelastic (pseudoelastic) phenomena very fruitful field of research, even in the medicine (e.g. orthodontics (Ferčec, Anžel, Rudolf, 2014)). Such an unusual behaviour of an alloy can be result of mechanical load and/or temperature change (Ferčec, Glišič, Šćepan, 2012). Shape changes are generated by martensitic phase transformations, rather than by conventional elastic or plastic dislocation glide deformation. The most common SMA is NiTi. Martensitic phase transformation is a phase change between two solid phases and involves rearrangement of atoms within the crystal lattice and is associated with an inelastic deformation of the crystal lattice with no diffusive process involved. The absence of diffusion makes the martensitic phase transformation almost instantaneous (first – order transition). But there exist a class of transitions in martensites and ferroelectrics named "nucleation type" which can be continuous (in some control parameter, e.g. stress field) (de Gennes, 1973). The phase transformation itself is an example of a displacive transition, in which there is cooperative motion of a relatively large number of atoms, each being displaced by only a small distance relative to its neighbours. As such the martensitic phase transformation can be characterised also as a structural phase transitionbn (Cowley, 1980, Ferčec, Jenko, Buchmeister, 2014).

Phase transition from high-temperature austenitic phase towards low-temperature martensitic phase takes place if the temperature of the system is changed from M_s to M_f. The same phase transformation e.g. of the NiTi wire can occur if the martensitic transformation stress σ_{M_f} is applied and increased to σ_{M_f}. When the stress is reduced it is thermodynamically more stable for the alloy to revert back to the parent phase exhibiting hysteresis because extra driving force is required due to the stored elastic strain energy contribution.

Landau mean - field theory provides a relatively simple picture of many structural phase transitions in terms of relatively few phenomenological constants (de Gennes, 1973, Landau, Lifshitz, 1980). In spite of neglecting fluctuations the phenomenological theories are very successful in describing a lot of phase transition phenomena. First attempts to describe martensitic phase transformation using Landau approach have been made in 1978 by Bhatt (Bhatt, 1978). Some review about following work in the "early years" of mean field description of the martensitic

phase transition was given in (Falk, 1982). There has been some very comprehensive research work using Landau approach to discuss (weakly) first order (martensitic) phase transformation with or without an external field e.g. (Falk, 1982, Fradkin, 1994, Sanati, Saxena, 2003), but there is not very much done using Landau approach in respect of the influence of the emerging martensitic phase on the character of the phase transformation. It is known that as the SMA enters from austenitic into martensitic phase in the process of transformation due to thermo-mechanical coupling macroscopic domains are formed, which strongly depend on loading (strain) rate $\dot{\varepsilon}$ (Bruno, Leo, Reitich, 1995, Sun, Zhong, 2000). Here point over the strain (ε) represents the time derivative. Moreover the number of emerging domains is strongly connected to $\dot{\varepsilon}$ (He, Sun, 2010).

In the following we will use a Landau mean-field approach to study the effect of elastic distortions as the consequence of the spatial strain inhomogeneity on the character of the phase transformation. Strain inhomogeneity will be introduced as the free energy "gradient term", and then it will turn out to be an essential part of the local thermo-mechanical coupling of the system. We first introduce our model in sec. II, then we discuss our result in sec. III, and finally in sec. IV we summarise and present our conclusions.

2 Model

We begin with our considerations assuming homogeneous order parameter field with no elastic distortions. Landau in his theory of continuous phase transitions assumes that free energy is an analytic function of the order parameter and of temperature. Therefore, he expanded the free energy density function *f*, with respect to the order parameter into a power series. Although Landau developed his theory for continuous (second order) phase transitions, albeit modified free energy density function (Devonshire theory (Falk, 1982)) can be used for the phase transition of the first order. The order parameter is an internal variable of the system (Landau, Lifshitz, 1980, Falk, 1982). In martensitic phase transitions the order parameter is the strain ε (for simplicity reasons we treat strain as a scalar quantity). Now the free energy density reads as

$$f(\varepsilon, T) = \alpha(T - T_*)\varepsilon^2 - \beta\,\varepsilon^4 + \gamma\,\varepsilon^6 - \sigma_E\varepsilon. \tag{1}$$

Here α, β and σ_E are positive coefficients and T_* is a characteristic temperature. Their values depend on the characteristics of the system. The last term represents "external field" conjugated to the order parameter. In our case the external field is "external" stress. Meanwhile

$$\sigma_i = \frac{\partial f_0(\varepsilon, T)}{\partial \varepsilon} \tag{2}$$

represents energetic response of the system due to a changing internal state (Falk, 1982). It can be designated as an "internal" stress. In eq. (2): $f_0 = \alpha(T - T_*)\varepsilon^2 - \beta\varepsilon^3 + \gamma\varepsilon^6$. In equilibrium, where $\partial(\varepsilon, T)/\partial\varepsilon = 0$, we have $\sigma_i = \sigma_E$ or

$$\sigma_E = \sigma = 2\alpha(T - T_*)\varepsilon - 4\beta\varepsilon^3 + 6\gamma\varepsilon^5 \tag{3}$$

Now eq. (3) represents our strain-stress relation. To make our calculations clearer, we introduce dimensionless free energy expression as

$$\varphi = (t-1)\eta^2 - 2\eta^4 + \eta^6 - h_E\eta, \tag{4}$$

where $\eta = \sqrt{\frac{2\gamma}{\beta}}\varepsilon$ is dimensionless strain, $h_E = 2\sigma_E\gamma^{3/2}\beta^{-5/2}$ is dimensionless external stress, $\varphi = 8\gamma^2\beta^{-3}f$, and $t = 4T\alpha\gamma\beta^{-2}$. At $T = 0$ we have then $t = 0$, and for $T = T_*$, there is $t = 1$. Therefore$T_*^{-1} = 4\alpha\gamma\beta^{-2}$.

3 Results and discussion

The equivalent of the eq. (3) reads as

$$h_E = h(\eta, t) = 2(t-1)\eta - 8\eta^3 + 6\eta^5\,. \tag{5}$$

Differentiating eq. (5) with respect to h, gives us $\frac{\partial h}{\partial \eta} = \frac{\partial^2 \varphi}{\partial \eta^2}$. In the Figure 1 we can see a characteristic plot of $h(\eta)$ at $t > 1$. In the section AA' there is $\frac{\partial h}{\partial \eta} < 0$ meaning also $\frac{\partial^2 \varphi}{\partial \eta^2} < 0$. Therefore, free energy there has its maximum and not a minimum. In the sections BA and B'A' the thermodynamic potential has a minimum, but its value is greater than for the minima corresponding to sections represented by full line (Landau, Lifshitz, 1980). Equilibrium form of the function $h(\eta)$ therefore follows the full line rather than a dashed one. If the material (let's say NiTi wire) would be

perfect (homogeneous, no defects in the crystal structure) the system would follow $h(\eta, t)$ function until the point A would be reached, but in reality we see that stress increases up to nucleation stress $h_N > h_B$ (He, Sun, 2010), and then due to nucleation it drops to the level of h_B.

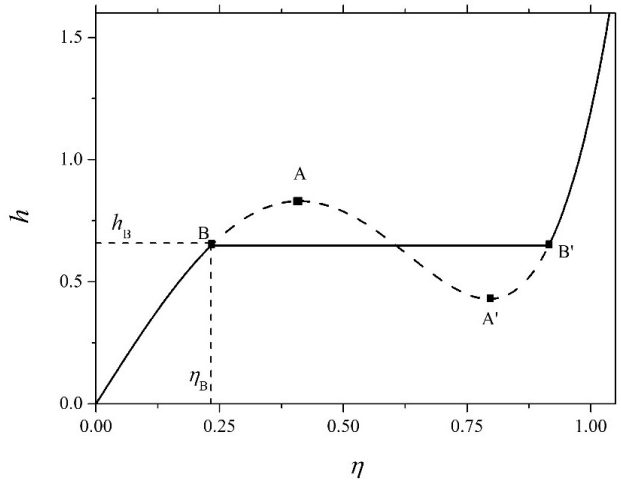

Figure 1: Typical plot of h(η), where dashed line represents metastable states of the system, as an opposite full line represents thermodynamically stable states. h_B and η_B represent σ_{MS} point.
Source: own.

The points A and A' we can calculate using $\frac{\partial h}{\partial \eta} = 0$. We get then

$$A'\colon\ \eta_1 = \sqrt{\frac{6 + \sqrt{51 - 15t}}{15}} \tag{6a}$$

$$A\colon\ \eta_2 = \sqrt{\frac{6 - \sqrt{51 - 15t}}{15}} \tag{6b}$$

If for a moment we discuss the solutions (6a) and (6b), and suppose that the system is at the temperature $t = 1$ (or equivalently $T = T_*$), then we would get $\eta_1 = \sqrt{\frac{4}{5}}$ and $\eta_2 = 0$ meaning that at that temperature we have only one solution $\eta \neq 0$ and therefore T_* is "maximum undercooling" temperature. In other words, beyond that temperature the system cannot exist not even theoretically in some meta-stabile

austenitic phase regardless to how much load our system is exposed. To discuss temperature range where (6a) and (6b) are being physically reasonable, we first introduce the critical point.

3.1 Critical point

There exists a critical value of the field at which the transition is continuous and beyond which no transition occurs. The critical field and the corresponding transition temperature are located by the conditions (Cowley, 1980):

$$\left(\frac{\partial\varphi}{\partial\eta}\right)_h = \left(\frac{\partial^2\varphi}{\partial\eta^2}\right)_h = \left(\frac{\partial^3\varphi}{\partial\eta^3}\right) = 0 \tag{7}$$

as

$$h_C = \sqrt{\frac{2}{5}\frac{64}{25}} = 1.618. \tag{8a}$$

$$t_C = \frac{17}{5} = 3.40. \tag{8b}$$

There is no symmetry breaking at the critical point, since η has there a nonzero value

$$\eta_C = \sqrt{\frac{2}{5}} = 0.632\,. \tag{8c}$$

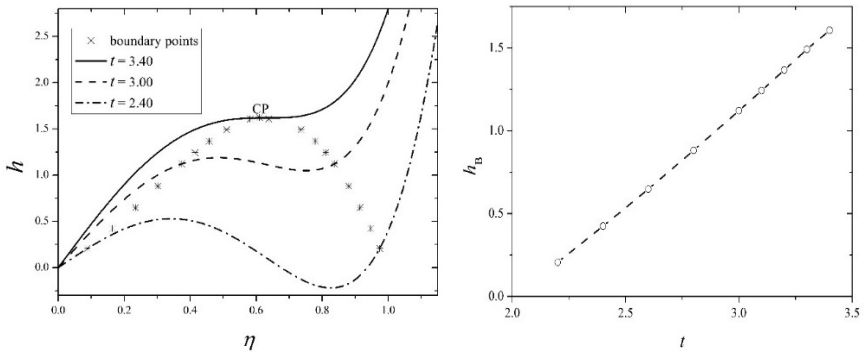

Figure 2: a) Plot of the stress-strain function for several temperatures. Here stars represent B and B' points from the Figure 1. CP is the critical point (ηc,hc). b) The boundary points h_B (sometimes called plateau stress) dependence on the temperature t.
Source: own.

In the Figure 2a we can see how strain-stress relation depends on the temperature. In other words, on the Figure 2a we draw some isotherms of the $h(\eta)$ function. The stars represent "boundary points" for every isotherm in the sense of B and B' boundaries of the thermodynamically stable $h(\eta)$ curve progression. CP is the critical point, $(\eta c, hc)$ on the t_C isotherm. On the Figure 2b we can see that the h_B points are nearly linearly dependent on *t*. Such kind of dependence was actually already shown (see (Shaw, Kyriakides, 1997)).

Eq. (6a) and (6b) represent minima and maxima of the function $h(\eta)$. These solutions are physically valid for $51 - 15t \geq 0$ or $t \leq t_C$. At $t = t_C$ we get $\eta_1 = \eta_2 = \eta_C$. At the same time for the solutions being reasonable, there has to be true that $\sqrt{6 - \sqrt{51 - 15t}} \geq 0$ or equivalently $t \geq 1$. Therefore, temperature has to belong to the interval: $1 \leq t \leq t_C$ if the phase transformation from austenitic to the martensitic phase is going to be of the first order.

3.2 Ginzburg term

We spoke about formation of the domains after the system enters into transformation stage at h_B and η_B (see Figure 1). The same is reported by experimental research (e.g. (Bruno, Leo, Reitich, 1995, Sun, Zhong, 2000, He, Sun, 2010)). The formation of domains is connected to distortions of the strain field. Therefore a gradient term has to be included into the Landau free energy expression. In eq. (1) we have to add an additional (Ginzburg) term of the form: $-L(\nabla\varepsilon)^2$. Here *L* is some elastic constant, which depends on the system properties. In fact it is a tensor quantity but for simplicity reasons let us suppose that it is a scalar quantity. Negative gradient term favours spatially modulated order parameter field. In our case this means distortions of the strain field as a consequence of the inclusions and defects in the crystal lattice. As the free energy potential should be thermodynamically stable, the elastic constant has to be limited. If we further suppose that locally perturbed order parameter recovers its equilibrium value on a length given by the relevant order parameter correlation length, for the gradient we can roughly write: $\nabla\varepsilon \sim \varepsilon/\xi$, where ξ is order parameter correlation length of the system, then eq. (1) can be rewritten in the following form

$$f(\varepsilon, T) = \alpha(T - T_*)\varepsilon^2 - \beta\,\varepsilon^4 + \gamma\,\varepsilon^6 - \sigma_E\varepsilon - \frac{L}{\xi^2}\varepsilon^2\,. \tag{9}$$

Now we can combine the terms with ε^2 into $\alpha(T - T_* - \frac{L}{\alpha\xi^2})\varepsilon^2$, where $T_* - \frac{L}{\alpha\xi^2}$ can be seen as some "effective temperature". To recognise how that effective temperature affects the stress-strain relation, we return to our dimensionless model. Now the counterpart of the eq. (4) is

$$\varphi = (t-1)\eta^2 - 2\eta^4 + \eta^6 - h_E\eta - \frac{\lambda}{1+x^2}\eta^2\,, \tag{10}$$

where $\lambda = L/L_0$ is dimensionless "elastic constant" if L_0 is some characteristic elastic constant of the system. Further in eq. (10) $= \xi_\varepsilon/\xi_0$, where ξ_0 is the smallest possible size of the domain, and ξ_ε represents strain rate contribution to the size of the typical domain. It roughly holds $\xi_\varepsilon \propto \dot{\varepsilon}^{-1}$ [13]. Strain rate contribution includes also some other factors that influence the size of the domains formed (e.g. defects in the crystal lattice structure, inclusions etc.). The smallest possible size of a domain equals

$$\xi_0 = \sqrt{\frac{2\alpha T_* L_0}{\beta}}\,. \tag{11}$$

We collect now the terms with η^2 and get

$$\varphi = (t - t_*)\eta^2 - 2\eta^4 + \eta^6 - h_E\eta\,, \tag{12}$$

where

$$t_* = 1 + \frac{\lambda}{1+x^2} \tag{13}$$

is now "effective temperature".

In the Figure 3 we can see that effective temperature t_* reaches the value of 1 when $x \gg 1$. That means if we want our system to work as if there would be no elastic distortions the contribution of ξ_ε has to be extensive. On the other side, if the system is stiff (λ is very low) then also system behaves like a bulk (no elastic contribution). The behaviour of the system changes comprehensively with small domains and large elastic response.

Although the critical point ($\eta c, hc$) in that new situation does not change, the critical isotherm isn't the same. Now holds $t_C = t_* + 2.4$.

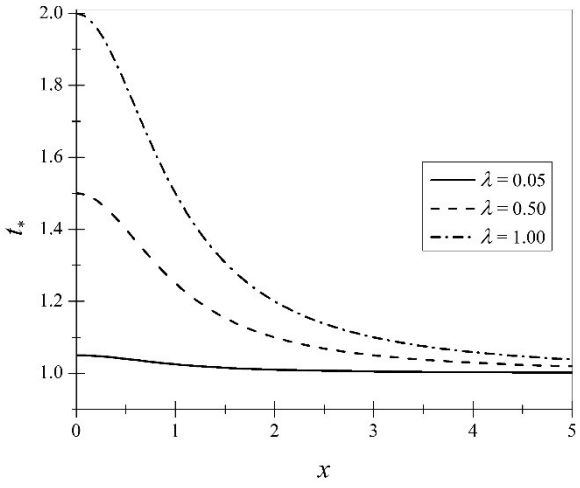

Figure 3: Effective temperature for larger elastic constants can influence the behaviour of the system in great manner if the size of the domains is low.
Source: own.

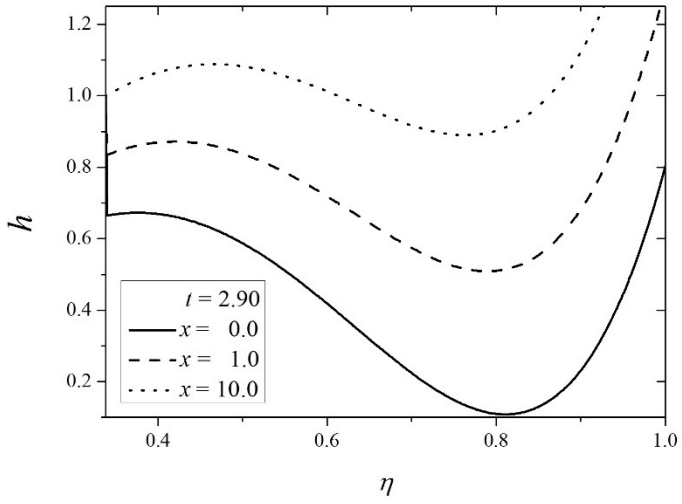

Figure 4: Influence of the domain size on the character of the phase transformation.
Soure: own.

In the Figure 4 we can observe how the size of the typical domain influences the behaviour of the system after it reaches the transformation point (η_B, h_B) into martensitic phase. On Figure 4 we keep $\lambda = 0.5$. Although temperature is constant

the stress-strain behaviour is very similar to that on Figure 2a where temperature was changed. This indicates that we have to do with a thermo-mechanical coupling within our system. The curves on Figure 4 were calculated as if the size of domains would be constant up to the point where the system reaches the martensitic state, but in the reality, domains increase and/or merge, and therefore the number and the size of the domains change.

In the previous research (e.g.(Sun, Zhong, 2000, He, Sun, 2010, Shaw, Kyriakides, 1997)) of the stress-induced phase transition behaviour of NiTi quasi one-dimensional structures under isothermal tensile loading the stress drop in the domain-nucleation was observed. In the Figure 4 we chose $t = 2.90$ where $\eta_B = 1.0$, therefore the stress drop at the entering into the austenite-martensite transformation stage is clearly evident also in our model. At the η_B the relation between (5) where stress is not affected by distortions of the strain field, and $h(x)$ where strain field distortions are taken into account can be written as

$$\frac{h(x)}{h} = 1 - 2\eta_B \frac{\lambda}{1 + x^2}. \tag{14}$$

From (14) we can infer that stress drop entering the transformation stage is less pronounced if x is very large. In other words, if the system is inclined not to build more than a few domains the stress drop would be held small. On opposite if the system entering the transformation stage builds many domains, the result is severe drop of the stress. If the factor x is relatively small the stress drop can be varied by elastic properties of the system. For growing λ the drop of stress would also increase as if the domain would be smaller. For large x, the elastic properties of the system are less important because only slight changes of stress drop can be achieved.

4 Conclusions

In this paper using Landau mean field approach we investigated the influence of the Ginzburg term on the description of a phase transformation between austenitic and martensitic phase in shape memory alloys. Distortions of the strain field, which are described by the Ginzburg gradient term, generate domain-like structure of the originating martensitic phase. We showed that distortions of the strain field are coupled with the thermo-mechanical response of the system. In the model the 'size'

of the domains was measured by x. For $x \gg 1$ the system entering into martensitic state developed only few domains and therefore practically no change was perceived comparing the system with no distortions of the strain field. For $x < 1$ significant changes in behaviour were obtained. The system produced many domains and therefore mimicked e.g. large concentration of lattice defects (vacancies, dislocations, stacking faults, trapped solute atoms etc.). The result was a drop of stress and consequently lower transformation temperature (see Figure 4). For growing elastic response of the system, the drop of stress would also increase as if the domains would be smaller. For large x, the elastic properties of the system are less important.

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