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Martensite deformation and phenomenon of hysteretic shape change in TiNi-based alloys

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ABSTRACT

The brief overview of published articles on Nitinol studies reflects, in fact, a little misunderstanding of a thermodynamic importance since there is no whole concept or paradigm considering the martensite transition and related effects in terms of thermodynamic arguments. TiNi-based alloys are basically functional materials. They're more important for what they do than for what they are. In order to make it easier to understand complicated behavior of TiNi-based alloys under general and special conditions, a new approach is introduced. This work was aimed at studying the hysteretic behavior of TiNi-based alloys. Mechanism of hysteretic phenomenon in TiNi-based alloys showing shape memory effect, superelasticity and ferroelasticity has been considered. Hysteretic behavior in repeatable shape memory effect was thermodynamically analyzed with the aid of Helmholtz potential formalism. Correlation of deformation, temperature and latent heat of phase transition under the constant load was established. Maximum hysteresis width achieves when the product $\varepsilon\Delta\sigma$ during phase transition tends to ΔH, and when the product $\varepsilon\Delta\sigma$ tends to zero the value of ΔT approximates the difference $(A_s - M_f)$ or $(A_f - M_s)$. Copyright © 2014 VBRI press.

Keywords: Martesite deformation; martensite transition; shape memory effect; superelasticity; ferroelasticity; TiNi-based alloy.

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Introduction

Martensite phase transformation under external stress is considered to be a specific shear deformation mechanism based on moving of the interface (martensitic) accompanied by cooperative transition of atoms from the parent phase to the produced one. External stress is one of the four parameters (T, V, s, p), which have an influence on the moving of interface. Moreover, external stress determines the preferential crystallographic orientation of martensite phase and prevents the formation of other variants of martensitic structure. As a result of this, when the temperature varies under conditions of constant loading, the macroscopic shear occurs and leads to the transformation of material shape **[1]**.

The main feature of the martensitic phase transformation among the other types of phase transformation is that the transition occurs due to crystallographic shear rather than dislocation sliding and mechanical twinning, resulting in deformation of volume as well as in macroscopic shape change. The deformation mechanism of martensitic phase itself in the SMA takes place by thermoelastic transformation based on not only the interface motion but also movement of domain boundaries (within the martensite interface), when the growth of one type of crystallographic variants happens due to the collapsing of others **[2]**.

Martensitic phase transformations under loading and deformation of martensitic phase have similar fundamental features, and in many experimental situations both mechanisms occur simultaneously. This allows combining them under one term *“martensite deformation”*. Since the crystal lattice dilation during martensite transformation is negligible, this type of deformation substantially appears to be shear deformation and could also be called *martensite shear*. The aim of this article is an attempt to move from theoretical consideration to practical application by studying the stress-induced martensitic transformation as energy-dissipative processes, i.e., hysteretic between the forward and reverse processes in TiNi-based alloys and to draw general rules governing the hysteretic behavior of these alloys.

The understanding of these rules is fundamentally important for the research of TiNi-based alloys in two respects. First, it improves the understanding of the mechanisms of the physical phenomena of shape memory effect and superelasticity. Secondly, it provides the theoretical framework for further experimental study to establish the constitutive models which take into account the effect of hysteresis on the thermo-mechanical response. In the near future, TiNi-based alloys are expected the second birth regarding to their practical application (especially for creation of a new material generation for medical goals). Such kind of approach is naturally supposed to introduce a number of assumptions described in the article, which don't bring any errors or derogate the physical meaning and essence. Calculations indicated are a manner and tool for designers to make the correct decision when solving the applied task **[3, 4]**.

Theoretical consideration

Martensite deformation in TiNi-based alloys under certain thermoelastic conditions is reversible and it can be recovered by isothermal unloading or by heating to the temperature of austenite transformation. Isothermal reversibility of martensitic deformation results in phenomenon of *superelasticity* within the temperature range $M_S<T<M_d$ (**Fig. 1, a**) or *ferroelasticity* in full martensitic state at the temperatures below M_f (**Fig. 1, b**). The reverse martensitic deformation (which remains after isothermal unloading) when heated to the temperature of reverse martensitic transformation (higher than M_f) is the basis of *shape memory effect* (**Fig. 1, c**). Only martensitic deformation in TiNi-based alloys occurs to be reversible in contrast to dislocation sliding and mechanical twinning. In thermodynamic sense, the martensite deformation is always irreversible because of energy dissipation during the process. In other words it is a substantially inelastic deformation. Studying the curve $\sigma(\varepsilon)$ in pure martensitic state within temperature range of M_S and M_d gives general qualitative description which has to be corrected in its details to applying to particular TiNi-based alloys (**Fig. 2**).

The initial section of the curve $\sigma(\varepsilon)$ is similar to elastic deformation in Hooke’s law. This section is completed by the abrupt change or “tooth” at point *B*. There is a significant deviation from linear behavior takes place after point *B* due to the accuracy of testing method and its value can be evaluated approximately at point *A*. This region of the curve $\sigma(\varepsilon)$ approximately corresponds to the observation of identical martensite crystals due to the surface relief: in cases of crystals are thin, single-domain, and elastically accommodated similar to the so called “elastic” twins. Abrupt change or “tooth” is followed by section *BC* which is the same level, and almost horizontal (depending on testing conditions).

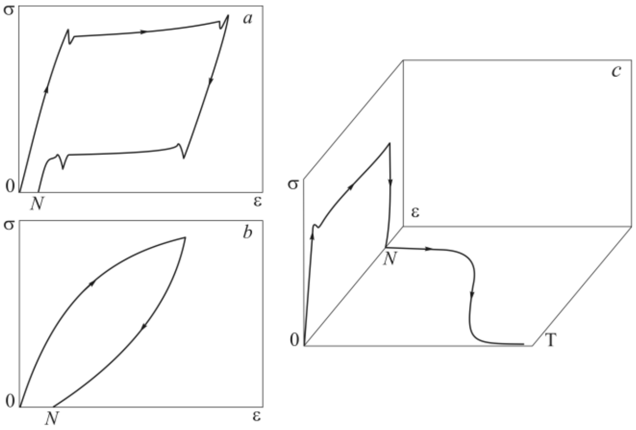

Fig. 1. The scheme of reversible martensite deformation at phase transitions in TiNi-based alloys: **(a)** – superelasticity; **(b)** – ferroelasticity; **(c)** – shape memory effect.

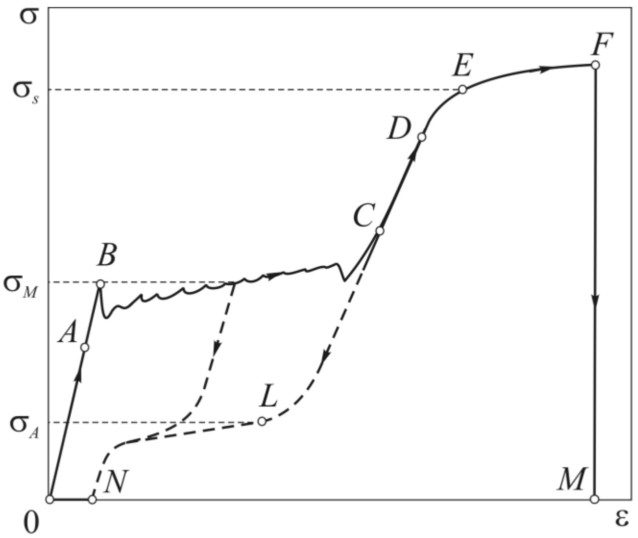

Fig. 2. Typical stress-strain behavior of TiNi-based alloys within temperature range $M_s<T<M_d$

When testing machine can provide sufficient rigidity, the stepwise behavior of stress-strain dependence can be easily detected within this section. Surface relief observation reveals avalanching formation of martensitic multi-domain crystals with certain internal structure and invariant habit plane. Around the end of section *BC* almost total cross-sectional area is covered with martensitic crystals reaching the surface of the sample. Following through point *C* the slope of the curve $\sigma(\varepsilon)$ is gradually increasing and then subsequently decreasing. In some cases the inflection point *E* is clearly seen in the curve, while in other cases linear section *CE* having the same slope similar to the Hooke’s section *OA*. At the beginning of section *CE,* the surface roughening can be observed on testing samples due to the de-twinning process in martensitic phase and growth of favorably oriented domains. In this process the invariant plane is lost and accommodation in polycrystalline TiNi-based alloy appears through the formation of “non-oriented” martensite variants near crystalline boundaries as well as through elastic and true plastic deformation **[3]**.

At higher stress from point *E*, the slope of the curve σ(ε) is decreasing and new surface patterns with different orientation starts to form on the cross-section area. This pattern is represented by slip bands, kink bands and deformation twins **[4]**. According to this stress the value at point *E* can be considered as macroscopic yield stress σ_s. However, the stress value σ_M at point *B* formally resembles the yield point; it is actually the ultimate stress value of martensitic deformation. When unloading from A_S the martensite deformation is partially restored in isothermal process and from A_f it is almost completely restored (neglecting contribution from true plastic deformation), and in this process energy dissipation occurred is expressed as mechanical hysteresis loop (**Fig. 2**). This section distinguishes the martensitic deformation substantially from plastic yielding of metals and alloys. The effect of complete martensitic transformation or almost complete shape recovery as a result of isothermal unloading under conditions described above is called *superelasticity*.

Certain residual strain remained after isothermal unloading (**Fig. 2**, section *NO*) formally makes martensitic deformation to be similar to plastic yielding; this explains the term “*plasticity of transformation*” sometimes used in literature **[1]**. Residual stress induced martensite after unloading and subsequent heating (higher than A_f) shows reverse transformation resulting in so-called shape memory effect **[5]**.

Another evidence of shape memory effect consists in the shape recovery of material, which was previously deformed at temperature below M_f, full martensitic state, and then to be heated in the temperature range of reverse transformation. The specific residual strain is due to not martensite appearance but its re-orientation, multi-domain structure formation, twinning and de-twinning of single-domain martensitic crystals. In this case σ_M can be called ultimate martensitic shear stress. When unloading on the alloy sample, which has been deformed at the temperature below M_f, certain portion of accumulated strain recovers isothermally (ferroelasticity effect), while remained martensitic deformation (section *NO*, **Fig. 1**) recovers when heating above the A_s temperature (shape memory effect). In general case the shape memory effect and ferroelasticity act as two competing effects. The correlation between these effects is determined by the degree of interface pinning. Mechanism of pinning of the interface and correlation values depend on the certain TiNi-based alloy and external conditions. Thus, under rapid unloading in some TiNi-based alloys at temperatures below M_f, ferroelasticity exhibits dominantly due to the lack of time for interface pinning. When unloading is slow or long time holding under the load the ferroelastic effect is suppressed **[6]**. Therefore, at temperatures below M_f, it is possible to find partial or complete ferroelasticity state of the alloy. The pinning of interface, which suppresses ferroelasticity, seems to be the result of the same basic phenomenon to stabilize the martensitic phase.

Martensite deformation and shape memory effect occur also in result of cooling and heating of the material under loading within temperature range of martensitic transitions. The loading initially promotes preferential formation of favorably oriented martensite during cooling process. Increasing of stress leads to decreasing a portion of “non-oriented” martensite in which formed by the results of internal stress distribution in the parent phase cannot be controlled externally. As a result of this maximum accumulation of martensite deformation occurs in direct martensitic transformation when cooling the material. Moreover, during further cooling at sufficiently high stresses can produce twinning propagation in multi-domain martensite and provide further accumulation of the deformation.

After cooling under loading to the temperature below M_f accumulated martensite deformation can be completely recovered only in heating above the A_f temperature. Deformation is able to be recovered many times, so this phenomenon is called repeatable shape memory effect (**Fig. 3)**. Basic patterns of martensite deformation are as follows: in cooling – favorably oriented martensite formation under external loading, re-orientation and single-domain formation, twinning of martensitic crystals; in heating – de-twinning, re-orientation, single-domain formation, and formation of the parent phase.

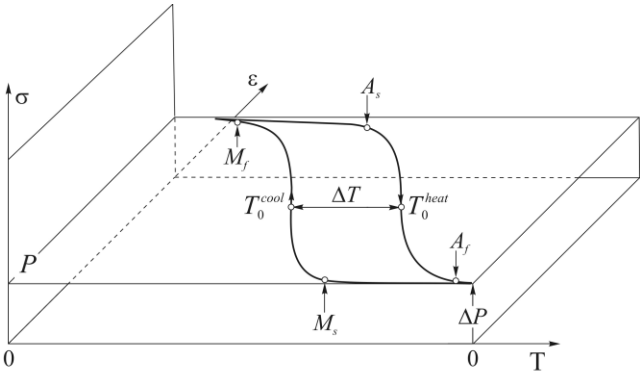

Fig. 3. Repeatable shape memory effect under loading in TiNi-based alloys

Discussion

Thermodynamic approach to the repeatable shape memory effect enables to establish the relation between such parameters as strain (ε), transformation temperatures (M_s, M_f, A_s, A_f), temperature hysteresis (ΔT) and the latent heat of phase transition (ΔH). In order to analyze repeatable shape memory effect we used Helmholtz thermodynamic potential (F) as $F=F_{s,p}(V,T)$. Independent variables V and T in Helmholtz potential allow to estimate the correlation between strain and temperature at the phase transition happening **[7-10]**. In a differential equation it can be formulated as follows:

$$dF = -SdT - PdV, \tag{1}$$

where S – entropy, P – pressure.

For two different phases (the parent (A) phase and the martensite (M) one) – the following can be defined:

$dF_A = -S_A dT - P_A dV;$

$dF_M = -S_M dT - P_M dV.$

For the interface when $dF_A \approx dF_M$, then

$-S_A dT - P_A dV = -S_M dT - P_M dV$

Or

$(S_A - S_M)dT = -(P_A - P_M)dV$

and after mathematical manipulation

$$dV = -\frac{\Delta S}{\Delta P} dT \qquad (2)$$

In case of shear strain, the change dV can be brought to $d\varepsilon$, under constant loading $\Delta P = \Delta\sigma = \text{const}$, the equation (2) can be written as follows:

$$d\varepsilon = -\frac{\Delta H}{T_0 \Delta\sigma} dT, \qquad (3)$$

since ε and T are independent variables, then

$$\Delta S = \frac{\Delta H}{T_0},$$

where ΔH – latent heat of phase transition, T_0 – equilibrium temperature. Equation (3) enables to estimate strain variation as a function of temperature change under constant loading $\Delta\sigma$. However, it should be taken into consideration that for direct martensitic transformation (in cooling) T_0 is determined as follows:

$$T_0^{cool} = (M_s + M_f)/2, \qquad (4)$$

and in heating

$$T_0^{heat} = (A_s + M_f)/2.$$

The curve $\varepsilon(T)$ for direct martensite transformation under loading can be expressed in integral form:

$$\varepsilon^{cool} = \frac{\Delta H^{cool}(T_1 - T_0^{cool})}{T_0^{cool}\Delta\sigma} \qquad (5)$$

For reverse martensite transformation the curve ε(T) is determined by the following equation:

$$\varepsilon^{heat} = \frac{\Delta H^{heat}(T_2 - T_0^{heat})}{T_0^{heat}\Delta\sigma} \qquad (6)$$

Equations (5) and (6) can be represented as follows:

$$\varepsilon^{cool} T_o^{cool} \Delta\sigma = -\Delta H^{cool}(T_1 - T_0^{cool}); \qquad (7)$$

$$\varepsilon^{heat} T_o^{heat} \Delta\sigma = -\Delta H^{heat}(T_2 - T_0^{heat}).$$

Since $\Delta H^{cool} \approx \Delta H^{heat} = \Delta H$, $\varepsilon^{cool} \approx \varepsilon^{heat} = \varepsilon$, then after mathematical transformation

$$T_0^{heat}(\varepsilon\Delta\sigma - \Delta H) = -\Delta H T_2;$$

$$(8)$$

$$T_0^{cool}(\varepsilon\Delta\sigma - \Delta H) = -\Delta H T_1.$$

By subtracting the second equation from the first one we obtain the following:

$$\Delta T = (T_0^{heat} - T_0^{cool}) = -\frac{\Delta H(T_2 - T_1)}{\Delta H - \varepsilon\Delta\sigma}, \qquad (9)$$

where $\varepsilon\Delta\sigma$ – mechanical work of crystal formation and re-orientation in martensitic and initial phases, T_2 and T_1 – current temperatures of direct and reverse martensitic transformation respectively, T_2 within $A_s \div A_f$ range and T_1 within $M_s \div M_f$ range.

Minimum values of T_2 and T_1 correspondent to A_s and M_f and their maximum ones do to A_f and M_s, respectively. In this case the width of hysteresis determined as $\Delta T = T_0^{heat} - T_0^{cool}$ for these boundary conditions in equation (9) can be expressed as follows:

$$\Delta T = \frac{\Delta H(A_S - M_f)}{\Delta H - \varepsilon\Delta\sigma}$$

or

$$\Delta T = \frac{\Delta H(A_f - M_S)}{\Delta H - \varepsilon\Delta\sigma}, \qquad (10)$$

i.e.;

$(A_s - M_f) = (A_f - M_s).$

Conclusion

The important conclusion one can made using equation (10) – in TiNi-based alloys the width of temperature hysteresis ΔT in phase transitions is proportional to the latent heat multiplied by difference between transformation temperatures of direct and reverse martensitic transformation, and inversely as the difference between the latent heat (ΔH) of phase transition and mechanical work ($\varepsilon\Delta\sigma$ – mechanical energy dissipation). Maximum hysteresis width is reached when the product $\varepsilon\Delta\sigma$ during phase transition tends to ΔH. In case when the product $\varepsilon\Delta\sigma$ tends to zero the value of ΔT approximates the difference ($A_s - M_f$) or ($A_f - M_s$). So the width of temperature hysteresis can be approximately estimated as equal to the difference between ultimate temperatures of martensite transformations: ($A_s - M_f$) or ($A_f - M_s$). It's often stated that the volume of applications using TiNi-based alloys is low compared to the amount of research and theoretical information available for such alloys. This may partly be explained by the fact that their technology requires considerable additional insight and understanding from the designer. Probably most attempts at product development have been made by Nitinol specialists, who are not primarily design oriented. On the other hand, not enough designers and engineers have yet got the insight and understanding of TiNi-based alloys knowledge necessary for a volume expansion of a new generation implants. This is in turn crucially important for the successful practical medical applications. Experimental studies and theoretical analyses are further required to accomplish a complete and systematic understanding of the hysteretic behaviour in TiNi-based alloys taking into consideration related effects in terms of thermodynamic arguments.

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Reference

1. Gunther, V.E.; Dambaev, G.Ts.; Sysolyatin, P.G. et al.; Delay law and new class of materials and implants in medicine, Northampton, MAA: STT, **2000**, pp. 432.
   ISBN: 0970235305
2. Jani, J.M.; Leary, M.; Subic, A.; Gibson, M.A.; A Review of Shape Memory Alloy Research, Applications and Opportunities, *Materials & Design*, **2014**, *56*, 1078–1113.
   DOI: 10.1016/j.matdes.2013.11.084
3. Gunther, V.E.; Hodorenko, V.N.; Chekalkin T.L. et al.; Medical materials and shape memory implants: In 14 vol. / Shape memory medical materials, Tomsk: MIC, **2011**, *1*, pp. 534.
   ISBN: 9785985890440
4. Gunther, V.E.; Hodorenko, V.N.; Chekalkin, T.L. et al.; Titanium nickelide – medical material of new generation, Tomsk: MITS, **2006**, pp. 296.
   ISBN: 9785985890201
5. Bhattacharya, K.; Crystallographic Attributes of a Shape-Memory Alloy, *Journal of Engineering Materials and Technology*, **1999**, *121*, 93-97.
   DOI: 10.1115/1.2816005
6. Ahlersa, M.; The martensitic transformation: Mechanisms and crystallography, *Philosophical Magazine A*, **2002**, *82*, 1093-1114.
   DOI: 10.1080/01418610208240019
7. Sun, L.; Huang, W.M.; Nature of the multistage transformation in shape memory alloys upon heating, *Metal Science and Heat Treatment*, **2010**, *51*, 573-578.
   DOI: 10.1007/s11041-010-9213-x
8. Otsuka, K.; Wayman, C.M.; Shape Memory Materials, Cambridge University Press, Cambridge, **1998**, pp. 284.
   ISBN 0521663849
9. Prigogine, J.; Defay, R.; Chemische Thermodynamik Übersetzung aus dem Englischen, Original französisch / VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, **1962**, pp 350.
   DOI: 10.1002/zfch.19630030124
10. Weigand, B.; Kohler, J; Jens von Wolfersdorf; Thermodynamik kompakt, Springer-Verlag, Berlin, **2008**, pp 206.
    DOI: 10.1007/978-3-540-71866-6