Shape Memory Alloys: Properties, Technologies, Opportunities

Natalia Resnina and Vasili Rubanik

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Edited by

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Preface

The collective monograph "Shape memory alloys: properties, technologies, opportunities" presents the scientific results obtained by leading scientific teams studying shape memory alloys in former Soviet Republics during the last decade. The scientists from Russia (Moscow, Saint Petersburg, Ekaterinburg, Chelyabinsk, Tomsk), Ukraine (Kiev) and Belarus (Vitebsk) together with their colleagues from other countries made contributions to prepare this monograph.

The collective monograph consists of five parts covering of all aspects of shape memory alloys from theory and modelling to applications. The first part is devoted to the theory of martensitic transformations and the modelling of functional properties of shape memory alloys. New methods for the simulation and prediction of the behaviour of shape memory alloys under different stress – temperature regimes are described. The wave model for the description of martensite crystal growth at different sequences of martensitic transformations and the analysis of recent achievements in theoretical description of phase transformation in Heusler alloys are presented. The second part is devoted to the physical basis for the development of shape memory alloys, including unique properties such as high-temperature shape memory alloys, high-strength single crystals of shape memory alloys and ferromagnetic shape memory alloys. The third part is devoted to the methods for controlling functional properties of shape memory alloys by thermomechanical treatment, warm deformation, electroplastic deformation, high strain rate loading, ultrasonic vibration and neutron irradiation. The fourth part is devoted to the study of martensitic transformation and shape memory effects in special objects such as porous alloys, thin ribbons, high-strength precipitation-hardening austenitic steels and alloying TiNi-based alloys. Finally, the fifth part contains a review of shape memory alloy applications in Russia.

All chapters were peer-reviewed by expert referees. As the guest editors of the volume, we are grateful to the authors who prepared the chapters. We wish to acknowledge all those who reviewed the papers submitted to the monograph.

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Possible Wave Processes Controlling the Growth of Martensite Crystals at B2-B19, B2-B19' and B2-R Transformations

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Abstract. Basic directions in the theory of martensitic transformations are briefly listed. Within the framework of the dynamic theory based on the synthesis of concepts of heterogeneous nucleation and wave growth of martensite crystals, the possibilities of description of morphological parameters during the B2→B19, B2→B19′, B2→R transformations are analyzed. It is demonstrated that the calculated and observed habit planes and orientation relationships can be matched.

In particular it is demonstrated that an introduction of the notion of the intermediate mesoscopic state during the B2 → B19′ transformation is expedient for a description of the observed morphological parameters. The $\{78\ 39\ 48\}_{B2}$ habit planes of the B19′ phase can be associated with standard dislocation nucleation centers.

It is noted that the exact inheriting of elastic fields of a dislocation nucleation center is possible. This is a necessary condition for explanation of the effect of transformation reversibility upon thermocycling.

The results obtained are briefly discussed.

Introduction

The phenomenon of martensitic transformation (MT) as a specific variant of the realization of a polymorphic transformation associated with a cooperative mechanism of atomic displacements attracts wide attention of researchers. On the one hand, an MT modifies the properties of a material and therefore plays an important practical role (it suffices to mention the process of quenching steels or a shape memory effect in NiTi alloys). On the other hand, it is quite interesting to construct a physical theory of MTs that would not be limited to fragmentary explanations of separate aspects of this phenomenon but rather would enjoy a high degree of completeness of description of all significant observable properties. It is obvious that such a theory should be based on a clear understanding of the physical nature of the mechanism of control of the structure rearrangement. It is evident that in the case of metals and alloys that represent electron-ion systems, we should first of all understand what features and states of the subsystems are necessary for the development of the MT. The issue is complicated by the fact that in different metallic systems, the MT can occur via different scenarios, which include the differentiation not only of the structures of the initial and final phases but also of the character of the phase transition, whose manifestations in some cases correspond to a limit version of a second-order transition, while in other cases, - to a clearly pronounced first-order transition. The understanding of both limit cases seems to be important. Until recently, the main problems are currently related precisely to the explanation of the MT mechanism in the case of distinctly pronounced first-order transitions.

This is not surprising because such a transition occurs upon a significant deviation from the point of equilibrium of the phases, and the strongly supercooled (or superheated) system is an active medium capable of liberating energy. Consequently, under nonequilibrium conditions, the MT mechanism that ensures the fastest rate of energy liberation may be unrivaled. Detecting such a mechanism requires revising familiar concepts of first-order phase transitions, in particular, revising the problem of the existence of equilibrium (quasi-equilibrium) nuclei of a new phase. It is obvious

that in a metallic system, the mechanism of propagation of the fastest relaxation of energy is related to a wave process, and the appearance of waves is related to the initial excited (oscillatory) state of ions, which is maximally efficient for triggering the process of rapid growth of the new phase. In turn, this initial state is localized in those regions of space where, owing to the influence of the elastic fields of defects (e.g., ordinary dislocations), a significant decrease occurs in the interphase energy barrier. This explains the specific character of heterogeneous nucleation. And, finally, the case that is richest in physical contents is where the maintenance of a high (threshold) level of deformations at the front of the control wave process (CWP) is possible due to the participation of the electronic subsystem.

The physically transparent picture described in an above general representation corresponds to a new paradigm of MTs that allows consistently describing a large body of observed facts and removing problems that seemed to be insurmountable for theoretical constructions based on the traditional quasi-equilibrium approach.

In making the final conclusions, we can state that the current model of the formation of a martensite crystal (including the stages of heterogeneous nucleation, wave growth, and accommodation of the coexisting phases) in the case of a spontaneous (in the process of cooling) $\gamma-\alpha$ martensitic transformation in iron alloys realized in single crystals or in polycrystals with large grain sizes D is generally complete [1-4]. The high degree of the completeness of the description of the observed features of the transformation suggests a new paradigm of the dynamic theory of the spontaneous $\gamma-\alpha$ MT.

The scheme in fig. 1 reflects an important role of the concept of initial exited state (IES) within the limits of new paradigm of MT. This concept has essentially completed the ideas of physics of first-order phase transitions on the initial stage of transformation. A deduction on the existence of the controlling wave process and its supersonic speed is a direct consequence of this.

IES is a region having the shape of an elongated rectangular parallelepiped with transverse dimensions d1, 2 ($d1 \sim d2 \sim d$) that is constructed on orthogonal eigenvectors of the tensor of elastic deformations of the defect (as a rule, a dislocation). It is important that d makes about one hundredth of the size of defect-free volume. The relation between spatial scales together with the condition for occupation of states of the electrons generating waves allows explaining an Ms dependence on D (Ms is the temperature of MT start and D is the size of austenite grain).

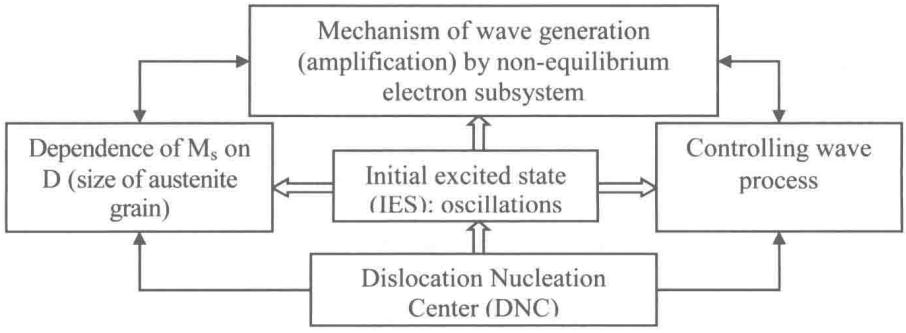

Fig. 1. Key position of the concept of Initial Excited State in dynamical theory of MT [2]

This conclusion can also be related to the dynamic theory of the formation of stress-assisted martensite (upon cooling in an external elastic field), in which case we simply observe a reduction in the number of realized variants of orientations of martensite crystals (compared to that observed in the case of a spontaneous transformation).

For the completeness of the analysis, we recall that at grain sizes exceeding the critical size D_c, apart from the above-considered cooling-induced martensite, crystals of deformation-induced martensite can be formed (at the stage of plastic flow), which is related to the carriers of threshold

deformation called crystons. The crystons (shear superdislocation carriers that arise upon the contact interaction of dislocations with intersecting slip planes) specify the orientations of habit planes during their propagation [5-7]. Fig. 2 displays the formation scheme of a cryston due to the interaction of n and m dislocations with different initial slip systems.

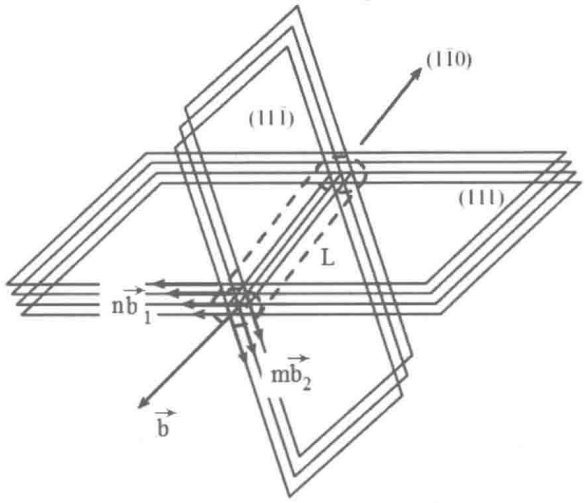

Fig. 2. Generalized Frank-Read source (typical of the fcc phase) of crystons each of which is characterized by a total (superposition) Burgers vector $\vec{b} = n\vec{b}_1 + m\vec{b}_2$.

The cryston concept is also efficient in describing shear bands with an arbitrary crystallographic orientation of planar boundaries.

Fig. 3 schematically shows the logical structure of the dynamic approach to the description of martensitic transformations.

The conformity of the theory to the observed picture of a $\gamma-\alpha$ MT is beyond doubt. Here is a list of the main obtained achievements and solved problems. 1. The new model of martensite nucleation in elastic fields of dislocations. 2. The concept of the initial exited state. 3. The identification of the characteristic spatial scales at the nucleation. 4. The mechanism of generation of elastic waves by nonequilibrium electrons. 5. The supersonic growth speed of martensite crystals. 6. The transition from threshold to ultimate deformations. 7. The interpretation of all observed macroscopic morphological features (habitus, macroshear and orientation relationships of the initial and final phase lattices). 8. The martensite crystal twinning in the course of $\gamma-\alpha$ martensitic transformation [4, 8]. 9. Analytical formula for the critical size of austenite grains D_c (M_s (D_c) = 0) has been obtained [1, 9, 10]. 10. The dependence of D_c on significant physical parameters was analyzed. 11. The existence of the special concentration C* (for $C \to C^*$, $M_s \to 0$, $D_c \to \infty$). 12. An explanation of the dependence of the size D_c on the strong magnetic field H and, as a result, the effect of destabilization of austenite preliminarily stabilized via grain refinement or severe plastic deformation. 13. An estimation of the macroscopic fraction of martensite for self-similar kinetics of ensembles of martensitic crystals in the model of symmetric orthogonal joints [11]. 14. The description of the profiles of martensite crystals formed in a medium containing planar inhomogeneities [12, 13]. 15. The calculation of critical rates of cooling of an austenite [14]. 16. The estimations of scales of incubatory times during the forming of a macroplate of bainitic ferrite [15].

This opens a wide field of activity for using the diverse tools of physical acoustics in the analysis of the morphological features of separate crystals (e.g., of plate-like or wedge-like forms), their junctions (acute and obtuse), mutual intersections, interactions with grain boundaries, etc., on the basis of the concepts of the CWP as a superposition of wave beams propagating in metastable austenite and capable of disturbing its stability. As regards other promising avenues of

investigations, we note the possibility of extending the applicability of the theory to bcc-hcp and hcp-bcc transitions [16, 17], which require an additional short-wavelength "reshuffling" of planes (which does not affect the macroscopic morphological features).

The purpose of this paper is to show that the concept of the controlling wave process is efficient also in the case of MTs in titanium nickelide-based alloys.

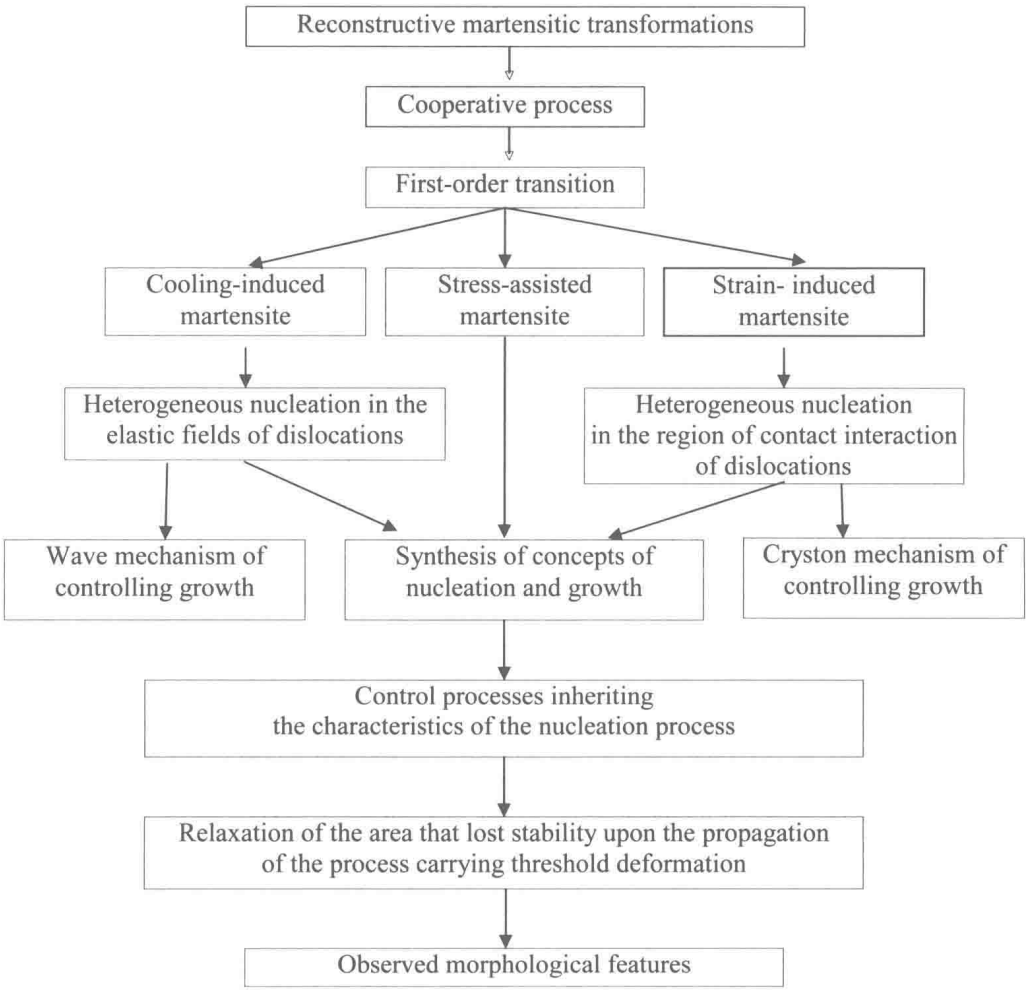

Fig. 3. Key points of the description of a martensitic reaction in single crystals and in polycrystalline materials with the grain size exceeding the critical size D_c.

Theory Procedure

The key role in a new paradigm is played by the concept of the IES appearing in the elastic field of a dislocation nucleation center (DNC). The oscillatory character of the IES generates a control wave process resulting in the threshold deformation disruption of the stability of the initial phase. In the simplest case the synthesis of concepts of heterogeneous nucleation and wave growth is reached if we consider that the wave normals $\vec{n}_1$ and $\vec{n}_2$ of wave beams in the CWP, describing in the superposition region the tensile ($\varepsilon_1 > 0$) and compression strain ($\varepsilon_2 < 0$), are collinear to the eigenvectors $\vec{\xi}_i$ ($i = 1, 2$) of the strain tensor of the elastic defect field in the nucleation region (see Fig.4):

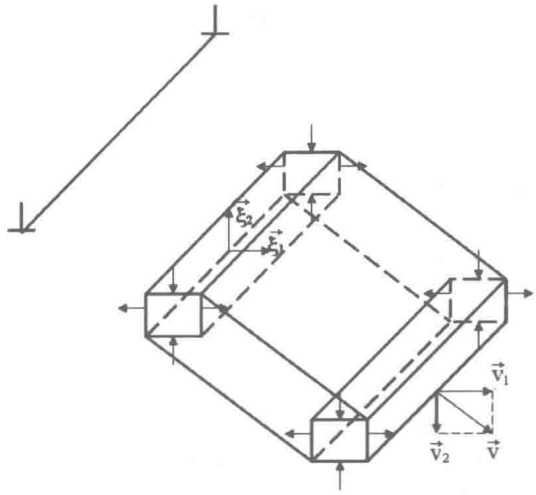

Fig. 4. Wave model of controlling growth of a martensite crystal (the segment bounded by the symbols ⊥ corresponds to a dislocation line).

$$\vec{n}_1 \| \vec{\xi}_1,\ \vec{n}_2 \| \vec{\xi}_2,\ \vec{n}_1 \perp \vec{n}_2,\ |\vec{n}_1| = |\vec{\xi}_i| = 1. \tag{1}$$

The normal $\vec{N}_w$ to the habit plane associated with CWP propagation is set by the relationship

$$\vec{N}_w \| \vec{n}_2 - \vec{n}_1 æ,\ æ = v_2/v_1, \tag{2}$$

where v_1 and v_2 are the moduli of the velocities of wave propagation in the $\vec{n}_1$ and $\vec{n}_2$ directions. For the small threshold strains ε_{th}, there holds true the relationship

$$æ = v_2/v_1 = k = \sqrt{\varepsilon_1/|\varepsilon_2|} \tag{3}$$

The reconstructive γ-α MT in iron-based alloys possess clearly pronounced properties of cooperative phase transitions of the first kind, whereas in the B2 titanium–nickelide-based alloys, the characteristics of transitions of the first kind are expressed to a lesser degree. From three widespread MT variants (B2 → B19, B2 → R, and B2 → B19′), we consider at first the B2 → B19 transition with the greatest relative change of the volume.

Results and Discussion

B2 → B19 MT for simplest variant (wave vectors along the axes of symmetry). Here the attention is focused on CWP cases [16-18] providing the fastest transformation of the $\{110\}_{B2}$ planes. The present paragraph is aimed at demonstration of the possibility of a choice of the deformable plane convenient for a description of the B2 → B19 (and B2 → B19′) MT through the intermediate mesoscopic state.

We begin by considering of expected habit planes and DNC for quenched martensitic crystals. Based on the data on the elastic moduli of Ti–Ni–Cu and Ti50–Ni38–Cu10–Fe2 systems presented in [19-22], the elastic moduli (in GPa) are assumed to be

$$C_{11} = 165,\ C_{12} = 139,\ C_{44} = 34. \tag{4}$$

Setting in Eq. (2) $\vec{n}_1 \| [110]_{B2}$ and $\vec{n}_2 \| [001]_{B2}$ (the $(1\,\bar{1}\,0)_{B2}$ plane is deformed), we find

$$\vec{N}_w \| [\,-æ\;-æ\;\sqrt{2}\,]_{B2},\; æ = \sqrt{\frac{2C_{11}}{C_{11}+C_{12}+2C_{44}}}. \tag{5}$$

Substitution of elastic moduli (4) into Eq. (5) yields

$$æ \approx 0.9419 \text{ and } \vec{N}_w \| [\bar{1}\;\bar{1}\;1.5015]_{B2} \tag{6}$$

that is, the $\{223\}_{B2}$ habit planes, as well as $\{334\}_{B2}$ ones (for small deviations of $\vec{n}_1$ and $\vec{n}_2$ from the symmetry axes), are easily realized in the wave description. It is well known (for example, see [23, 24]) that the necessary conditions for the formation of the corresponding IES exist in elastic fields of edge dislocations with a $[1\,\bar{1}\,0]_{B2}$ direction of dislocation lines. Recall that the habit planes, close to $\{223\}_{B2}$ and $\{334\}_{B2}$, are observed in Ti–Ni–Cu [25].

The B19 phase is orthorhombic; therefore, the additional requirement caused by the lattice symmetry during an α–ε MT (see [17]) is absent, and it is impossible to determine analytically the final strains only from the known ratio of their values. However, knowing the lattice parameters for the initial and final phases, it is possible to verify whether the observable ratio of final strains is in agreement with the ratio of threshold strains according to the requirement (3). Fig. 5 taken from [19] shows elementary cells of phases.

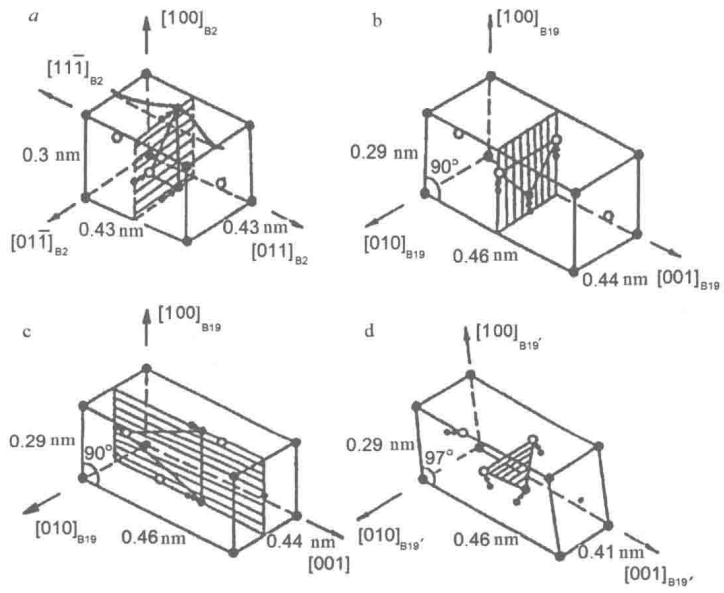

Fig. 5. Elementary cells of B2 (*a*), B19 (b and c), and B19′ phases (d) in titanium nickelide alloys and their size-orientation relations and reorganization schemes determined by shuffle (of $\{011\}\langle 100\rangle$ and $\{0\,1\,\bar{1}\}\langle 011\rangle$ types) displacements of atoms (the $\{011\}_{B2}$ shear planes are hatched). The Fig. 5 corresponds to Fig. 3.12 in [19].

It should be borne in mind that Fig. 5 displays only approximate correspondence of cell sizes of the initial B2 phase. For example, setting the cell size in the $[100]_{B2}$ direction equal to $a_{B2} = 0.3$ nm, the sizes in the $[011]_{B2}$ and $[0\,1\,\bar{1}]_{B2}$ directions must be set equal to $\sqrt{2}\,a_{B2} \approx 0.42426$ nm rather