The Peculiarities of Martensite Morphology in Nano- and Inhomogeneous Spaces

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The article describes certain experimental situations, in which the small volumes available for the phase transformation can dramatically affect the morphology, substructure of martensite, martensitic transformation itself. Martensitic structures in standalone nanoparticles as well as that one's embedded in extrinsic matrix, joint nanograins and multiply connected spaces, gradient structures are given consideration. Much attention is paid to the problem of nucleation and propagation of martensitic phase through peculiar spaces having inhomogeneities and complex 3D connectivity with each other. The conclusion is made about inconsistency of the observed ultimate martensite microstructure in nanosized and inhomogeneous spaces with the current conception of the propagation of martensite-austenite boundary through the available for the transformation volumes as the interface, which sustains the invariant plane strain condition.

1. INTRODUCTION

The martensitic transformation is a key attribute that makes available shape memory effect and related phenomena in some alloys. Despite the progress achieved in the recognition of its nature, some aspects concerning the possibility of martensitic transformation in finite-size and/or nonequilibrium structures are still shaded. Among the variety one can denote such problems as a) transformation peculiarities under constraints of various natures; b) the spreading of martensitic phase on whole available for the phase transformation space; c) the nucleation of the martesite. On the other hand the continuously developing shape memory material fabrication methods generate in most cases a set of nonequilibrium states of materials including inhomogeneous and/or gradient structures of different dimensions and topology. The various experimentally observed situations will be described in respect of above mentioned problems in current communication. The attempt elucidating the relevance of each of those factors for the realization martensitic transformation in ultra small and multiply connected and/or inhomogeneous spaces in actually observed structures will be made.

2. MARTENSITE MORPHOLOGY

Fig. 1 exemplify the main features of martensite morphology, which appear in most of the β-phase alloys (Ni-Al, Cu-base, Ti-Ni-base, Ni-Mn-Ga *etc*) undergoing transformation from ordered BCC structure into various type of martensites. The plate-like martensite crystals (domains) of different orientations indicated as M1, M2, M3 occupy two grains, which in turn are separated with the boundary decorated with the precipitation P1 of Ni_3Al phase. The martensite crystals do not touch the grain boundary because of gradient of Ni concentration exists nearby the boundary [1] and martensite crystals can't propagate in region enriched with Al.

The grain on the right is also divided on subgrains decorated with precipitation P2, which don't impede the martensite crystals propagation. Slight bending of martensite crystals appears on subgrains boundaries due to small reorientation between subgrains. Whilst the martensite crystals M2, apparently appeared first, impede effectively the propagation of M1 crystals through the grain.

Each of separate crystals produces large shear stresses in the surrounding matrix. According with the phenomenological theories of martensitic transformation [2,3] to minimize those stresses the homogeneous deformation of whole transformed volume **P₁** must satisfy the invariant plane strain condition – the interface (habit plane) between martensite and parent matrix (austenite) has to be undistorted and unrotated on average. It can be shown that matrix operator **P₁** is representing as follows:

$$P_1 = RP_2B, \qquad (2.1)$$

where **B** represents the lattice transformation matrix (Bain deformation) to transform a martensite crystal lattice from austenite lattice, **P₂** is a deformation with invariant lattice (shear) and **R** is a rotation matrix, which provides the orientation relationship between martensite and austenite. **P₂** is usually introducing as twining in β-phase alloys, which hereafter will be referred as microtwins. The example of such twin structure is shown in Fig. 1b. It is important that theory predicts strict relation between the twins width in the crystal. Other peculiarities of martensite morphology is that 24 habit plane variants of martensite crystals forms various self-accommodation schemes of mutual arrangement to eliminate the stresses appearing on the edges of separate martensite crystals. One of such self-accommodation scheme is presented on inset of Fig. 1a. Neighboring crystals are in the twin relation with each other, which hereafter will be referred as macrotwins. For the further purposes it should be noted that a) –

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invariant plane strain condition presuppose indirectly that growth and propagation of martensite ensemble always happens in the presence of austenite matrix and b) – theory don't give any restriction on the available twin systems, which realize deformation with invariant lattice. Among the different twinning elements, only those one that provide good fitting between theory and experimental observations are considered as invariant lattice shear systems.
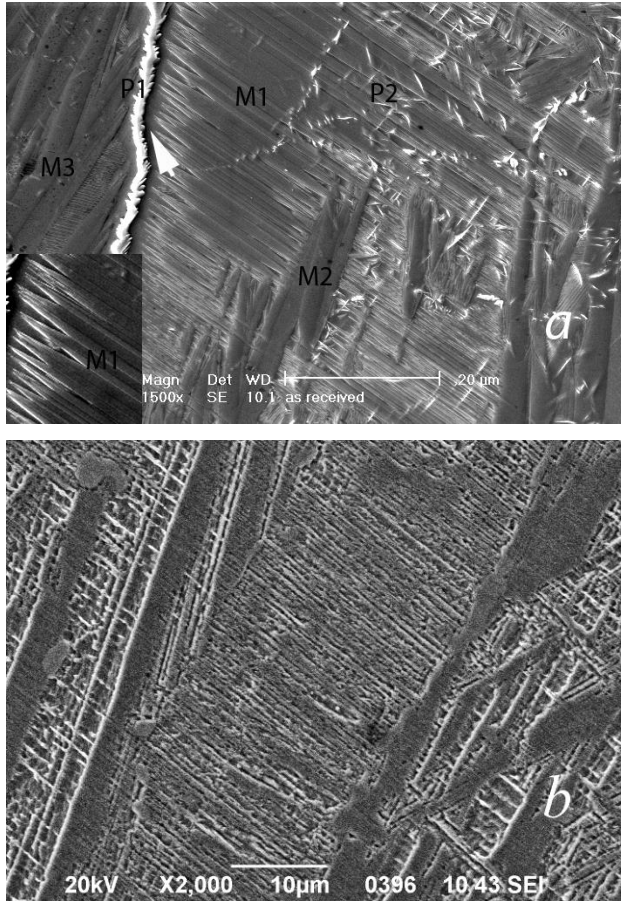

Fig. 1 – a) – SEM micrograph of the martensite structure in NiAlGa alloy [1]. Enlarged self-accommodated martensite ensemble with spear-like morphology is shown on inset; b) – SEM micrograph of the twin structure of martensite crystal in the severe chemically etched HfPd alloy [4].

3. SMALLNESS CRITERIA

In order to elucidate the peculiarities of martensitic morphology that could be critical for the shape memory effect in small volumes, it is naturally identify the inherent to martensite structure length scales comparing them with the volumes available for the transformation in each experimental situation. For the first glance the candidates on such scales are the characteristic length l or connected with it width b of the individual crystal, which is length of microtwins in fact. The width of microtwins w can be considered as other candidate. However detail examination of Fig. 1a shows that length of the crystals is controlled by the space, which is available for the transformation, being the aspect ratio l/a remains approximately constant for each crystals. The microtwin width in Ni-Al alloys decreases from about

10 nanometers down to about 2 nanometers with the decreasing microtwins length [5], being the relation between widths of adjacent microtwins inside martensite crystals remains approximately constant to attain the invariant plane strain condition. For other alloys microtwin width can achieve submicron sizes (see Fig. 1b) however trend of decreasing microtwin width with decreasing crystal length have to be retained owing the balance between the elastic strain energy at the austenite-martensite interface and the surface microtwin boundary energy [5-7]. The decreasing of length of crystal l controlled by external constraints (grain boundary e.g.) causes the decreasing of length of microtwins a consequently the decreasing of twins width w *virtually to zero value*. Thus, in such hierarchical scheme, no one of the above length scales is convenient as smallness criteria of volume available for the phase transformation.

Apparently one more inherent length scale exists that relates with the long period stacking order structure, which one martensite structure differs from another by itself. There are 2H and/or 9R(18R) structure in Cu-Al-base alloys, 3R and/or 7R in Ni-Al-based alloys, 5M(10M) and/or 7R(14R) structure in Ni-Mn-Ga. The digits in the notations indicate the modulation period of stacking order taken in interplanar distances. They are giving the natural lower limit of length scale, usually less than nanometer in order, above which the consideration of martensite structure per se makes sense. The objects of such volumes will not be considered in current communication. However it is length scale that confine from below hierarchical scheme and allows estimate the lower dimensions of system at least, where size effects could be expected.

4. STANDALLONE AND SEPARATE PARTICLES

The low magnification HRTEM image of standalone particle sized 18 nm with the composition $Ni_{64.6}Al_{35.4}$ is shown in Fig. 2. Particle is formed due to the condensation from vapor phase during spark erosion processing in liquid argon [8]. It is evident that width of $(111)_M$ microtwins alternates between 2 and 8 nm (as well as ratio between neighbor twins) that contradicts the predictions of phenomenological theory. It should be noted that similar differences in stacking fault sequences and twins widths has been observed in splat-cooled NiAl particles [9] also having nonequilibrium nature. Some irregularities have been documented even in bulk NiAl martensite [9]. However in current case *all* of the particles under proper diffraction conditions have irregular twins structure. It is useful to compare the structure of such martensitic particles with nanosized particles $Cu_{0.97}Al_{0.03}$, which are not undergoing martensitic transformation (Fig. 1b). They were obtained by the same technique as a result of the condensation from vapor phase. The origin of irregular stacking faults (or twins) seems to be the relaxation of stresses appearing from the relative thick oxide layer.

The similarity both pictures allowing suppose that the fine twins in $Ni_{64.6}Al_{35.4}$ standalone particles are rather internal defects of martensite appearing to minimize the transformation strain under the constraint of oxide layer and/or compensate the increasing in surface energy of particle due to the phase transformation. In-

deed, 1) – due to the Bain deformation **B** spherical particles have to transform in ellipsoid particles with obviously larger surface and 2) – so far as the surrounding austenite matrix don't be present anymore, there is no need to maintain the invariant plane strain condition. Irregular stacking faults have been observed also in nanocrystalline TiNi powder, prepared by the electro explosion of TiNi wire [10]. In that observation the type of defects were not studied in details.
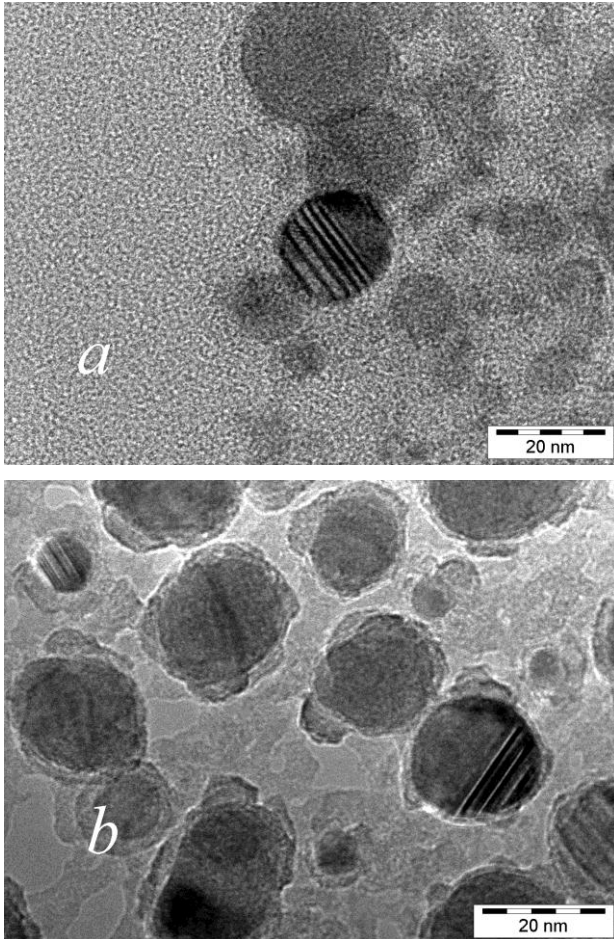

Fig. 2 – low magnification HRTEM image of a) standalone particle $Ni_{64.6}Al_{35.4}$. $EB||(011)_M$; b) the particles $Cu_{0.97}Al_{0.03}$.

How large can be standalone particle to observe above mentioned martensitic structure? Using the proportionality between width of microtwins and their length in form of $w \sim a1/2$ power low predicted by linear theory [6] or $w \sim a2/3$ predicted by nonlinear theory [7] one can estimate the length of microtwin corresponding to the width of martensitic crystal (macrotwin) that could be present in coarse-grained martensite. For the estimation both relations are suitable since both good fit the experimental data [5]. In case of Ni64.6Al35.4 nanoparticles taking microtwin width in 2nm one can obtain 100nm as lower limit of nanoparticles size where similar structures could be still expected. In fact it is underestimated value because the microtwins widths w increase with the increasing its length a at least in coarse-grained materials.
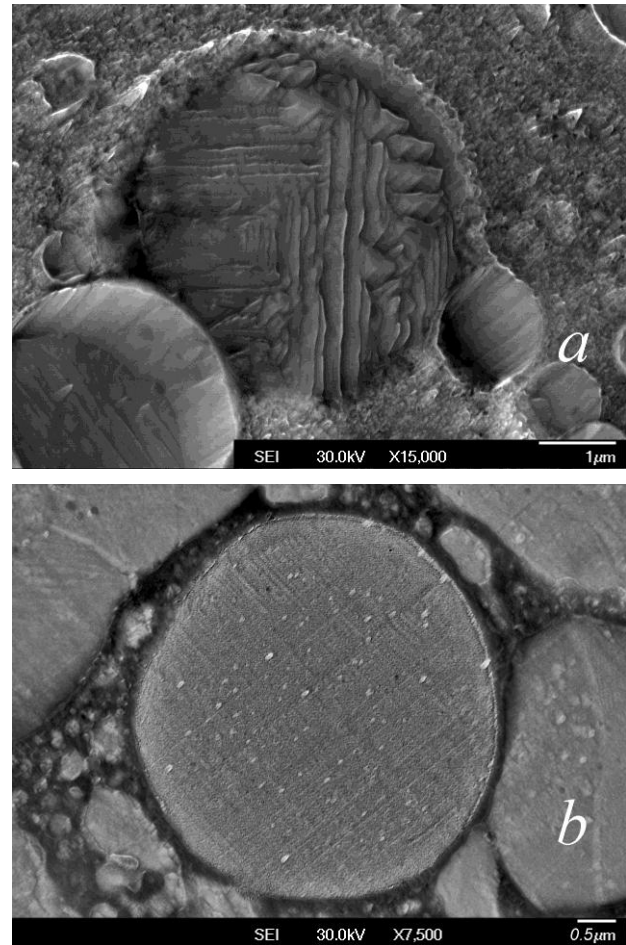

Fig. 3 – SEM micrograph of the SPS sintered alloys a) – the spherical CuAlNi particle occupied by the twinned martensite (on the left) [11]; b) – the spherical NiMnGa particle occupied by the twinned martensite [12]. Samples were etched in situ by the Ar^+ ions beam. Needle-like tips and striped walls around the etched particles are the artifacts of the Ar+ ion etching.

To make the accurate estimation the interplay between the chemical free energy per unit of volume, the microtwins boundary energy, the strain energy caused by the ends microtwins should be taken into account. In case of martensitic transformation in separate particles surrounded by extrinsic matrix such factors as the volume-related strain energy appearing in surrounding matrix due to the transformation and the changes of the particle interfacial energy upon the transformation have to be added into consideration. Good discussion of the problem of transformation is given in Refs. [13,14]. In [13] also shown that self-accommodation wedge scheme of B19' martensite crystals combining with the transformed in R-phase regions was present already in 100 nm spherical inclusions of NiTi obtained after partial devitrification of the amorphous phase. Still some experimental evidences obtained for separate particles surrounded by extrinsic matrix allowing claim that martensite can occupy whole volume available for the transformation even in relatively large micron sized objects (Fig. 3).

5. VOLUMES UNDER CONSTRAINTS

Other peculiarity of the martensitic transformation in nanosized volumes was revealed by many authors in nanograins of Ti-Ni-based alloys [13-16]. In addition to the absence of self-accommodating schemes of martensite it was found that dominant twinning systems was (100) compound twins, which does not give a solution of the phenomenological crystallography theory. These fine twinning platelets are rather the internal defects of the martensite to minimize the transformation strains under the constraint of grain boundaries [15]. These peculiarities and the acquisition of the shape of nanograins by the martensite presume that invariant plane strain condition is not sustained upon the martensitic transformation. On the other hand the calculations using the geometrically nonlinear theory of the martensitic transformation performed for the NiTi nanograins are in very good agreement with the *a posteriori* experimental observations [14]. Again, the statement 2 from previous section is undoubted for *a posteriori* observations. But, is the invariant plane strain condition still proper upon the propagation martensite through the whole volume of nanoparticle? Nevertheless, the condition of the minimum strain on the interface boundary has to be sustained during the propagation of martensite crystal to provide good conjunction on the martensite-austenite interface. But is it a really plane? The validity of these questions is becoming obvious following the detail examination of Fig. 4, where the twinned martensite plates occupy the whole $Ni_{65}Al_{35}$ particle. It is seen that martensite was spread through the 3D network, which was formed owing chemical stratification of the rapid quenched in liquid argon molten NiAl particle during spark erosion procession [8]. The martensite plates of two different morphologies with different orientations occupy dominantly 3D network formed from the cells with bright diffuse boundaries. Such boundaries are enriched with Ni that makes available martensitic transformation in it well above room temperature. It is obviously that there is strong correlation between the contrasts in different places of network separated by the area, where martensitic plates are not observed. How martensite plates in one cells boundary do "know" about the martensitic plate's orientations in others boundaries? The untransformed areas, as constraints, simultaneously transmit the transformation strains from one boundary to another. Due to the rapidity of martensitic transformation and its cooperative nature the interaction between different areas, where martensitic transformation is available at given temperature, can transmit only through the lattice oscillations. In that case the martensitic transformation can develop practically simultaneously in different areas of particle, maintaining the minima transformation strain conditions even in such inhomogeneous structure as shown on Fig. 4. Other questions where does the martensite nucleate in

such nano-particles? The dislocation walls or pile-ups are generally considered as possible place for nucleation in coarse-grained martensite [17]. However the observed standalone nanoparticles are free of such defects and only surface of particle remains as potential site for the nucleation in standalone particles. At the other hand the 1 nm modulated structure of γ'-martensite together with austenitic B2 phase has been observed in Au-Cd nanoparticles, prepared by wet-chemical synthesis [18], being the modulated structure was present inside the particles, not at the surface. Therefore, authors concluded the surfaces of the nanoparticles do not serve as preferential nucleation sites for the martensite. One of the possible ways to overcome these contradictions is to decline the conception of heterogeneous nucleation, at least for the standalone nanoparticles.
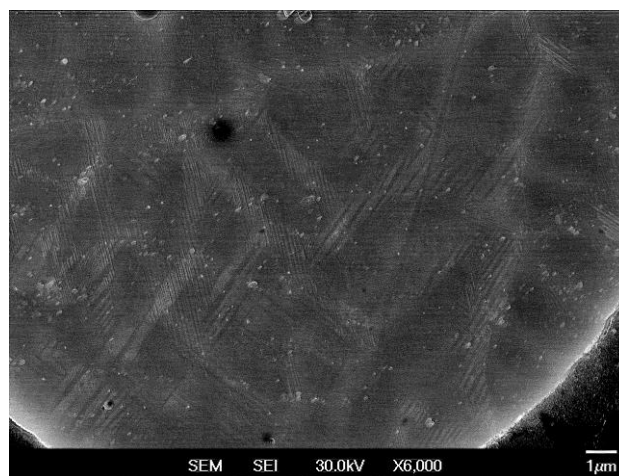

Fig. 4 – SEM micrograph of the twinned martensite in the NiAl particle. Particle was etched in situ by the Ar^+ ions beam.

6. CONCLUSIONS

Martensitic transformation in fine standalone and separated particles in some of B2 alloys is featured the absence of self-accommodating martensite and twin structure, which contradicts with the predictions of phenomenological theory. These twins, which rather are the internal defects of martensite, provide compensation the increasing in surface energy of particle due to the phase transformation and/or the minimization of the transformation strains under the constraints such as oxide layer or the extrinsic matrix or the neighboring untransformed regions. Observed ultimate martensite microstructure in nanosized and inhomogeneous spaces is not consistent with the current conception of the propagation of martensite-austenite boundary through the available for the transformation volumes as the interface, which sustains the invariant plane strain condition.

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