ISSN 0027-1349, Moscow University Physics Bulletin, 2010, Vol. 65, No. 3, pp. 184–188. © Allerton Press, Inc., 2010.
Original Russian Text © A.G. Khundjua, E.A. Brovkina, Shaotao Zheng, 2010, published in Vestnik Moskovskogo Universiteta. Fizika, 2010, No. 3, pp. 27–31.

Formation of Self-Accommodation Complexes of Martensite Crystals during Transformations of Distortion Type in Alloys with the Shape Memory Effect

A. G. Khundjua, E. A. Brovkina, and Shaotao Zheng
Department of Solid State Physics, Faculty of Physics, Moscow State University, Moscow, 119991 Russia
e-mail: khundjua@mail.ru, el-brov@rambler.ru

Received February 12, 2010; accepted February 17, 2010

Abstract—This work discusses the formation of self-accommodation complexes of martensite crystals during transformations of distortion type and experimentally observed shape memory effects in unordered solid solutions. A method for the analysis of orientation relationships between the lattices of austenite and martensite in terms of the possibility of formation of self-accommodation complexes is given.

Key words: shape memory effect; martensite transformations; inelastic deformation; twinning; orientation relationship.

DOI: 10.3103/S0027134910030069

INTRODUCTION

Shape memory effects cannot exist without crystallographic reversibility of inelastic deformations, assuming that during direct and reverse transformations one and the same atoms are shifted in opposite directions. An alternative is the shift during reverse transformation in a direction that is equivalent in terms of crystallography to the shift direction during direct transformation.

Crystallographic reversibility, i.e., the recovery of the structure at the atomic level and of the sample shape, is possible during inelastic deformations by twinning or by martensite transformation. During deformation by twinning the shape of elementary cell is not changed, and the deformation actually is converted to rotation of one part of the crystal relative to another part; this determines the macroscopic shape change. Removal of the external load can result in detwinning and the recovery of shape, provided that the deformed region is located inside a crystal medium that accumulates elastic strains and tends to recover the initial state [1, 2].

During martensite transformations the shape of the elementary cell is changed; this is accompanied by the shape change of the transformed region. However, without external anisotropy the martensite transformation is developed in different regions of a crystal, and formation of several variants of relative orientation of the lattices of austenite and martensite compensates for the shape change at the macroscopic level of the monocrystal (polycrystalline grain). The macroscopic shape change is related to the creation of advantages in the crystal for the formation of certain variants, i.e., of predetermined anisotropies originating by external mechanical strains or magnetic field promoted formation of domains with a determined orientation of atomic magnetic moments [3].

The causes of the crystallographic reversibility are not unique, which results in the nonuniqueness of the mechanisms of memory effects. Crystallographic reversibility exists without any exceptions in all alloys with ordered crystalline structures, because the shift of atoms during reverse transformation in crystallographic equivalent directions distorts the type of ordering and results in the formation of a structure with an increased level of cohesive energy. In unordered solid solutions crystallographic reversibility is associated with dislocations, which, within the course of direct (reverse) martensite transformation, are inherited by the lattice of martensite (austenite). Without crystallographic reversibility energetically unfavorable dislocations are formed regardless of the structure of austenite.

The inheritance of dislocations is only one possible mechanism of crystallographic reversibility in unordered solid solutions and cannot explain all varieties of the observed phenomena. The memory effect exist also during deformation in low temperature regions where a sample is completely in a martensite state, and inelastic deformation occurs via twinning of martensite crystals and growth of one domain at the expense of others by sliding of the domain border (twinning plane). This process can also involve various martensite crystals, provided that a twin bond between various variants of the orientation relationship exists. During the existence of such a bond a complex of domains is developed from the initial martensite crystal by twinning; such domains correspond to several variants of the orientation relationship—self-accommodation complex. Deformation of the shape averaged over such a complex is described by an almost unit matrix, that is, the compensation of shape deformation and minimization of elastic energy occur not only at the level of a polycrystalline grain but also at the microlevel of the self-accommodation complex of martensite crystals.

Therefore, in alloys with unordered lattices the crystallographic reversibility of the transformation can be determined by the ability to form self-accommodation complexes. The present work aims at an analysis of the ability to form self-accommodation complexes during martensite transformations of the distortion type from the crystallographic point of view, that is, during tetragonal, orthorhombic, rhombohedral, and monoclinic distortions of the initial cubic lattice of austenite.

CALCULATION PROCEDURE

The number of crystallographic and equivalent variants of relative orientation of crystalline lattices depends on their syngony and actual type of orientation relationship set by defining of parallel planes and directions in the lattices:

$$\{H, K, L\}\langle h, k, l\rangle_A \parallel \{H', K', L'\}\langle h', k', l'\rangle_M.$$

The number of the relative orientation cannot exceed the maximal value of the multiplicity factor of an austenite lattice (24 for cubic structures); however, the number of the variants is usually lower, since, as a rule, the planes of dense packing are parallel, and their multiplicity factor does not reach the maximal value.

On the basis of the orientation relationship and parameters of the lattices the matrix of the orientation relationship $\hat{A}$ is built; its columns are projections of basic vectors of the martensite lattice to the basis of the austenite lattice. The twinning transforms one variant of orientation relationship to another; the twinning plane of the martensite crystal is parallel to one of the nine planes of symmetry of the austenite lattice (planes of the {100} and {110} type). In mathematical terms, this condition is reduced to the matrix equation $\hat{S}_i\hat{A} = \hat{A}\hat{D}_{UVW}$, where $\hat{S}_i$ is the symmetry operator of an austenite lattice, and $\hat{D}_{UVW}$ is the twinning operator of a martensite lattice over the (UVW) plane [4].

The calculation of the ability to form self-accommodation complexes amounts to determination of the indices of martensite lattice planes that are parallel to the symmetry planes of an austenite cubic lattice, as well as to the analysis of the reliability of twinning over these planes [5]. The transformation of distortion type is characterized by continuous variations of the parameters of an elementary cell upon a temperature decrease below the M_s value, resulting in variations of the symmetry. Herewith, the orientation relationships are maximally simple, but not unique, because it is not always clear over which planes the lattices are contiguous. Therefore, it is obvious that during low distortions the lowest angles to the symmetry planes of austenite will form nine planes of martensite with the same indices (100), (010), (001), (110), (101), (011), $(1\bar{1}0)$, $(10\bar{1})$, and $(01\bar{1})$. The question of whether the limit values of these angles prevent the formation of self-accommodation complexes in solid solutions with memory effects is a very significant issue.

It should be noted that the role of distortion consists not only of “parallelizing” the lattices of austenite and martensite, but also of the fact that the a decrease of symmetry creates the possibility of twinning over these planes, i.e., the twinning over the planes of lattice symmetry is a similar operation.

The calculations were aided by a software package for the simulation of spot diffraction patterns in dual-phase crystals. After entering of initial data in the interactive window (orientation relationship, parameters of the lattices of austenite and martensite phases, indices of twinning plane of martensite phase, and conditions for acquiring a diffraction pattern) the software performs calculations of the diffraction pattern accompanied by visual presentation on the monitor screen, including the matrices $\hat{A}$ and $\hat{D}_{UVW}$ [6]. Comparison of the diffraction patterns with and without consideration of twinning allows one to make a conclusion as to whether the twinning results in the occurrence of new orientations, i.e., additional reflections in the diffraction patterns.

ANALYSIS OF TWINNING OF CRYSTALS DURING DISTORTION TRANSFORMATIONS

Upon tetragonal distortion of a cubic lattice the lengths of the edges of an elementary cell are changed and the measure of the distortion rate can be expressed as the c/a ratio. The possibility of the formation of self-accommodation complexes is determined only by the parallelism of the planes; therefore, the absolute values of the lattice parameters do not effect the final result of the calculations, which depend only on the ratio of the lattice parameters of the tetragonal shape: $c_\tau/a_\tau = \tau$. For low distortions, several methods can be proposed for conjugating the lattices over the planes {100}, {110}, and {111}. In general, the elements of the matrix of an orientation relationship can be expressed in terms of the parameter τ; these matrices are simple when nondiagonal elements equal zero, e.g., the matrices of the two following relationships (the matrix was calculated on the basis of the assumption that $a_\tau = b_\tau = a_0$, and $c_\tau = \tau a_0$:

$$\{100\}\langle 001\rangle_A \parallel (100)[001]_M$$

$$\text{or}\ \ \{110\}\langle 001\rangle_A \parallel \{110\}\langle 001\rangle_M;$$

$$\hat{A}_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \tau \end{pmatrix}. \tag{1}$$

For other orientation relationships nondiagonal elements appear in the matrices, which are rather complicated expressed in terms of τ (by fractions and radicals). It is more convenient to calculate matrices for the numerical values of $\tau = 0.968$ (c_τ/a_τ ratio for the martensite lattice in Cu–Mn alloy [3, 7]). The respective orientation relationships and their matrices are as follows:

$$\{100\}\langle 0\bar{1}1\rangle_A \parallel \{100\}\langle 0\bar{1}1\rangle_M$$

$$\text{and}\ \ \{011\}\langle 0\bar{1}1\rangle_A \parallel \{011\}\langle 0\bar{1}1\rangle_M$$

$$\hat{A}_2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & -0.016 \\ 0 & -0.016 & 0.968 \end{pmatrix}, \tag{2}$$

$$\{111\}\langle 1\bar{1}0\rangle_A \parallel (111)[1\bar{1}0]_M$$

$$\hat{A}_3 = \begin{pmatrix} 1 & 0 & 0.010 \\ 0 & 1 & 0.010 \\ -0.010 & -0.010 & 0.968 \end{pmatrix}, \tag{3}$$

$$\{011\}\langle 1\bar{1}1\rangle_A \parallel (011)[1\bar{1}1]_M$$

$$\hat{A}_4 = \begin{pmatrix} 1 & 0.005 & -0.005 \\ -0.005 & 1 & 0.016 \\ 0.005 & -0.016 & 0.968 \end{pmatrix}, \tag{4}$$

$$\{111\}\langle 10\bar{1}\rangle_A \parallel (111)[10\bar{1}]_M$$

$$\hat{A}_5 = \begin{pmatrix} 1 & 0.005 & 0.016 \\ 0.005 & 1 & 0.005 \\ -0.016 & -0.005 & 0.968 \end{pmatrix}. \tag{5}$$

Other forms of expression of the orientation relationships are possible, and such matrices will vary only in the signs of nondiagonal elements or their position in the matrix, in a similar manner to variations between the matrices $\hat{A}_4$ and $\hat{A}_5$. Therefore, in fact, there are four different matrices $\hat{A}_1$–$\hat{A}_4$ with various numbers of zero nondiagonal elements. (In the mentioned matrices the sum of squared elements, e.g., of the first column does not remain unchanged, which is stipulated by preset accuracy of calculation of the matrix elements, this can be verified by calculations of the length of the respective basis vector of the martensite lattice.

In tetragonal lattice the planes $(01\bar{1})$, (011), $(10\bar{1})$, and (101) are not planes of symmetry and twinning over them is possible. By means of the matrices it is finally possible to calculate the angles between the planes of symmetry of austenite and the planes of twinning of martensite, which for the orientation relationship (5) equals:

$$\angle(10\bar{1})_A(10\bar{1})_M = 1.86°;\ \ \angle(101)_A(101)_M = 0.41°;$$

$$\angle(011)_A(011)_M = 0.78°;\ \ \angle(01\bar{1})_A(01\bar{1})_M = 1.49°.$$

The algorithm of calculations performed for tetragonal lattice can also be applied for orthorhombic distortion. In this case the parameters of the lattice of orthorhombic martensite can be assumed to equal $a_r = a_0$, $b_r = \mu a_0$, and $c_r = \chi a_0$, then the problem of parallelism can be approached in a general form or for certain values of the parameters obtained from the experiment. Orthorhombic martensite with lattice parameters that continuously vary with temperature is formed in an Mn–Ni alloy. For the calculations let us take the values of the parameters equaling to $a_r = 0.3678$ nm, $b_r = 0.3695$ nm, and $c_r = 0.3735$ nm corresponding to the temperature $T = 313$ K [3]. The lattices can be conjugated over the planes {100}, {110}, and {111} by at least twelve methods. Let us select the conjugation of the lattices over the planes of face-centered cubic cell of the austenite lattice. In this variant three orientation relationships should be considered:

$$\{111\}\langle 1\bar{1}0\rangle_A \parallel (111)[1\bar{1}0]_M$$

$$\hat{A}_6 = \begin{pmatrix} 1 & -0.002 & -0.004 \\ 0.002 & 1.005 & -0.004 \\ 0.004 & 0.004 & 1.015 \end{pmatrix}; \tag{6}$$

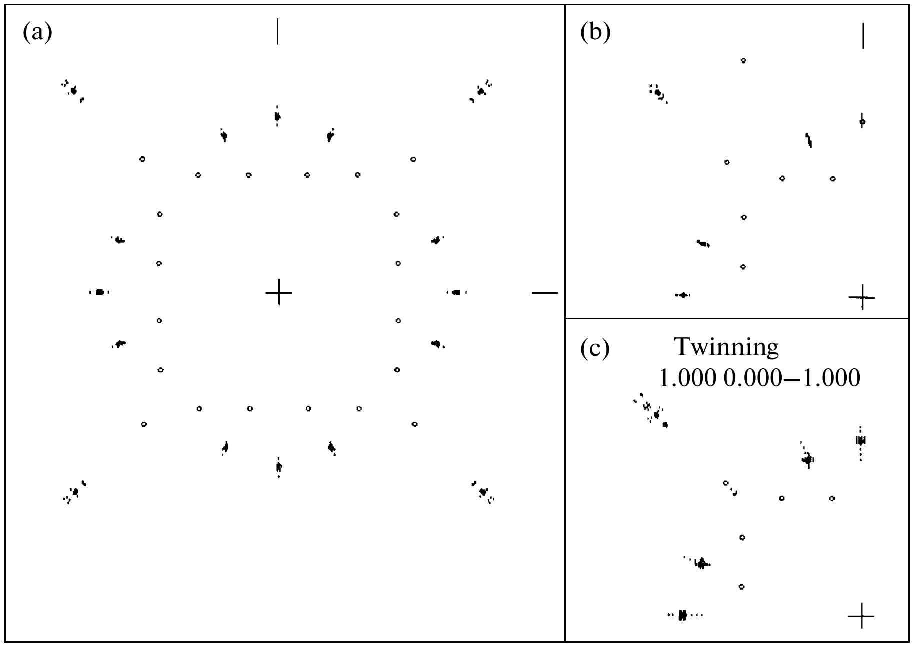
$$\{111\}\langle 10\bar{1}\rangle_A \parallel (111)[10\bar{1}]_M$$

$$\hat{A}_7 = \begin{pmatrix} 1 & 0.001 & -0.008 \\ -0.001 & 1.005 & -0.001 \\ 0.008 & 0.001 & 1.015 \end{pmatrix}; \tag{7}$$

$$\{111\}\langle 0\bar{1}1\rangle_A \parallel (111)[0\bar{1}1]_M$$

$$\hat{A}_8 = \begin{pmatrix} 1 & -0.003 & -0.003 \\ 0.003 & 1.005 & -0.005 \\ 0.003 & 0.005 & 1.015 \end{pmatrix}. \tag{8}$$

The orientation relationships (1)–(5) can also be applied to orthorhombic martensite. All of them describe close mutual orientations, which can be easily confirmed by element-wise comparison of the matrices, or, more clearly, by comparison of the simulated patterns of diffraction of X-rays for various ori-



Simulated X-ray pattern of a crystal of cubic austenite with segregated orthorhombic martensite without consideration of twinning for orientation relationships (7) (a), (8) (b) and with consideration of the twinning over the plane $(10\bar{1})$ (c).

entation relationships (figure). Taking into account the asterism of reflections in experimental X-ray patterns, it is nearly impossible to estimate the occurrence of any of the mentioned relationships.

In addition, during the formation of martensite crystal inside the initial phase, the energy minimum is achieved upon deviation of the habit from the invariant plane; in this case the martensite lattice experiences supplemental rotation, and therefore, none of the rational orientation relationships exist.

The orthorhombic lattice can be twinned over any plane of the {110} type. The angles between the relevant planes of martensite and austenite lattices for the given orientation relationships are presented in the table.

The performed calculations show that during the martensite transformations of tetragonal and orthorhombic distortions of the lattice (similar to the distortion in the γ-manganese based alloys) there are no obstacles of a crystal-geometric character for the formation of self-accommodation complexes of martensite crystals, which is in conformity with the observed situation [3].

The algorithm that was applied during calculations of orthorhombic martensite can also be extended for monoclinic distortion by modification of one of the angles of an elementary cell. General calculation is too complicated and not reasonable even for orthorhombic distortion; the situation would hardly be improved for monoclinic distortion, because it would be necessary to introduce one more additional variable parameter. The problem of parallelism of the respective planes should be solved for certain lattice parameters obtained from experiments. The only aspect to be mentioned as a general approach is the possibility of twinning of the monoclinic lattice ($a \neq b \neq c$; $\alpha = \gamma = 90°$; $\beta \neq 90°$) in addition to the twinning planes of an orthorhombic lattice over two more planes (100) and (001).

During rhombohedral distortion the cubic cell is elongated or compressed along the (111) direction due to simultaneous distortion of three angles of an elementary cell ($a = b = c$; $\alpha = \beta = \gamma \neq 90°$). For low distortions, that is, upon low deviation of the angles from 90°, the angles between the symmetry planes of austenite and the twinning planes of martensite are not high. e.g., for $\alpha = \beta = \gamma = 89°$) the matrix of orientation relationship between the lattices of austenite and martensite is as follows:

Angles between the lattices of austenite and martensite

Indices of the planes	Orientation relationship		
	(6)	(7)	(8)
$\angle(110)_A(110)_M$	0.32°	0.41°	0.32°
$\angle(1\bar{1}0)_A(1\bar{1}0)_M$	0.26°	0.29°	0.32°
$\angle(101)_A(101)_M$	0.22°	0.09°	0.27°
$\angle(10\bar{1})_A(10\bar{1})_M$	0.70°	0.88°	0.68°
$\angle(011)_A(011)_M$	0.25°	0.36°	0.24°
$\angle(01\bar{1})_A(01\bar{1})_M$	0.52°	0.50°	0.57°

$$\{111\}\langle 10\bar{1}\rangle_A \parallel (111)[10\bar{1}]_M$$

$$\hat{A}_R = \begin{pmatrix} 1 & 0.009 & 0.009 \\ 0.009 & 1 & 0.009 \\ 0.009 & 0.009 & 1 \end{pmatrix} \quad (9)$$

and the angles between the respective planes do not exceed 1°:

$$\angle(110)_A(110)_M = \angle(101)_A(101)_M$$
$$= \angle(011)_A(011)_M = 0.73°;$$
$$\angle(100)_A(100)_M = \angle(010)_A(010)_M$$
$$= \angle(001)_A(001)_M = 0.72°.$$

The rhombohedral lattice can be twinned over the planes (100), (010), (001), (110), (101), and (011). The planes $(1\bar{1}0)$, $(10\bar{1})$, and $(01\bar{1})$ are the symmetry planes of the rhombohedral lattice and the twinning over these planes is impossible.

The formation of crystals of rhombohedral martensite that were twinned over the (100) and (110) planes was observed in experiments with titanium nickelide and its alloys [1, 2, 8].

CONCLUSIONS

The comparison of the calculation results with experimental data [3, 8] demonstrates the possibility of the formation of self-accommodation complexes of martensite crystals with tetragonal, orthorhombic, and rhombohedral lattices upon deviation of parallelism of the symmetry planes of austenite from the twinning planes of martensite by angles of ~1.5°.

The distortion type of martensite transformations is supported by the parallelism of complete systems of twinning planes of martensite with the symmetry planes of austenite (six planes in the case of orthorhombic and rhombohedral martensite and four planes in the case of tetragonal one), which provides the formation of not only twins, but of a self-accommodation complex of martensite crystals.

REFERENCES

1. K. Ootsuka, K. Simidzu, Yu. Sudzuki, et al., *Alloys with Shape Memory Effect* (Moscow, 1990) [in Russian].
2. K. Otsuka and C. M. Wayman, *Shape Memory Materials* (Cambridge Univ., Cambridge, 1998).
3. E. Z. Vintaikin, V. A. Udovenko, D. F. Litvin, et al., Izv. Vyssh. Uchebn. Zaved., No. 5, 104 (1985).
4. A. G. Khundzhua, A. V. Sorokin, and E. V. Chernov, Vestn. Mosk. Un-ta, Ser. Fiz. Astron., No. 5, 86 (1991).
5. A. G. Hundjua, E. A. Brovkina, and A. G. Pticyn, Vestn. Mosk. Un-ta, Ser. Fiz. Astron., No. 6, 25 (2008) [Mosc. Univ. Phys. Bull. **63**, 393 (2008)].
6. M. M. Mel'nikov, A. G. Khundzhua, and E. A. Brovkina, in *Proc. of the 6th Nation. Conf. RSNE* (Moscow, 2007), p. 433.
7. G. Nosova and E. Vintaikin, Scr. Mater. **40**, 347 (1999).
8. *Titanium Nickelide Alloys with Shape Memory, part I: Structure, Phase Transitions, and Properties)*, Ed. by V. G. Pushin (UrO RAN, Yekaterinburg, 2006) [in Russian].