

Conference paper

## X-ray Diffraction Studies of Martensitic Transformations in Situ of the Parameters of a Thin Crystalline Structure in TiNi Under External Loading

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### Abstract

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The paper presents the results of the X-ray diffraction study of martensitic transformations B2-R-B19' in a wide temperature range under the simultaneous action of the applied stress in the alloy based on titanium nickelide. Temperature dependences of the crystal structure parameters in phases B2, R, B19' in samples under the action of the external applied stress have been determined. It has been found that heating of a TiNi-based alloy under loading leads to a rapprochement of atomic volumes of coexisting martensitic and austenitic phases.

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### 1 Introduction

Today, alloys based on titanium nickelide find wide application in various fields of technology and new medical technologies. This is due to unique physical and mechanical properties possessed by such alloys. In alloys used in medicine, the parameters in characteristics are similar to the behavior of biological tissues [1]. In real constructions that exhibit the shape memory effect (SME), the external resistance limits the shape recovery and causes the development of internal stresses in the material. In the marginal situation of a rigidly predeformed material (at a fixed deformation) the strain recovery is completely prevented and internal stresses reach the highest values. These stresses may correspond to equilibrium stresses of martensitic and austenitic phases in the alloy at a given temperature. Martensitic transformation (MT) in the presence of an external stress acts as a

specific shear deformation mechanism, which is based on the motion of interphase boundaries of the section and the cooperative transition of atoms from one phase to another. The external stress favors the formation of some crystallographic variants of martensite (for which the action of external stresses has a maximum value) and prevents the formation of others [1, 2]. Under the action of the applied stress in the temperature interval  $M_H < T < M_d$ , ( $M_d$  is the highest temperature at which a transformation is still taking place under the applied load,  $M_H$  is the temperature of the martensitic transformation at cooling in the absence of the external stress) the area of phase equilibrium shifts towards high temperatures and it is well described by the Klaperton-Clausius equation [1, 3]. Formation of a new phase in contact with the initial phase creates a deformation incompatibility at the phase boundary, acting as a source of internal stresses determining the thermodynamics and the formation kinetics of phases and structures formed during the transformation [2, 4].

The goal of this paper is, using the X-ray diffraction method in situ, to study the changes occurring in a crystalline structure of martensitic and austenitic phases in a wide temperature range under the simultaneous action of the applied stress in TiNi-based alloys.

## 2 Materials and Methods

Alloys based on titanium nickelide with chemical composition TiNi(Mo, Fe) (Mo, Fe vary from 0 to 2.0 at.%) were used in the study [5]. The ingots, obtained as a result of a smelting process were hot rolled, then cut using the electroerosive method to form samples in the shape of thin plates and annealed at 800 °C during 1 hour. Structural studies were carried out on a diffraction meter DRON-2 using  $CuK\alpha$ -radiation with the use of a special temperature console [6] allowing to simultaneously change the temperature in the range of -100 °C to +250 °C and to carry out tensile deformation. X-ray surveys were carried out in the point scanning mode with an exposure time of 100 seconds at each point.

## 3 Results and discussion

The following sequence is observed in the studied TiNi-based alloy: B2-R-B19 '[1]. This is reflected in the temperature curve of the electrical resistance (Fig. 1). At room temperature the alloy is biphasic: TiNi phase with a crystalline structure B2 (type CsCl) and a small amount of the phase  $Ti_2Ni$  (about ~5%). The crystalline

structure of martensite is described differently by different authors. In this paper, we used the conventional structure of martensite phases B19' and R (elementary cell R of martensite is rhombohedral with parameters  $a=0,903$  nm and  $\alpha=89,4^\circ$ , elementary cell B19' of martensite is monoclinic) [1, 2]. Characteristic temperatures of the MT were determined by temperature dependences of electrical resistivity curves and are as follows:  $T_R=12^\circ\text{C}$  (MT  $B2 \Rightarrow R$ );  $M_H= -6 \pm 3^\circ\text{C}$ ;  $M_K= -37 \pm 3^\circ\text{C}$ ;  $A_H= 6^\circ \pm 3^\circ\text{C}$ ;  $A_H= 28 \pm 3^\circ\text{C}$  (MT  $R \Rightarrow B19'$ ).

With a decrease in the temperature, a natural splitting of reflexes of the phase B2 has been detected, which was due to the MT  $B2 \Rightarrow R$ . With a further decrease in the temperature, X-ray diffraction patterns have revealed reflexes of the phase B19', i.e. MT  $R \Rightarrow B19'$  takes place. The temperature dependences of reflex intensities of phases B2, R, and B19' (Fig. 1*b,c,d,e*) reflect the change in the phase composition (Fig. 1*e*). The change in the volume fraction of the phase B19' has been calculated by the ratio of reflex intensities of phases R, and B19'. The phase composition most intensively changes in a temperature range from  $-20$  to  $-100^\circ\text{C}$ . It can be seen that the results of the X-ray diffraction study on the measurement in the region of the MT  $B2 \Rightarrow R \Rightarrow B19'$  do not coincide with data obtained from the curves  $\rho(T)$ .

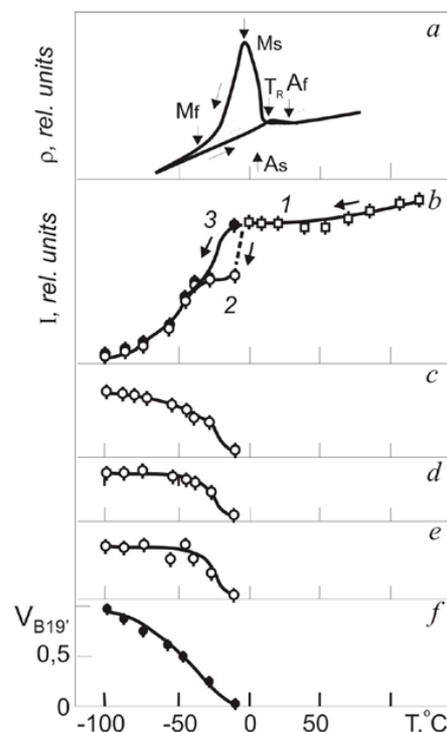


Fig. 1. Temperature dependences of the electrical resistivity (a), of intensities of reflexes of phases B2, R, and B19' (b is curve 1  $(110)_{B2}$ , curve 2  $(330)_R$ , curve 3  $(303)_R$ ; c is  $(111)_{B19'}$ ;  $(020)_{B19'}$ ;  $(111)_{B19'}$ ) and the change on the volume fraction of the phase B19' in the alloy TN-10 at cooling.

Temperature dependences of the parameters of elementary cells of phases B<sub>2</sub>, R, B<sub>19'</sub>, and temperature dependences of atomic volumes of structures B<sub>2</sub> and B<sub>19'</sub> (Fig. 2) have been identified. There is a violation of the linear dependence of the lattice parameter of the phase B<sub>2</sub> in the temperature region prior to the MT. Then, the nonlinear dependence most strongly manifested itself at the temperature dependence of the parameters of the elementary cell of the R-phase in the region of the PT B<sub>2</sub>→R. The temperature dependence of the reflex half-width of the phase B<sub>2</sub> (110)<sub>B<sub>2</sub></sub> shows that the widening of the reflex takes place long before the reflex (110)<sub>B<sub>2</sub></sub> splits into a doublet (330)<sub>R</sub>, (30 $\bar{3}$ )<sub>R</sub>. It can serve as evidence of small distortions in the crystalline structure of the phase B<sub>2</sub>. With further development of the PT B<sub>2</sub>→R, a splitting of the reflex (110)<sub>B<sub>2</sub></sub> into a doublet(330)<sub>R</sub>, (30 $\bar{3}$ )<sub>R</sub> takes place, which is associated with strong distortions in the lattice. The rhombohedral angle significantly differs from 90° (Fig. 2a).

Temperature dependences of atomic volumes of structures B<sub>2</sub>, R, and B<sub>19'</sub> allow to judge on the state of the crystalline lattice in the transition region and to carry out a comparison of the degree of space filling in such different structures. The atomic volume of the martensitic phase B<sub>19'</sub>  $\Omega_{B_{19'}}$  has a higher value than the atomic volume of the R-phase. The value of the atomic volume of the phase B<sub>19'</sub> is very close to values of the atomic volumes of phases B<sub>2</sub> and R. The extrapolated curve from the high-temperature region of the atomic volume in the phase B<sub>2</sub> is higher than the curve of the atomic volume in the phase B<sub>19'</sub> (Fig. 2b).

Thus, the following sequence is observed in the studied alloy in the temperature range from ~ 0 °C to -100 °C: MT B<sub>2</sub> - R - B<sub>19'</sub>. A non-linear nature of the behavior of the above listed parameters is found on temperature dependences of parameters of elementary cells and atomic volumes of phases B<sub>2</sub>, R и B<sub>19'</sub> in the region preceding the transition and in the MT region itself (Fig. 3). It has been found that the atomic volume of the martensitic phase B<sub>19'</sub> is greater than the atomic volume of the R-phase, and in the temperature range corresponding to the beginning of the MT B<sub>2</sub>→B<sub>19'</sub> it coincides with atomic volumes of phases B<sub>2</sub> and R.

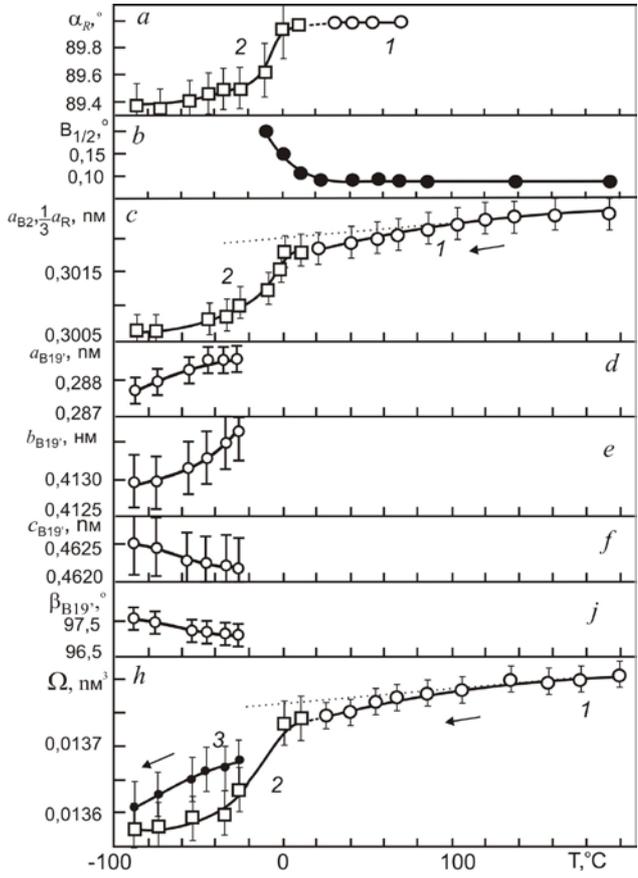


Fig. 2. Temperature dependences of parameters of elementary cells in phases B2 (*curve 1*) R (*curve 2*) (*a*, *c*), half-widths of the line (110)<sub>B2</sub>, of parameters elementary cells in the phase B19' and atomic volumes in phases B2 (*curve 1*), R (*curve 2*), and a B19' (*curve 3*) at cooling of TN-10 alloy

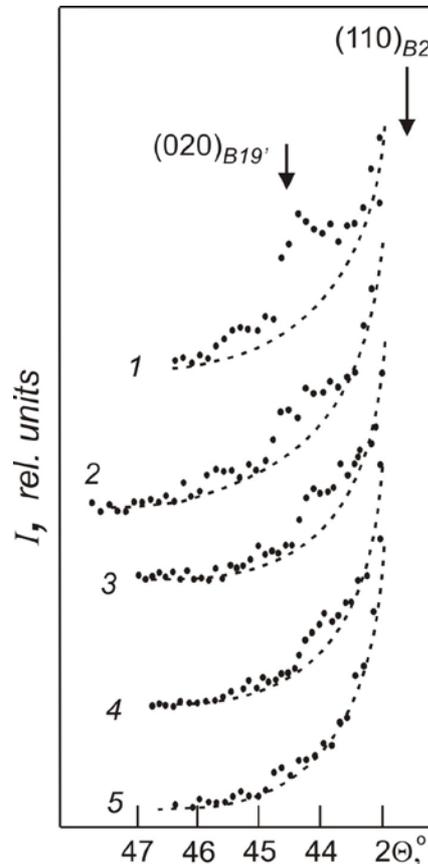


Fig. 3. Areas of X-ray diffraction patterns of the alloy TN-10 predeformed by stretching ( $\epsilon=10\%$ ) and being in the predeformed state at heating: 1 - 120 °C; 2 - 135 °C; 3 - 151 °C; 4 - 167 °C; 5 - 186 °C

Phase transition under the load  $B2 \rightarrow B19'$  takes place during tensile deformation at room temperature. Nearly 90% of the martensitic phase is formed during plastic deformation of the order of 10%. Further cooling of the deformed alloy in the predeformed state (external stress is not removed) leads to a complete MT, i.e. 100% of the martensitic phase with the structure  $B19'$  is formed. When heated, there is a reverse MT  $B19'-B2$ . This martensitic phase  $B19'$  is retained up to temperatures of about 200 °C, significantly exceeding the temperature of the end of the reverse martensitic transformation  $A_k$  in the initial non-deformed alloy (Fig. 3 and Fig. 4). The temperature dependence of the volume fraction of the phase  $B19'$  at the final stage of transformation is similar to the exponential dependence (Fig. 4).

As known, one of the main mechanical characteristics of the material is the yield strength. When the yield strength is reached, the elastic stresses occurring in the material during the deformation relax by means of a plastic shear [1]. Fig. 5 shows a typical temperature dependence of the yield strength for materials experiencing

MT. At a temperature below  $M_H$ , the experimentally determined yield strength is essentially a stress of the martensitic shear, and the actual resistance to plastic shear is determined by an extrapolation curve from high temperatures to low (dashed line in the figure). The region near the minimum on the curve  $\sigma(T)$  corresponds to  $M_H$ , and the region of maximum to the temperature  $M_d$ , at which the curve characterizing the true resistance to plastic deformation and the curve of the temperature dependence of the martensitic shear stress coincide. The difference  $\sigma_{\max} - \sigma_{\min}$  characterizes the susceptibility of the material to plastic deformation, and the larger it is, the less likely the relaxation of elastic stresses accumulated at the MT through plastic shear [1].

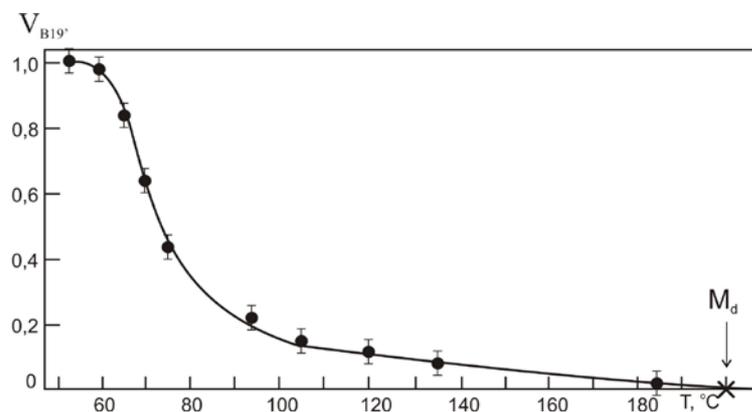


Fig. 4. The temperature dependence of the change in the volume fraction of the phase B19' at heating of the alloy TN-10, predeformed by stretching up to the deformation of 10% and being in the predeformed state

In the temperature range below  $M_d$ , the equilibrium stress states of the martensitic and the high temperature phase coincide at a certain temperature and correspond to the martensitic shear stress determined, mainly, by the value of martensitic and elastic deformations. However, the closer the material deformation to  $M_d$ , the more intense the plastic deformation processes. An insignificant deformation of the alloy near  $M_d$  leads to the fact that the stress relaxation is carried out not only with the formation of the martensitic phase, but with the plastic shear as well. At a temperature  $M_d$ , the martensitic shear stress coincides with the macroscopic yield strength, and at a deformation higher than  $M_d$  the deformation is carried out only with a plastic shear.

These results confirm the findings of the coincidence of the temperature  $M_d$  and the temperature of a complete disappearance of martensitic crystals during

heating of the preliminary deformed alloy. This experiment is one of the methods for determining the temperature  $M_d$  [7].

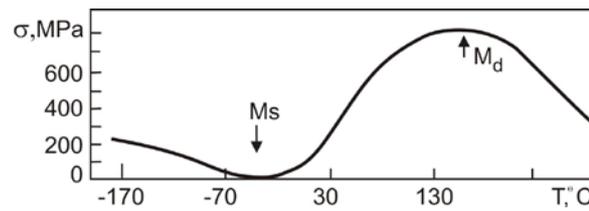


Fig. 5. The temperature dependence of martensitic shear stresses of the alloy TN-10

More information on the behavior of temperature dependences of atomic volumes of structures B2 and B19' under the load can be found in studies on heating the alloy in the predeformed state after the MT B2-V19' (Fig. 6). Temperature dependences of atomic volumes of structures B2 and B19' (Fig. 6) allow to judge on the state of the crystalline lattice in the transition region and to characterize the degree of space filling in such structures. The atomic volume of the martensitic phase B19' is greater than the atomic volume of the austenitic phase B2. A greater value of the atomic volume of the phase B19' indicates the fact that the structure of the martensitic phase is more "loos" than the austenitic, or indicates the growth of the anisotropy of interatomic interactions in the B2 phase. The difference of atomic volumes  $\Omega_{B19'} - \Omega_{B2}$  does not change abruptly in a narrow temperature range, but is rather stretched out in the extended temperature range. At the end of the reverse MT there is a convergence of values of atomic volumes. In different temperature intervals, there are various types of peculiarities on temperature curves of atomic volumes. The main peculiarity on the curve  $\Omega_{B2}$  appears in the temperature region where the main change in the phase composition takes place. According to the theories developed in [8], this phenomenon may indicate an interphase transition in the B2 structure, which occurs simultaneously with the main transition B2-B19'.

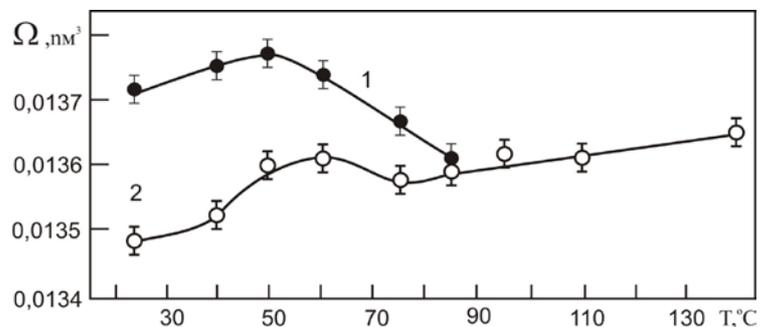


Fig. 6. Temperature dependences of atomic volumes in phases B2 (curve 1) and B19' (curve 2) at heating

## 4 Summary

In the end, the following conclusions can be made.

The experimental X-ray diffraction studies show that heating of the predeformed alloy based on titanium nickelide leads to a complete disappearance of the martensitic phase at temperatures close to  $M_d$ .

With the use of X-ray diffraction in situ methods it has been found that in the temperature region of the end of the reverse martensitic transformation there is a rapprochement of atomic volumes of coexisting martensitic and austenitic phases. A decrease in the value of the lattice deformation with the disappearance of martensitic crystals, and the mutual "fitting" of the initial and the target structures, are observed. At this point, the phase transition of the first kind begins to assume the features of the second-order transition. These data are consistent with the general idea about the features of structural changes in martensitic transformations [9].

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