

Conference paper

Dilatation Changes in the Phase Transition Region in TiNi-based Alloys

A.A. Klopotov^{1,2*}, A.I. Potekaev¹, Yu.A. Kakushkin³, E.S Marchenko^{1,2}, G.A. Baigonakova^{1,2}, V.E. Gunther^{1,2}

¹Tomsk State University, Tomsk, Russia

²Research Institute of Medical Materials and Implants with Shape Memory, Tomsk, Russia

³Tomsk State University of Architecture and Building, Tomsk, Russia

*Corresponding author:
A.A. Klopotov, email:
Klopotovaa@tsuab.ru

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Abstract

The paper presents the data obtained as a result of the X-ray diffraction in situ study of the parameter structure of a thin crystalline structure in the of phase transition region in alloys based on titanium nickelide depending on the deformation influence. It has been shown that dilatation changes during the transition B2-R(ω) depend on the arrangement of atoms in the doping element.

1 Introduction

TiNi-based alloys have unusual properties associated with the manifestation of shape memory and superelasticity effects. These properties have found an effective application primarily in medicine and robotics [1, 2]. Martensitic transformation is accompanied by structural changes that manifest themselves in the change of atomic volumes. Therefore, the use of TiNi-based alloys in various constructions requires the knowledge on structural changes that occur in alloys during the application of an external load. When TiNi-based alloys with SME are applied in practice, this process is carried out partially or in a completely predeformed state, and is associated with the overcoming by the material of the external resistance during the shape recovery after a preliminary deformation. 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 shape 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. Therefore, the information on dilatation changes in the MP region is needed, as these changes play an important role in the manifestation of SME.

It seemed appropriate to conduct a direct experimental study on the influence of the external stress on a fine crystalline structure in the region of phase transitions (PT) in TiNi-based alloys. In this regard, the changes of the structure in the PT region have been studied using the method of X-ray diffraction in situ analysis. The temperature dependences of elementary cell parameters of austenitic and martensitic phases in the PT region in the alloy TiNi(Mo), widely used in medicine as implants, have been obtained [1].

2 Experimental

X-ray diffraction studies were carried out on a diffraction meter DRON-2 in a mono-hromatized $\text{CuK}\alpha$ radiation using a specially designed console. The console design allowed to simultaneously carry out the expansion of samples in different temperature ranges.

Ingots of the alloy $\text{Ti}_{50}\text{Ni}_{48}\text{Rh}_2$, $\text{Ti}_{50}\text{Ni}_{47}\text{Fe}_3$, and TiNi(Mo) with a uniform chemical and phase composition were produced by double electric-arc melting in a cooled crucible of a vacuum skull furnace. Nickel NO or N₁, as well as an iodide titanium or a pure titanium sponge, were used as charging materials. Ingot forging was performed using a hammer under pressure in the temperature range of 500-900 °C. Then, the ingots were rolled with a decrease in the thickness of plates by 10% in one pass. In conclusion, the annealing at 800 °C for 1 hour was carried out.

The composition of the alloy TiNi(Mo) corresponds to the formula $\text{Ti}_{51,2-l}\text{Ni}_{48,8-y-z-k}\text{Mo}_y\text{Fe}_z\text{Cu}_k\text{Al}_l$, where y, z, k, l may have the following values: $y=0; 0,1; 0,2; \dots; 2,0$ at%; $z=0; 0,5; 0,6; \dots; 1,5$ at%; $k=0; 2,0; 6,0; \dots; 20$ at%; $l=0; 1,0; 2,0; \dots; 10$ at%.

3 Results and discussion

The temperature dependences of atomic volumes have been examined in TiNi-based alloys, the non-linear nature of these dependences and the jumps of atomic volumes in the phase transition region have been established (Fig. 1-3).

Phase transitions B2-R(ω)-B19' that have a thermoelastic martensitic transformation nature and occur in different temperature ranges are observed in all the investigated alloys. It draws attention to the fact that the nature changes

depending on atomic volumes in the PT region in deformed alloys relative to the original – non-deformed. All this indicates a significant role of the deformation effect on structural characteristics of alloys in the PT region.

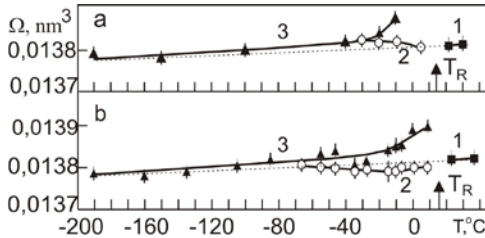


Fig. 1. Temperature dependences of atomic volumes in phases B2 (1), R(ω) (2), and B19' (3) in the initial state (a: $\epsilon=0\%$) in deformed (b: $\epsilon=6,6\%$) samples of the alloy $Ti_{50}Ni_{48}Rh_2$

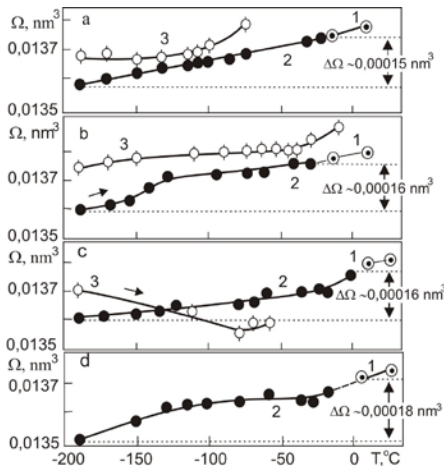


Fig. 2. Temperature dependences of atomic volumes in phases B2 (τ), R(ω) (2), and B19' (3) in the initial state (a: $\epsilon=0\%$) in deformed (b: $\epsilon=4\%$; c: $\epsilon=9,4\%$; d: $\epsilon=9,4\%$) samples of the alloy $Ti_{50}Ni_{47}Fe_3$

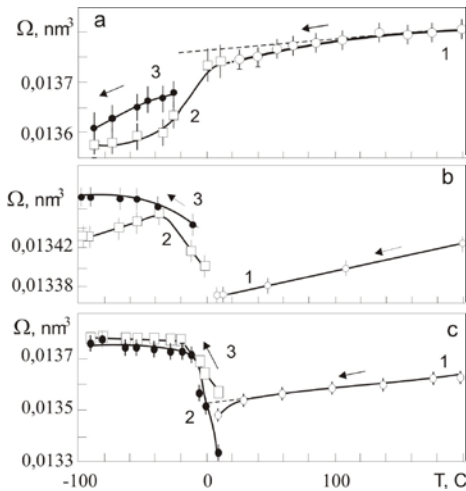


Fig. 3. Temperature dependences of atomic volumes in phases B2 (1), R(ω) (2), and

B19' (3) in the initial state (a: $\epsilon=0\%$) in deformed and predeformed (b: $\epsilon=3,7\%$; c: $\epsilon=10\%$) samples of the alloy TiNi(Mo)

Phase transitions B2-R(ω)-B19' that have a thermoelastic martensitic transformation nature and occur in different temperature ranges are observed in all the investigated alloys. It draws attention to the fact that the nature changes depending on atomic volumes in the PT region in deformed alloys relative to the original - non-deformed. All this indicates a significant role of the deformation effect on structural characteristics of alloys in the PT region.

The change in the structure and phase composition associated with the PT B2 \leftrightarrow R(ω) \leftrightarrow B19' is observed in the alloy TiNi(Mo) in the temperature range from $\sim 0^\circ\text{C}$ to -100°C ($T_R=0^\circ\text{C}$). Features of the non-linear nature of structural parameters manifest themselves on temperature curves of the parameters of elementary cells and atomic volumes of phases B2, R(ω) and B19' in the pre-transition region and in the PT region itself. The atomic volumes of phases B2, R(ω) and B19' are quite close in the temperature range corresponding to the beginning of the PT B2 \rightarrow R(ω) and R(ω) \rightarrow B19'. This is reflected in non-deformed alloys on temperature dependences of atomic volumes in phases B2, R(ω) and B19' (Fig. 3), which practically coincide at the initial stage of transition B2 \rightarrow R(ω) and the stage of martensite crystal formation B19', and then the atomic volumes of phases R(ω) and B19' have values smaller than volumes of the original phase B2. A reverse situation is observed in deformed alloys. The applied deformation leads to a significant change in the nature of temperature dependences of the elementary cell parameters in the alloy with respect to the initial state. The atomic volume of the phase B19', which occurred as a result of the deformation influence, is higher than the atomic volume of the phase B2. Upon cooling, there is a significant decrease in the atomic volume of the phase B19', which is almost the same as the atomic volume of the R(ω)-phase in the low-temperature region. Transition from the phase B2 to the R(ω)-phase occurs virtually without a jump in the atomic volume. Such behavior of atomic volumes in the restructuring of crystalline structures in the PT region reflects slight dilatation changes, indicating the energy proximity of austenitic and martensitic phases in the transition region. The difference between phases increases at a distance from T_R (T_R is the temperature at the beginning of the PT B2 \rightarrow R(ω)).

Crystallographic model of the transition B2-R(ω)

In order to find out what has caused this unusual behavior of temperature dependences of atomic volumes in the PT region $B2-R(\omega)$, a simple crystallographic modeling of the restructuring of the crystalline lattice in the transition $B2-R(\omega)$ has been carried out using the concept of atoms as «rigid» spheres with a constant diameter D . An assessment of the influence of the arrangement of atoms in doping elements in the nodes of the crystalline lattice in alloys based on titanium nickelide on the parameters of the elementary cell and, as a result, on the change in atomic volumes during the restructuring of the crystalline lattice at the PT $B2-R(\omega)$ has been carried out.

The basis of our study was the comparison of the transition $A2-\omega$ as a transition BCC – HCP [3], and the presence of displacements that may transform one lattice into another. In this representation, the BCC-lattice is very similar in shape to the lattice of the ω -phase, and the difference is only in the position of internal atoms (Fig. 4). For the PT $A2 \leftrightarrow \omega$, the only necessary condition is the displacement of atoms inside the cell along the axis $\langle 111 \rangle_{BCC}$ at a distance of a fraction of the interatomic distance (Fig. 5). These displacements can be represented as a shift of atomic rows $[111]_{BCC}$ towards each other, and such cooperative atomic displacements have a feature that is manifested in the fact that a shift in this displacement is not accumulated. It should be noted that the proposed in [5] crystallographic transition mechanism $A2 \leftrightarrow \omega$ has found a continuation in the work [5], which, based on electron microscopy data, suggested a transition mechanism that uses longitudinal waves of atomic displacements $2/3 \langle 111 \rangle$, the correlation of which determines the transition from the BCC phase into the $R(\omega)$ -phase. However, there are small dilatation changes that occur in the crystalline structure. This is caused by the fact that such atom shifts result in an increase in the density of packing, due to a more compact arrangement of atoms in the space.

The structure of the $R(\omega)$ -phase, obtained as a result of the PT $B2 \leftrightarrow R(\omega)$ in TiNi-based alloys, differs from the structure of the ω -phase in the presence of a long-range order in the mutual arrangement of atoms of various components [3]. The presence of a long-range order in the R-phase leads to doubling of planes along cubic axes, as compared to the ω -phase. Therefore, in literature the R-phase in TiNi-based alloys is often represented as the $R(\omega)$ -phase.

Fig. 6 shows the calculation results of the compression value Δ in the restructuring of the crystalline lattice $B2-R(\omega)$ depending on the grade of doping elements and

on the arrangement of atoms in the doping element in the crystalline lattice. Line 1 (insertion 1 in Fig. 6) corresponds to the compression value Δ at a hypothetical B₂-R(ω) in binary Ti-based alloys. Lines 2-6 (insertions 2-6 in Fig. 6) have been obtained by calculation of the compression Δ at real and hypothetical PT B₂↔R(ω) in ternary alloys TiNi(Me). Insertions 2 – 6 in Fig. 6 show different arrangements of atoms in the doping element in titanium nickelide. It can be seen that when atoms of the doping element are arranged as shown in insertions 2 and 3 (Fig. 6), the compression value Δ increases with an increase in the radius of the doping element. In the case when atoms of the doping element occupy positions in the crystalline lattice as shown in insertions 4 – 6 (Fig. 6), the compression value Δ decreases with an increase in the radius of the doping element. The obtained dependences indicate that dilatation changes at the PT B₂↔R(ω) are highly dependent not only on the size of doping elements, but also on the atom arrangement in the nodes of the crystalline lattice. A large compression value Δ should lead to large dilatation changes at the B₂-R(ω) and, consequently, to high stresses in the crystalline lattice. In this case, the energy gain related to the restructuring of the crystalline lattice decreases during the transition due to elastic distortions that occur at the interface of the old and the new phase. This may contribute to suppression of the restructuring “channel” of the crystalline lattice toward B₂↔R(ω). The smallest “start” dilatation changes at the PT B₂↔R(ω) occur in cases when atoms of the doping element occupy the position as shown in the insertion 2 (Fig. 6), but there is an intensive increase in the compression value Δ with a decrease in the ratio between the atomic size of the doping element and Ti. On the other hand, the arrangement of atoms in the doping element as shown in the insertion 5 (Fig. 6) leads to an intensive decrease of Δ with a decrease in the ratio between the atomic size of the doping element and Ti.

On the basis of pure crystallographic considerations, without regard to the interatomic interaction between similar and unsimilar atoms, the following assumption can be made. The most preferred arrangement of atoms in the doping element is as shown in insertions 2 or 6 (Fig. 6), which will result in minimum distortions in the crystalline structure at the transition B₂↔R(ω). In fact, it can be much more difficult when taking into account all the other contributions.

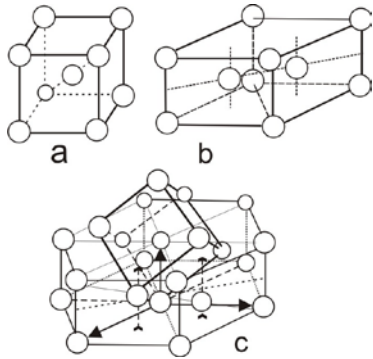


Fig. 4. Elementary cells of the structure $A_2(a)$, ω -phase (b), and its relation to the BCC-lattice (c)

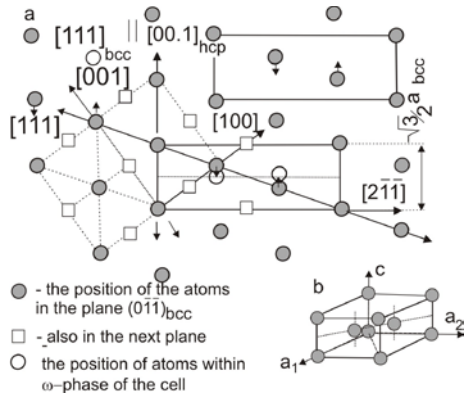


Fig. 5. The atom arrangement in the A_2 phase in the plane $(110)_{BCC}$ and the ω -phase in the plane $(01\bar{1})_{\omega}$. The arrows indicate displacements of atoms necessary for the rearrangement $A_{\kappa} \rightarrow \omega$.

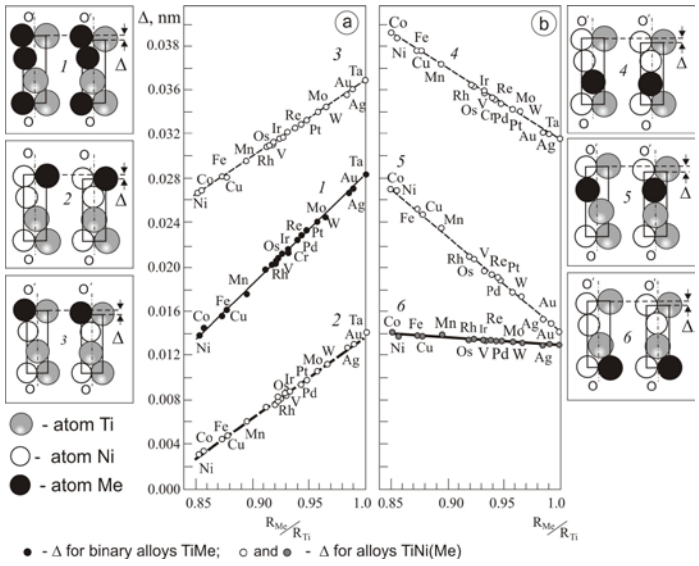


Fig. 6. The compression value Δ in the elementary cell of the phase $R(\omega)$ in the direction of $[211]_{B_2}$ after the transition $B_2 - R(\omega)$ depending on the arrangement of atoms in the doping element (insertions 1 - 6, left fragment of the insertion is before)

the rearrangement, right is after the rearrangement) in the elementary cell and on the ratio of atomic radii of titanium and doping elements

In alloys $Ti_{50}Ni_{48}Rh_2$, $Ti_{50}Ni_{47}Fe_3$, and $TiNi(Mo)$ the concentration of doping elements is not high. But doping with a third element has a significant influence on the electron structure [1], which is manifested in the change of the interatomic interaction forces and in the change of the atomic size. According to data presented in Fig. 6, different value of the dimensions of doping atoms relative to the dimensions of atoms of main alloy-forming elements leads to reduction of dilatation changes at the PT $B2 \rightarrow R(\omega)$. This phenomenon is consistent with the features on temperature dependences of atomic volumes in alloys based on titanium nickelide in the transition region (Fig. 1-3).

On the other hand, doping of NiTi with a third component leads to significant changes in the parameters of elementary cells of martensitic and austenitic phases [6]. Therefore, in ternary alloys based on titanium nickelide the manifestation of dilatation effects may have a significant influence on martensitic transformations due to the redistribution of the third component.

The additional studies on the size of Ti and Ni atoms using the space-filling analysis in the superstructure B2 in alloys based on Ti and Ni atoms has allowed revealing that the space-filling coefficient increases with an increase in the superstructure compression value (Fig. 7). Here, the space-filling coefficient ψ was determined by Laves-Parte [7], and the superstructure compression by the value of the atomic volume deviation from Zen law [3]. The revealed correlation suggests that the size of Ni and Ti atoms depends on the alloy with a superstructure B2 in which they are present.

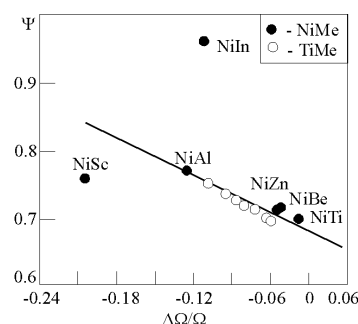


Fig. 7. The dependence of the space-filling coefficient ψ on the relative value of the superstructure compression in the superstructure B2 in alloys based on Ti and Ni atoms

The deformation influence in the alloy TiNi(Mo) leads to formation of various kinds of defects (planar, linear, and point) that have a significant impact on the PT $B2 \leftrightarrow R(\omega) \leftrightarrow B19'$. On the other hand, phase transitions result in the interaction of elastic internal stresses, caused by defects formed during the deformation influence, with stress fields that occurred during the PT. Own internal fields of elastic stresses during the PT occur due to the appearance of interface boundaries. The occurrence is caused by the discrepancy of crystalline lattices of the initial and the new phase. This, in turn, is caused by dilatation changes during the transition. Such interaction of deformation defects and interphase boundaries is well shown experimentally on the change in the type of temperature dependences of atomic volumes in the PT region, as compared to similar dependences obtained for non-deformed alloys (Fig. 1–3). The accumulation of defects, for example in the alloy TiNi(Mo), leads to the fact that the jump of the atomic volume in the $R(\omega)$ -phase $\Delta\Omega = \Omega^{B2} - \Omega^{R(\omega)}$ changes its sign during the transition. In the non-deformed alloy, the jump of the atomic volume is positive ($\Delta\Omega > 0$). In the alloy subjected to the deformation influence, $\Delta\Omega < 0$ (Fig. 3). In the alloy $Ti_{50}Ni_{47}Fe_3$, such a significant influence of the deformation effect on the value and the sign of the jump $\Delta\Omega = \Omega^{B2} - \Omega^{R(\omega)}$ is not observed. However, there is a change in the jump sign of the atomic volume in the PT region between $B2$ and $B19'$ phases.

4 Summary

On the basis of the analysis of temperature dependences of the elementary cell parameters in martensitic and austenitic phases ($B2$, $R(\omega)$ and $B19'$) in alloys $Ti_{50}Ni_{48}Rh_2$, $Ti_{50}Ni_{47}Fe_3$, and TiNi(Mo) a number of laws has been revealed. The obtained results confirm the assumption that deformation effects in alloys based on titanium nickelide result in the redistribution of atoms along the nodes of the crystalline lattice being in the weakly-stable state in the PT region [3,8,9], and in the increase in the contribution of deformation defects on the value of atom displacements at the PT $B2 \leftrightarrow R(\omega)$ [3].

1. A significant effect of the preliminary deformation influence on the change in the atomic volume in martensitic and austenitic phases in the phase transition region in alloys $Ti_{50}Ni_{48}Rh_2$ and $Ti_{50}Ni_{47}Fe_3$ has been established.
2. Minimum "jumps" of atomic volumes in the phase transition region $B2 \leftrightarrow R(\omega) \leftrightarrow B19'$ in the non-deformed alloy TiNi(Mo) have been detected.

Meanwhile, the temperature dependences of atomic volumes undergo a significant evolution under the action of external applied stresses.

3. The evaluation of dilatation distortions during the restructuring of the crystalline lattice during the phase transition $B_2 \leftrightarrow R(\omega)$ in TiNi-based alloys has been carried out on the basis of a simple crystallogometric modeling in the framework of representing the atoms in the form of "rigid" spheres with a constant diameter D . It has been shown that dilatation changes during the transition $B_2 \leftrightarrow R(\omega)$ depend both, on the atomic size of the third component and their position in the nodes of the crystalline lattice in the initial phase B_2 .
4. Different variants of the arrangement of atoms in doping elements in the nodes of the crystalline lattice have been examined. The variants which under the proposed model would provide minimal distortions of the crystalline lattice during the transition, and weakly depend on the ratio between the radii of atoms of doping elements and the main alloy-forming atom Ti, have been found.

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