

Orthorhombic Martensite and the ω Phase in Quenched and Deformed Titanium Alloys with 20–24 at % Nb

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Abstract—X-ray diffraction is used to study phase transformations in quenched and cold-worked titanium alloys with 20–24 at % Nb in a temperature range of 80–373 K and to determine the volume fraction of the orthorhombic martensite and its lattice parameters. As the temperature decreases, the martensite lattice parameter b is found to increase reversibly. This increase leads to a change in the ratio of the orthorhombic lattice parameters, and this change agrees with the tendency of bcc \rightarrow hcp transition that proceeds as the temperature decreases. In the same temperature range, the fine structure of the retained bcc phase changes reversibly, and these changes are related to the formation of the athermal ω phase during cooling.

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INTRODUCTION

Ti–Nb alloys have recently attracted attention as a possible substitution for TiNi-based shape memory alloys in medicine, since the latter alloys contain nickel, which is harmful to the human body and has allergenic and carcinogenic properties. The shape memory effect in Ti–Nb alloys is related to the formation of the orthorhombic martensite [1]. These alloys exhibit anomalies in the temperature dependence of the linear thermal expansion coefficient (LTEC) that are also related to the martensitic transformation [2, 3].

The orthorhombic martensite (α'' phase) forms in quenched Ti–Nb alloys in the concentration range 7–23 at % Nb [4] or in deformed Ti–Nb alloys with a higher niobium content, in which a high-temperature bcc phase is fixed upon quenching [4]. The structure of the orthorhombic martensite can be represented as an intermediate structure between the titanium-based hcp α phase and the niobium-based bcc β phase. The orientation relationships for the α'' phase formed from the bcc matrix are as follows: $[100]\alpha''$ is parallel to $\langle 100 \rangle\beta$ to an accuracy of 2° , $[010]\alpha'' \parallel \langle 110 \rangle\beta$, and $[001]\alpha'' \parallel \langle 110 \rangle\beta$. The transformation from the bcc into the α'' lattice requires small compression along the a axis and tension along the b axis of the α'' phase (the lattice parameters depend on the alloy composition), as well as alternating displacements of atomic planes normal to the c axis, so that, for a plane fixed at level $z = 0$, the plane at level $z = c/2$ moves y along the b axis. In the limiting case, where $y = 0.17b$ and $b = a\sqrt{3}$, the orthorhombic lattice transforms into the hcp-phase lattice and $y = 0$ and $b = a\sqrt{2}$ correspond to the bcc lattice. As the niobium concentration changes, the b/a ratio of the

α'' -phase lattice and y change in a certain narrow range located between these limiting values [4].

Moreover, a metastable “athermal” ω phase can form in quenched titanium alloys with transition metals approximately in the same electron-concentration range. It has a rhombohedral structure and the following orientation relationships with the bcc matrix [4]: $(0001)\omega \parallel (111)\beta$ and $[1120]\omega \parallel [110]\beta$. In contrast to martensitic transformations, the bcc phase– ω transition proceeds via atomic recombination at short distances (within one unit cell) without a macroscopic shift. The structure of the ω phase can be represented as the bcc lattice distorted by a longitudinal atomic-displacement wave with a wave vector parallel to $[111]\beta$ and a wavelength equal to three interplanar spacings along this direction. As the alloying-element concentration increases, the reflections of the ω phase in X-ray diffraction patterns broaden gradually, weaken, and shift from their positions. This behavior corresponds to a structure that can be described as a phase with the bcc lattice containing coherent ω configurations that form a certain short-range order.

Unlike the equilibrium α phase and the metastable thermal ω phase (which have related structures), both the α'' and athermal ω phases form in a diffusionless manner.

In this work, we use X-ray diffraction to study structural transitions with the participation of the α'' and ω phases in quenched and deformed titanium alloys with 20–24 at % Nb (or 32–38 wt % Nb). Prominence is given to two alloys; they contain 20 at % Nb (the temperature of the onset of the martensite transformation M_s is above room temperature) and 24 at % Nb (martensite is virtually absent after quenching). We estimate

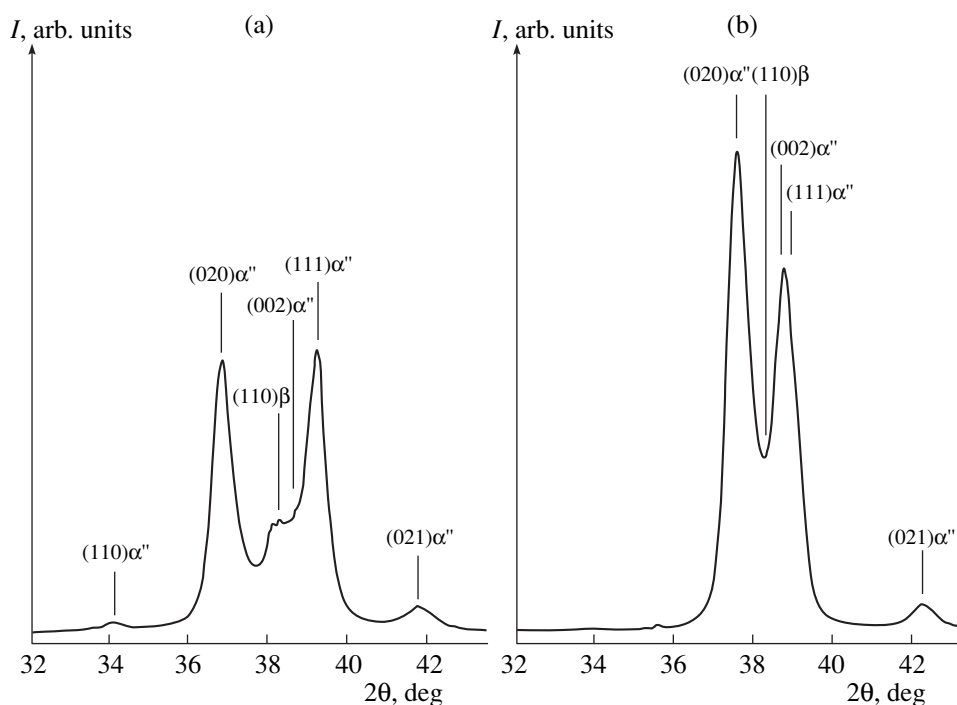


Fig. 1. X-ray diffraction patterns of the deformed (a) Ti-20 at % Nb and (b) Ti-24 at % Nb alloys at room temperature (patterns were taken in reflection geometry from the planes normal to the rolling direction).

the changes of the lattice parameters and the volume fraction of the α'' martensite in the temperature range 83–373 K.

EXPERIMENTAL

Titanium-alloy ingots were prepared by double melting in an arc vacuum furnace from the following starting materials: MBSH-0 niobium and TG-100 titanium sponge. The ingots were deformed via free forging in air in a temperature range of 1100–1000°C. To protect the workpiece surface from oxidation, it was covered with boron silicate enamel; as a result, we decreased the total oxygen absorption during heating for forging by a factor of 150 and the gas content by a factor of 30. The rest of the enamel on the surface and oxidized and gas-saturated layers were removed mechanically. After hot deformation, the alloys were vacuum-annealed at 900°C, water-quenched, and subjected to cold rolling at a 40% reduction. X-ray diffraction studies were mainly performed on samples of the Ti-20 at % Nb and Ti-24 at % Nb alloys in the cold-rolled state and in the state after repeated quenching from 900°C (after cold rolling). The phase composition and lattice parameters were determined on an X-ray diffractometer using monochromatized $\text{CuK}\alpha$ or $\text{CrK}\alpha$ radiation. The temperature coefficient of the change of the i -phase (α'' - or β -phase) lattice parameter was determined from the formula

$$k_{a_i} = (\Delta a_i / a_i) / \Delta T,$$

where Δa_i is the difference in the lattice parameter a at measurement temperatures $T_1 = 293$ K and $T_2 = 83$ K and $\Delta T = T_1 - T_2$. The volume fractions of the phases were estimated from the integrated-intensity ratio of the (200) reflection of the β phase to the related (200) and (022) reflections of the α'' phase.

EXPERIMENTAL RESULTS

Phase Composition and Texture at Room Temperature

The quenched Ti-20 at % Nb alloy consists of the orthorhombic α'' martensite and insignificant amounts of the β and ω phases. The main phase constituent in the Ti-24 at % Nb alloy is the β phase; the volume fraction of the α'' phase is about 5%; and the reflections of the ω phase are weak and diffuse.

After cold rolling at a 40% reduction, the main phase in both alloys is the orthorhombic martensite (Fig. 1). The noticeable difference in the X-ray diffraction patterns of these two alloys is related to the dependence of the ratio of the orthorhombic-martensite lattice parameters on the composition and to the differences between the martensite textures and volume fractions.

The texture of the α'' phase in the cold-rolled samples is different for the alloys of the two compositions, although it is characterized by a preferred [010] orientation along the rolling direction in both cases. This is indicated by the high intensity of the (020) reflection from the planes normal to the rolling direction as com-

Table 1. Effects of the Ti–Nb alloy composition, treatment conditions, and T_{meas} on the lattice parameters of the α'' and β phases and coefficient k

[Nb], at %	Treatment	T_{meas} , K	Lattice parameter, nm				k (10^{-5} K^{-1}) of the lattice parameter		
			a_{β}	$a_{\alpha''}$	$b_{\alpha''}$	$c_{\alpha''}$	a_{β}	$a_{\alpha''}$	$b_{\alpha''}$
20	Quenching	293	0.328	0.314	0.486	0.464	1.0	3.7	–2.6
		103	0.327	0.311	0.488	0.463			
20	Deformation	293	–	0.312	0.485	0.464	–	3.5	–1.9
		80	–	0.310	0.487	0.463			
24	Deformation	293	0.328	0.319	0.478	0.463	1.0	3.9	–3.6
		123	0.327	0.317	0.463	0.463			

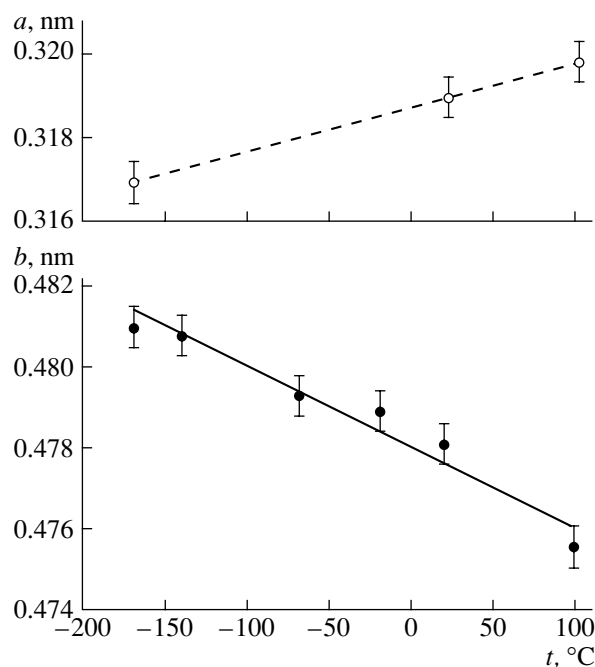
pared to the reflection from the planes parallel to the rolling plane. The comparatively high intensity of the $(200)\alpha''$ line in the X-ray diffraction pattern of the Ti–24 at % Nb alloy taken in symmetric reflection geometry from the planes parallel to the rolling plane and the absence of reflections from the planes whose normals make a small angle with the $[010]$ direction suggest that the main texture component in this case is $(100)[010]$. The X-ray diffraction pattern of the Ti–20 at % Nb alloy (see, e.g., Fig. 1) contains all the lines of the α'' phase that are present in this angular range; that is, the texture is more scattered. Although we did not analyze texture formation within the framework of this study, it should be taken into account to interpret the results obtained.

Temperature Dependence of the Lattice Parameters

Table 1 gives the lattice parameters of the α'' and β phases in the alloys under study at room temperature. These results agree with the data in [4–6]. The martensite lattice parameters in the quenched and deformed alloys of the same composition are the same within the limits of measurement error.

The lattice parameters of the deformed samples containing the orthorhombic phase cannot be determined with a high accuracy, since the diffraction lines are broadened and the groups of closely spaced lines at high scattering angles cannot be resolved. We had to calculate the lattice parameters from the lines located in the angular range $50\text{--}70^\circ$, which cannot give accuracy better than 0.001 nm. Nevertheless, the relative values of the lattice parameters can be determined with a higher accuracy. Since the adjustment of the device is the same within one measurement series, the main contribution to the random error is induced by inaccurate arrangement of a sample with respect to the primary beam and the goniometer axis. We estimated the random error when measuring the lattice parameters in a sample that was repeatedly placed in the initial position according to a standard procedure. The scatter of the interplanar spacings in the angular range $50\text{--}70^\circ$ did not exceed 0.0002 nm, which corresponds to a random error of about 0.0004 for the lattice parameter.

In the temperature range from room temperature to the liquid-nitrogen temperature, all samples exhibit reversible changes in the lattice parameters of the orthorhombic martensite: as the temperature decreases, the parameters a and c decrease and the parameter b increases (Table 1, Fig. 2). This effect is weak, and its reliable detection requires special measures to increase the accuracy of the diffraction-line position measurement. To this end, we measured the interplanar spacings in the quenched Ti–20 at % Nb alloy and the deformed Ti–24 at % Nb alloy using $\text{CrK}\alpha$ radiation to increase the scattering angle. The Ti–20 at % Nb alloy sample has no pronounced texture, and the lines that shift toward opposite directions with decreasing temperature can be detected in a narrow X-ray diffraction pattern range. These shifts are reliably reproduced when the experiment is repeated; however, the shift measurement

**Fig. 2.** Variation of the lattice parameters of Ti–Nb alloys with the measurement temperature.

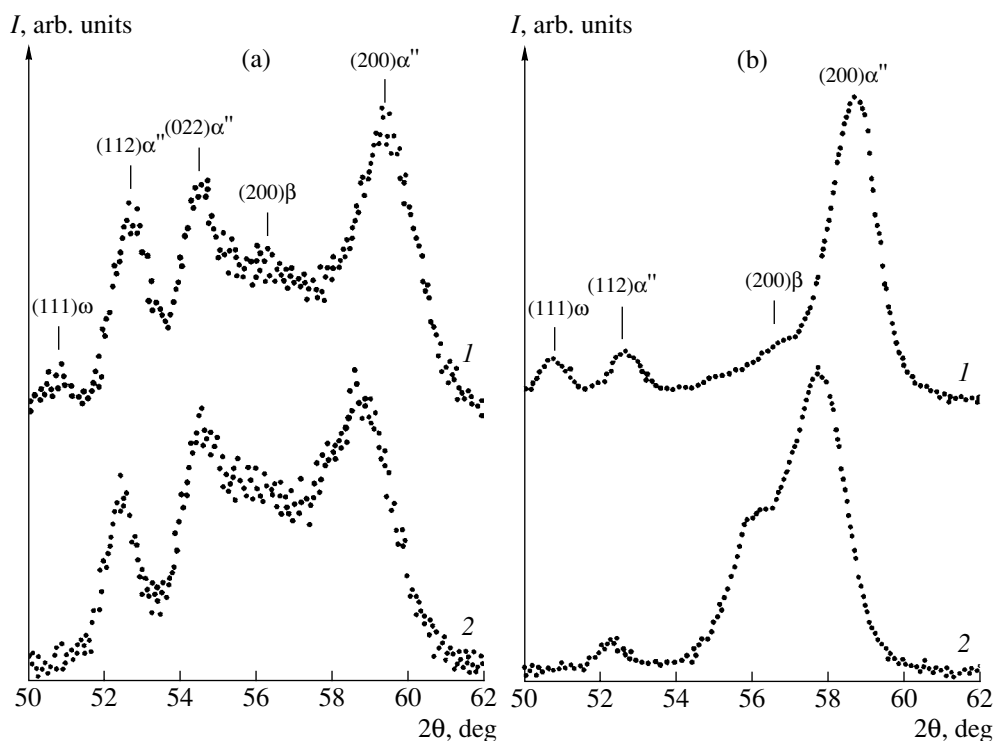


Fig. 3. X-ray diffraction patterns of the deformed titanium alloys with (a) 20 and (b) 22.5 at % Nb. Patterns were taken in reflection geometry from the planes parallel to the rolling plane at temperatures of (1) 83 and (2) 293 K.

accuracy is insufficient to establish the presence or absence of a small hysteresis upon cooling and subsequent heating.

For the deformed Ti–24 at % Nb alloy, we determined the temperature dependence of the parameter b of the α'' phase using a sample whose surface was cut normal to the rolling direction. In this case, we were able to determine the position of the $(040)\alpha''$ line, which has a small structure factor (for $\text{CuK}\alpha$ radiation), due to a pronounced texture; as a result, we calculated the parameter b with a high accuracy.

Thus, the temperature coefficients of the lattice parameters of the orthorhombic martensite are positive for the parameters a and c (Table 1), the value of $k_{a_{\alpha''}}$ being higher than $k_{c_{\alpha''}}$. The temperature coefficient of the parameter a of the α'' phase is higher than that of the bcc β phase, which is clearly visible from the variation of their difference with the temperature in the Ti–24 at % Nb alloy (see Table 1). The temperature coefficient of the parameter b of the α'' phase is negative and its absolute value is lower than that of $k_{a_{\alpha''}}$. The anomalous change in the parameter b in the deformed Ti–20 at % Nb alloy sample is slightly lower than that in the quenched alloy; however, the difference in the values of $k_{b_{\alpha''}}$ is close to the determination error. As a result of these changes in the lattice parameters, the changes in the martensite volume have a normal temperature

dependence and are close to the value characteristic of the bcc lattice (about $2 \times 10^{-5} \text{ K}^{-1}$).

Volume Fraction of Martensite

During cooling, the volume fraction of the α'' phase in the quenched alloys does not change within the limits of measurement error.

In the deformed alloys, the intensity ratios of the diffraction lines of the α'' and β phases change significantly (Figs. 3, 4), which can indicate a change in their volume fractions. To quantitatively estimate this effect, we measured the intensity of the $(200)\beta$ line, which lies between the (022) and (200) lines of the α'' phase (Figs. 3, 4). We chose these groups of lines since their partial broadening-induced overlap is smaller than for the other lines of the bcc phase. Moreover, the (022) line of the α'' phase is virtually absent in the X-ray diffraction patterns taken from the rolled samples containing 22.5 and 24 at % Nb in reflection geometry because of texture. The experimental intensity distributions of these samples can be well described as the sum of two Gaussian curves corresponding to the $(200)\alpha''$ and $(200)\beta$ lines with the parameters calculated by the least squares method.

As a result, we find that the intensity ratio of the $(200)\beta$ to $(200)\alpha''$ line at the maximum decreases noticeably as the temperature decreases from room temperature to 83 K: from 0.50 to 0.21 for the Ti–

22.5 at % Nb alloy and from 0.68 to 0.54 for the Ti–24 at % Nb alloy. However, the integrated-intensity ratio in the Ti–24 at % Nb alloy decreases less significantly, namely, from 0.62 to 0.56 (the corresponding volume fractions of martensite are given in Table 2). As the temperature decreases, the $(200)\beta$ reflection of the Ti–22.5 at % Nb alloy, which coincides with (201) -type reflections of the ω phase, broadens substantially, which is likely due to a sharp increase in the reflection intensities of the ω phase (see Fig. 3). It is difficult to estimate the integrated intensity in this case; however, we found that the integrated-intensity ratio slightly increases (approximately from 0.6 to 0.7) rather than decreasing as the temperature decreases.

As seen in Figs. 3 and 4, the $(200)\beta$ line intensity for the deformed alloys with 22.5 and 24 at % Nb decreases slightly with decreasing temperature; however, it should increase due to the weakening of the thermal vibrations. This phenomenon can be associated with two factors, namely, an increase in the volume fraction of the α'' phase and a change in the volume fraction or structural parameters of the athermal ω phase. We first analyze the former factor.

If orientation relationships take place for the $\beta \rightarrow \alpha''$ transformation, then the (100) planes of the bcc lattice transform into the (100) or (011) planes of the α'' phase. The scattering intensity of planes of this type, which are parallel to the sample surface, passes from the $(200)\beta$ reflection to the (200) and (022) reflections of the α'' phase in X-ray diffraction patterns taken in symmetric reflection geometry. The integrated intensity of the $(022)\alpha''$ line decreases because of a change in the structure factor induced by atomic displacements; however, this reflection is virtually absent for the Ti–24 at % Nb alloy sample at the given texture and at both room and liquid-nitrogen temperatures. The decrease in the volume fraction of the β phase is likely to be caused by the growth of existing α'' -phase crystallites (which have a certain texture). If we neglect the possible difference in the Debye–Waller temperature factors of the β and α'' phases and the possible dependence of the $\beta \rightarrow \alpha''$ transformation on the orientation of the initial crystallites, then we can estimate the volume fractions of these phases from the intensity ratio of the $(200)\beta$ to the $(200)\alpha''$ reflection. The volume fraction of the β phase thus calculated for the deformed Ti–24 at % Nb alloy decreases by 2% upon cooling to 83 K (Table 2).

Changes in the $\beta + \omega$ Structural State

When the quenched alloys are cooled to 83 K, the lines of the ω phase strengthen. For example, the (00.1) line intensity of the Ti–24 at % Nb alloy sample increases twofold, and its width decreases by a factor of 1.1.

The X-ray diffraction patterns of the deformed Ti–20 at % Nb alloy taken at room temperature contain weak lines of the ω phase; in particular, the (111) line,

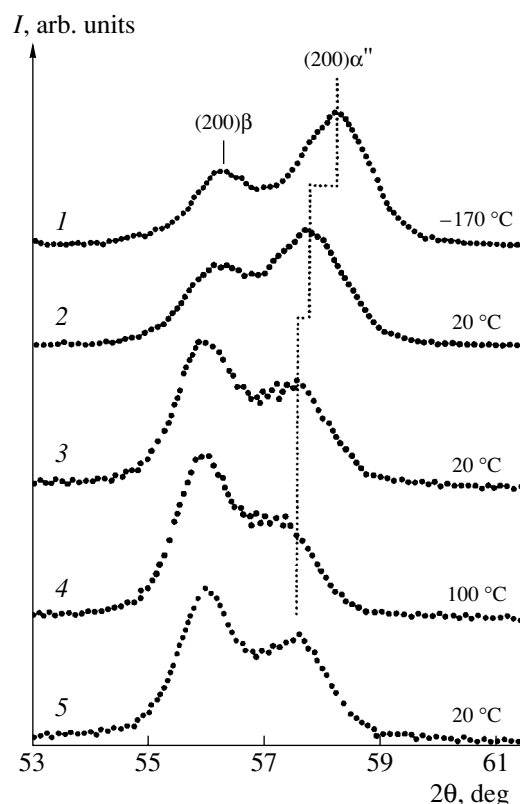


Fig. 4. X-ray diffraction patterns of the deformed Ti–24 at % Nb alloy after (1, 2) quenching and (3–5) subsequent annealing at 200°C for 1 h. Patterns were taken in reflection geometry from the planes parallel to the rolling plane at temperatures of (1) 103, (2) 293, (3) 293 before heating to 373, (4) 373, and (5) 293 after heating to 373 K.

which does not overlap with the lines of the α'' phase, is visible. As the temperature of this sample decreases, the $(111)\omega$ line intensity increases by a factor of 1.3. More pronounced effects are observed upon cooling of the deformed Ti–22.5 at % Nb alloy (see Fig. 3). At room temperature, the reflections of the ω phase are virtually absent. However, rather strong (111) , (002) , and

Table 2. Variation in the volume fraction of the α'' martensite of the Ti–24 at % Nb alloy with the treatment conditions and the measurement temperature

Treatment	T_{meas} , K	Volume fraction, %
Quenching + rolling at $\epsilon = 40\%$	293	62
	103	64
Annealing at 150°C, 30 min	293 (before heating)	56
	373	54
	293 (after heating)	56
Annealing at 200°C, 1 h	293 (before heating)	46
	373	43
	293 (after heating)	44

(301)+(112) reflections of the ω phase appear at 100 K, and they again disappear upon subsequent heating to room temperature. The deformed Ti–24 at % Nb alloy does not exhibit reflections of the ω phase both at room temperature and upon cooling to 100 K. This behavior can be related to the fact that the volume fraction of the β phase is low compared to the quenched state and that its lines and the lines of the ω phase are broadened because of deformation.

Reverse Martensitic Transformation

When the deformed alloys are subjected to heat treatment at temperatures up to 200°C, the α'' phase is retained, and its lattice parameters determined at room temperature are identical to those calculated in the initial state. In the deformed Ti–24 at % Nb alloy, heat treatment at 150–200°C leads to a relative increase in the (200) β line intensity (Fig. 4, Table 1), which indicates partial reverse martensitic transformation. Upon subsequent thermal cycling in a temperature range below the annealing temperature, the lattice parameters and the line intensities change reversibly (Fig. 4, Table 1).

DISCUSSION OF THE RESULTS

When X-ray diffraction patterns were taken in the temperature range 80–293 K, no substantial changes in the volume fraction of martensite was detected in all samples under study. This is true of both the alloys whose martensitic point M_s is above room temperature and the alloys that have a $\beta + \omega$ structure upon quenching. In the latter case, M_s decreases below 80 K. In the alloys with 22.5 and 24 at % Nb, the α'' phase forms in significant amounts only upon deformation, and its volume fraction remains virtually unchanged as the temperature changes in the temperature range under study (a reversible ~2% change in the volume fraction can only occur).

This is likely to be related to a sharp decrease in the temperature of the onset of the martensite transformation M_s with increasing alloying-element concentration, which is typical of martensitic transformations in the general case [7]. However, unlike other systems, Ti–Nb alloys do not exhibit martensitic transformation at temperatures below room temperature. The authors of [6, 8] supposed that this is associated with the competition of the $\beta \rightarrow \alpha''$ and $\beta \rightarrow \omega$ diffusionless transformations. As the niobium content increases, the M_s temperature of the α'' phase decreases, and the $\beta \rightarrow \omega$ transformation can occur at a sufficient niobium concentration above this temperature, which hinders the martensitic transformation. This approach is thought to be correct on the whole; however, we have to refine some points related to the specific features of the $\beta \rightarrow \omega$ transformation, which differs from usual martensitic transformations.

Structural changes as functions of the concentration and temperature are caused by a gradual change in the

intraprase parameters of the $\beta + \omega$ structural state [9, 10]. At an alloying-element concentration close to a “critical” concentration, these changes occur at temperatures below room temperature over a wide temperature range. The changes in the X-ray diffraction pattern are most pronounced upon cooling of the Ti–22.5 at % Nb alloy. By analogy with other titanium alloys with transition metals, such as Ti–V and Ti–Mo alloys [9, 10], we propose the following interpretation of the results obtained.

An increase in the reflection intensities of the ω phase with decreasing temperature that is significantly larger than the increase induced by a change in the Debye–Waller factor was also detected earlier for Ti–V and Ti–Mo alloys [9, 10]. It is also known that the electron concentration (the sum of $s + d$ electrons) plays a key role in the formation of the structure of the athermal ω phase [4, 10, 11]. In Ti–V alloys, the reflection intensities of the ω phase increase anomalously in the concentration range 18–24 at % V, i.e., in the electron-concentration range that includes the compositions of the Ti–Nb alloys under study. In [9], we studied Ti–V single crystals and showed that the strong increase in the ω -reflection intensities (by a factor of three to five) was mainly related to an increase in the correlation of ω configurations, which manifested itself in the narrowing of the diffraction lines without substantial changes in their integrated intensities and in the volume fraction of the ω configurations. (Many researchers interpret such structural changes as the $\beta \rightarrow$ athermal ω transformation, since diffuse reflections from the ω configurations are absent in the X-ray diffraction patterns of polycrystals at higher temperatures.)

The corresponding change in the fine structure should not weaken the integrated intensities of the reflections common for the bcc and ω phases, but this change can cause their broadening because of a certain mismatch between the interplanar spacings in the β and ω phases along various directions. This phenomenon is likely to occur in the Ti–22.5 at % Nb alloy during cooling, since the diffraction line in the (200) β position (see Fig. 3b) for a $\beta +$ athermal ω phase structure is the superposition of the (200) β line and (201) ω -type lines from four orientations of the ω phase. Moreover, the formation of configurations characteristic of the ω phase can be accompanied by a change in the atomic displacements, which can cause a small decrease in the (200) β line intensity that is comparable with the changes detected in this work at low temperatures. Therefore, the volume fractions of the α'' phase found in this work (Table 2) should only be considered as a rough estimation; nevertheless, it is clear that the changes in the volume fraction of the α'' phase are small.

Thus, in terms of the concept in [6, 8], the competition between the $\beta \rightarrow \alpha''$ and $\beta \rightarrow \omega$ transformations is controlled by changes in the intraprase parameters of the $\beta + \omega$ state. These changes stabilize a $\beta + \omega$ struc-

ture as the temperature decreases, thus hindering the $\beta \rightarrow \alpha''$ transformation. At room temperature, the α'' phase forms during deformation from the less stable $\beta + \omega$ state.

In the deformed Ti–Nb alloys, the [010] direction of the α'' phase is mainly oriented along the rolling direction. Therefore, as the temperature decreases, we can expect anomalous changes in the thermal expansion along this direction due to, first, the $\beta \rightarrow \alpha''$ transformation and, second, the anomalous temperature dependence of the parameter b of the α'' phase. With these results, we can estimate the effect of these two factors on the LTEC and compare it with the experimental data in [2, 3].

Let the [010] direction of the α'' phase be oriented strictly along the rolling direction. Then, the volume fraction of the β decreases upon cooling to 80 K by 2%, from 38 to 36% (Table 1, Ti–24 at % Nb alloy), and the LTEC calculated in the rolling direction is positive ($(\Delta l/l)/\Delta T \approx 1 \times 10^{-6} \text{ K}^{-1}$) in the absence of the anomalous temperature dependence of the parameter b of the α'' phase ($(\Delta b/b)/\Delta T = 0$) and in the presence of the normal temperature dependence of the parameter of the β phase ($(\Delta a/a)/\Delta T \approx 1 \times 10^{-5} \text{ K}^{-1}$). If we take into account the increase in the parameter b of the α'' phase with decreasing temperature, the LTEC is found to be negative: it is approximately $(\Delta l/l)/\Delta T = -2 \times 10^{-5} \text{ K}^{-1}$ for the ideal orientation and about $-1 \times 10^{-5} \text{ K}^{-1}$ with allowance for texture scatter.

Thus, at temperatures below room temperature, the anomalous change in the lattice parameter b of the α'' phase mainly contributes to the LTEC of the textured Ti–24 at % Nb alloy sample. At temperatures above room temperature and below approximately 373 K (at which the contribution of the diffuse phase transformations with the formation of the thermal ω and α phases is insignificant), the LTEC is also controlled by the change in the lattice parameters, the volume fraction of martensite, and the texture. In this temperature range, the volume fraction of the α'' phase changes significantly in the Ti–24 at % Nb alloy, which results in an LTEC of about $-1.5 \times 10^{-5} \text{ K}^{-1}$.

In the Ti–20 at % Nb alloy, we have not detected a change in the volume fraction of the α'' phase in the temperature range 80–293 K. However, for a proper texture, the negative LTEC along the rolling direction can also reach $-1 \times 10^{-5} \text{ K}^{-1}$ due to the anomalous change in the lattice parameter of the α'' phase even if the anomalies of the temperature coefficient of the parameter b in the deformed alloy are somewhat smaller than those in the quenched alloy. These estimates agree qualitatively with the results of [2, 3]: in the temperature range 293–373 K, the LTEC of cold-rolled Ti–Nb (30–35 wt % Nb) alloys was found to be $-1 \times 10^{-5} \text{ K}^{-1}$ along the rolling direction and to be negative in the perpendicular direction.

Since the temperature dependences of the parameters a and b of the α'' phase are different, the a/b ratio

increases with decreasing temperature. Similar changes in the b/a ratio occur as the niobium concentration decreases. This change in the degree of orthorhombic distortion corresponds to the tendency of the transition from the bcc β into the hcp α phase, whose field in the equilibrium phase diagram occupies low temperatures and niobium concentrations compared to the β -phase field. A similar change in the martensite lattice parameters, i.e., an increase in the parameter c with decreasing temperature for the normal temperature dependences of the parameters a and b of the monoclinic martensite, was detected in TiNi alloys in the temperature range 20–80°C [12]. As in our case, the temperature dependence of the parameter c was close to a linear dependence, and the corresponding temperature coefficient of the lattice parameter was close to the value obtained in our work (see Table 1). The specific feature of Ti–Nb alloys is a large temperature range (about 300 K) in which $db/dT < 0$. For a favorable texture, one can produce a material with a given LTEC by changing the volume fraction of martensite via low-temperature annealing [3].

Titanium alloys with 3d and 4d metals exhibit near-linear temperature dependences of electrical resistivity; in a certain composition range, they are characterized by negative temperature coefficients of resistivity (TCRs). In [10], we showed that the TCR is related to an increase in the ω -reflection intensities in the X-ray diffraction patterns of Ti–V, Ti–Mo, and Ti–Fe alloys, which indicates that the anomalies of electrical conductivity are caused by electron scattering by ω configurations. For quenched Ti–(20–25) at % Nb alloys, a negative TCR having a small absolute value was also detected in the temperature range from –190 to +20°C [13]. A negative TCR, in this case, is likely to be also associated with an increase in the correlation of ω configurations, which manifests itself in the growth and narrowing of the ω reflections with decreasing temperature in the volume of the alloy occupied by a $\beta + \omega$ structure.

Thus, the alloys under study simultaneously contain two phases that form in a diffusionless manner from the high-temperature bcc phase, namely, the martensitic α'' phase and the athermal $\beta + \omega$ structure. In the temperature range below room temperature, the intraphase characteristics of both phases change reversibly and gradually. In the case of the α'' phase, such changes represent oppositely directed changes in the lattice parameters, and, in the case of the ω phase, such changes represent an increase in the correlation of the spatial distribution of ω displacements. These changes manifest themselves in anomalous temperature dependences of the alloy properties: in the case of the α'' phase, a negative LTEC is detected at a proper texture; in the case of the athermal ω phase, a negative TCR is detected.

CONCLUSIONS

Ti–(20–24) at % Nb alloys exhibit an anomalous temperature dependence of the lattice parameter of the orthorhombic martensite in the temperature range 80–373 K: as the temperature decreases, the parameter b increases and the parameters a and c decrease. This phenomenon is observed for the martensite formed upon both quenching and deformation. The reversible changes in the lattice parameters of the orthorhombic martensite, i.e., a strong decrease in the parameter a and an increase in the parameter b with decreasing temperature, agree with the tendency of a transition from the high-temperature bcc phase into the low-temperature hcp phase. The main contribution to the formation of a negative LTEC in the deformed Ti–(20–24) at % Nb alloys is associated with the anomalous temperature dependence of the lattice parameter rather than to the volume fraction of martensite, which is virtually unchanged in the temperature range under study. The suppression of the martensitic transformation related to the formation of the athermal ω phase at temperatures below room temperature in the alloys containing 22–24 at % Nb can be caused by the reversible restructuring of their $\beta + \omega$ structure as the temperature changes in the range 80–293 K.

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