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DYNAMIC THERMAL ANALYSIS OF STRUCTURAL TRANSFORMATIONS IN α-TITANIUM WITH MICROIMPURITIES

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Structural and phase transformations at elevated temperatures in α-titanium containing trace nonmetallic impurities are studied by the methods of differential scanning calorimetry and x-ray diffraction analysis. The microstructural and energy characteristics of such transformations are determined.

Key words: titanium, nonstoichiometric interstitial phases, structural and phase transformations, differential scanning calorimetry, x-ray diffraction analysis.

INTRODUCTION

Commercial titanium commonly contains a comparatively low content of nonmetallic microimpurities [1]. Such impurities may enter congruently the hcp lattice of α-titanium and have the form of interstitial atoms forming the solid solution. They may also precipitate in the titanium matrix in the form of foreign phases such as Ti_xA_y and $Ti_xB_yC_z$ that differ from α-titanium in the structure of the crystal lattice [2]. It is obvious that these structural features should affect the temperature behavior of titanium. Specifically, the variation of the temperature may give rise to structural and phase transformations not affecting the crystal lattices of both α-titanium and of the foreign phases [3 – 6]. It is especially important to allow for such transitions in the development of numerous processes for fabrication of aerospace and medical alloys where titanium is used as the initial material [7 – 10]. At the same time, the relevant literature is chiefly devoted to investigations of the structural and phase transformations ($\alpha \rightarrow \beta$ or $\alpha \rightarrow \omega$) changing the crystal lattice of α-titanium at elevated temperatures, pressures or impact loads [11 – 16], and to analysis of $\alpha \rightarrow \omega$ phase transitions occurring at high concentrations of the oxygen impurity in titanium [17]. As far as we know, no study has been devoted yet to the effect of microimpurities on the structural and phase transformations occurring without changes in the crystal lattice of α-titanium.

The aim of the present work[3] was to study the structural and phase transformations that may develop in titanium containing nonmetallic microimpurities at the temperatures of the range of stability of its α-phase.

METHODS OF STUDY

We studied titanium powder PTM-1 of industrial production (TU 14-22-57–92), which was obtained by reduction of the metal oxides by calcium hydride. The chemical composition of the powder is given in Table 1.

TABLE 1. Chemical Composition of Titanium Powder Particles

Impurities	Content elements,* wt.%			
Interstitial	H	C	O	N
	0.30	0.12	0.25	0.10
Substitutional	Ca	Fe	Ni	Si
	0.1	0.05	0.06	0.04

* The remainder titanium.

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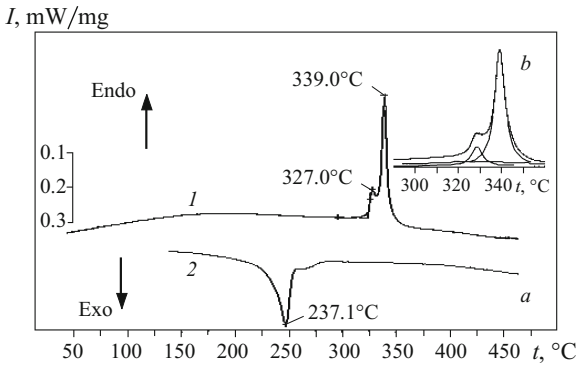

Fig. 1. DSC curves obtained in heating (*1*) and cooling (*2*) of powder titanium at a rate of 10 K/min (*a*) and four elementary components obtained due to decomposition of the resulting endopeak in the Lorentz approximation (*b*). Each component corresponds to a partial phase transition in the sublattice of α-titanium formed by atoms *i* of one kind.

The changes in the thermal flows in the samples upon variation of the temperature were studied with the help of a NETZSCH DSC 204 F1 Phoenix differential scanning calorimeter in a continuous-flow atmosphere of purified and dried argon (at flow rate 30 – 50 ml/min). The heating (and cooling) rate of the samples was varied within 2.5 – 20 K/min. The microstructure and the phase composition of the powder particles was determined with the help of an Empyrean x-ray diffractometer. The tests were conducted in an HTK-1200N high-temperature vacuum chamber with layout geometry "for reflection" (copper K_α radiation, nickel filter, corundum substrate sample holder). The sample temperature during heating and cooling of the powder samples for the x-ray analysis was changed stepwise with a step of 20°C. The rate of variation of the temperature between the steps was 10 K/min. The exposure at every fixed temperature for taking the diffraction pattern was 30 min. Two wavelengths (0.1540598 and 0.1544426 nm) with proportion 2 : 1 of the line intensities in the doublet were used for computing the diffraction patterns. The measurements were made for reflection angles $2\theta = 25 – 120°$.

TABLE 2. Energy Characteristics of Elementary Endopeaks

Peak	T_i, °C	ΔH_i, J/g
1	300.9	1.5
2	328.6	1.5
3	328.7	2.7
4	339.2	13.3
Σ	270 – 370	19.0

Notations: T_i is the temperature of the peak; ΔH is the enthalpy.

RESULTS AND DISCUSSION

As an example, we present in Fig. 1*a* the results of the DSC analysis of titanium powder heated and cooled successively within 50 – 500°C. The DSC curves exhibit complex-configuration endothermic and exothermic peaks shifted with respect to each other over the temperature scale due to hysteresis. The peaks correspond to equilibrium phase transitions of the first kind occurring in the structure of the samples at 300 – 400°C (during heating) and 300 – 200°C (during cooling). Figure 1*b* presents the results of decomposition of an endopeak into four elementary components in the Lorentz approximation. The peak temperatures T_i of these components and the corresponding enthalpies ΔH_i (recalculated per unit mass of titanium) are presented in Table 2.

It is known that interstitial impurities in the hcp-lattice of α-titanium may be located in octahedral (O) or tetrahedral (T) interstitial voids (O- and T-nanopores) (Fig. 2). Six atoms of the metal (with radius R_m) in an elementary cell of titanium correspond to six octahedral ($r_O = 0.41R_m$) and 12 tetrahedral ($r_T = 0.228R_m$) nanopores. They form two O- and T-sublattices in the crystal lattice of titanium, which are filled with impurity atoms only partially due to their quite low concentrations not exceeding several percent in total (Table 1). In this case the "impurity atoms – vacancies" subsystem may be classified as a substitutional solid solution, in which we may expect formation of long-range ordering yielding superstructural phases [3 – 6]. Since the powder material studied has four kinds of interstitial impurities (Ta-

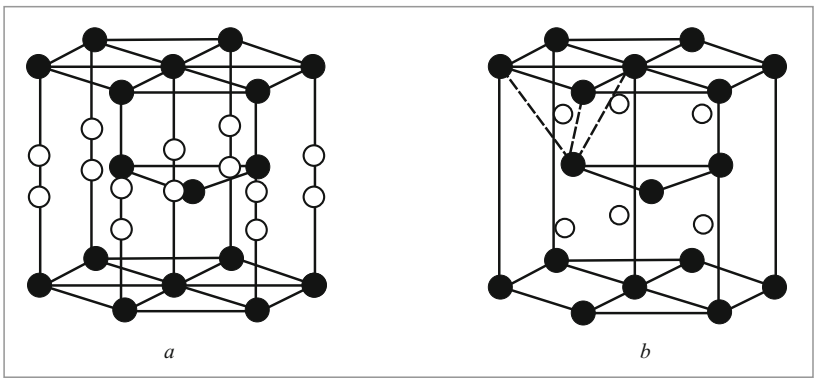

Fig. 2. Octahedral (*a*) and tetrahedral (*b*) interstitial voids (○) in the hcp-lattice of α-titanium (●).

ble 1), four types of superstructure can form in the O- and T-sublattices [4] at low enough temperatures; the corresponding four parameters of their long-range ordering are η_i, where the subscript i may take values corresponding to the H, C, N and O impurity atoms.

The interstitial atoms i occupy sets of geometrically and energetically inequivalent positions in the O- and T-sublattices, which differ for each kind of impurity, and this results in different temperatures of occurrence of the structural and phase transformations in them (Table 2). However, since the energies of the interaction u_{ii}^{O} and u_{ii}^{T} between unlike atoms introduced into the respective sublattices are relatively close, as well as the interaction energy between them and the atoms of the titanium matrix U_{Mi}^{j} (where j = O or T), the temperatures of these transitions differ inconsiderably. This allows us to use the approximation of a mean field not requiring concretization of the kind of the interstitial atoms for estimating the energy characteristics of the system. Assessment of the energy of interaction of such "averaged" atoms between each other in terms of the results of the calculation of $\sum_i \Delta H_i$ within the approximation mentioned, gives us a value $\overline{U_{ii}^{jj}} \approx 0.5k_{\mathrm{B}} = 0.052$ eV (here k_{B} is the Boltzmann constant) averaged with respect to the kinds i of impurity atoms and to the types j of the interstices.

It is obvious that the phase transformations mentioned should also find reflection in the temperature dependences of the lattice constants (a and c) of the α-phase of titanium. Figure 3 presents such curves obtained due to continuous-step heating of the powder of α-titanium. The lattice constants vary nonmonotonically in the range $\Delta T_{\mathrm{tr}} = 300 - 400$°C, which corresponds to the temperature range of the transformations considered above. The basic parameter a [100] of the Bravais lattice of α-titanium continues to increase with growth of the temperature in this range after a short-term lowering (which follows from the negative value of the respective component of the tensor of the thermal expansion coefficients). The prismatic parameter c [0001] decreases monotonically with growth of the temperature in this range. The ratio c/a decreases from the standard value $c/a = 1.588$ [18] at 25°C to $c/a = 1.585$ at the start of the phase transformation and to $c/a = 1.582$ at its end. This indicates appearance of tetrahedral distortions in the elementary cell of the crystal lattice of the α-titanium. They are caused by displacement of a part of the interstitial atoms localized earlier primarily in the coarser octahedral nanopores belonging to the prismatic planes into small-size tetrahedral nanopores in the basal planes.

We used the method of [4] to analyze the equations of thermodynamic equilibrium of a system constructed in the approximation of effective medium field for an averaged ordering parameter $\eta = \overline{\eta}_i$. The analysis showed that the distribution of impurity atoms in the lattice of titanium should be

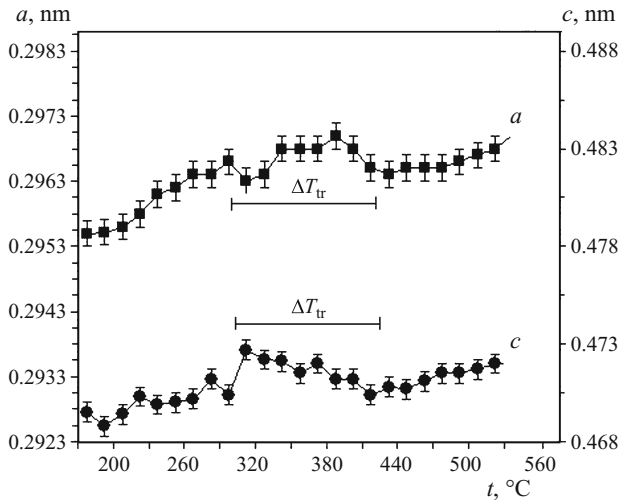

Fig. 3. Temperature dependence of lattice parameters (a and c) of α-titanium obtained during heating of a powder sample: ΔT_{tr}) temperature range of phase transitions.

substantially heterogeneous. At a low enough temperature, the lattice of α-titanium has regions of a submicrometer size forming an ultramicrofine phase (microphase) enriched considerably with impurity atoms. This microphase may be associated with a set precipitates of colloidal sizes in the matrix hcp-lattice of α-titanium which serves a dispersion medium for it. From the standpoint of the science of metals, this microphase is an analog of a set of nanosize Guinier–Preston zones observed in aluminum and some other alloys in their aging [19].

The number density of n of impurity atoms in the interstices of N sublattices in nanovolumes of a colloidal-disperse microphase with hcp-structure of α-titanium attains $n/N = 0.3 - 0.4$. Structural and phase transformations of the first kind occur just in nanovolumes of the microphase in the respective O- and T-sublattices of the hcp-structure under heating and cooling of the samples. The transformations are accompanied by marked variation of the value of η from the positive values of $\eta_{\mathrm{O}} \approx +0.7 \div +0.8$, which characterize the distribution of the interstitial atoms and vacancies in the O-sublattice of the microphase, to the negative values of $\eta_{\mathrm{T}} \approx +0.7 \div -0.2$ describing the distribution of the same structural components in the T-sublattice of the microphase. Computations show that $|\eta_{\mathrm{O}}| > |\eta_{\mathrm{T}}|$, and therefore such transitions occur with noticeable absorption of energy in the material. Further growth of the temperature in the region of $T \geq T_{\mathrm{tr}}$ results in gradual disordering of the mutual arrangement of the interstitial atoms now localized primarily in the T-sublattice of the microphase and of the vacancies in it ($\eta_{\mathrm{T}} \to 0$). The absorption of energy in the material with growth of the temperature becomes insubstantial or even zero.

Estimation of the energies $\overline{U_{ii}^{jj}}$ within the local-coordination approximation with allowance for the energy contribu-

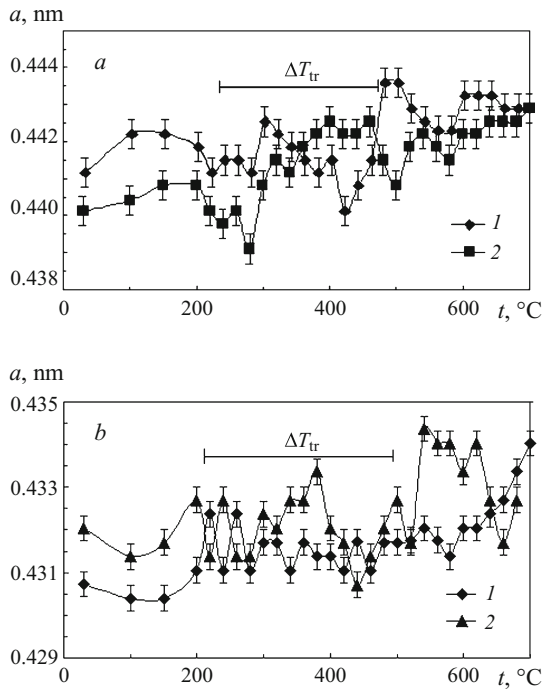

Fig. 4. Variation of the lattice parameters of $TiN_{1-x}\square_x$ titanium mononitride (*a*) and $Ti_2C_{1-y}\eta_yN_{1-x}\square_x$ carbonitride under heating (*1*) and cooling (*2*) of a powder sample; □ is a standard depiction of a vacancy: ΔT_{tr}) temperature range of phase transitions.

tions of the interatomic bonds belonging to only the first coordination sphere in the absence of a deformation impact and of close-range ordering in the system [4, 5] in the median field approximation (for $\eta = \overline{\eta}_i$) and under the conditions $\left|\overline{U^O_{Mi}} - \overline{U^T_{Mi}}\right| \ll \left|\overline{U^{OT}_{ii}}\right| \ll \left|\overline{U^{OO}_{ii}}\right| \approx \left|0.5\overline{U^{TT}_{ii}}\right| \approx 0.5k_B T_{tr}$ gives $\overline{U^{OO}_{ii}} \approx 0.5\overline{U^{TT}_{ii}} \approx -0.02 \div -0.03$ eV. Since $\overline{U^{ij}_{ii}} < 0$, the interstitial atoms in the O- and T-sublattices in an ordered state are surrounded with dominantly single-type atoms, and the "ordering – disordering" phase transformations are accompanied by processes formally similar to melting.

Opposite changes in the lattice parameter of α-titanium are observed when the sample is cooled in a temperature range corresponding to the endopeak in Fig. 1. It is obvious that in this case, the O- and T-sublattices of the microphase undergo structural transformations inverse to those described above. They consist in the appearance of long-range ordering in the system of atoms and vacancies located in the T-sublattice of α-titanium at $T \geq T_{tr}$ in the disordered state due to cooling of the sample below T_{tr}. With further cooling of the system, the interstitial atoms transfer massively from the T-sublattice into the O-sublattice of α-titanium, and the system undergoes gradual long-range ordering with respect to the corresponding vacancies. This process is formally similar to condensation of impurity atoms in particles of a colloidal-disperse microphase, i.e., multiple nucleation of ordered Guinier–Preston microzones in the mother lattice of α-titanium.

In addition to the colloidal-disperse microphase described, nanosize volumes of which are incorporated coherently into the crystal lattice of the α-phase of titanium, the powder particles contain microinclusions of phases Ti_xA_y and $Ti_xB_yC_z$ containing interstitial atoms. The letters A, B and C are used here to denote the impurity atoms (H, C, N and O), while the subscripts *x*, *y* and *z* are their concentrations in the respective microphases. These microphases foreign with respect to the α-phase of titanium and having a hcp crystal lattice differing from the hcp-lattice of α-titanium, may also undergo structural and phase transformations, which are possible due to deviation of the compositions of the microphases from stoichiometry [3 – 5]. Such transitions are obviously a result of an insufficient concentration of interstitial atoms in the microphases. As an example, we present in Fig. 4 the temperature dependences of the lattice parameters of the nonstoichiometric microphases detected in the powder particles, i.e., cubic titanium mononitrides $TiN_{1-x}\eta_x$ and titanium carbonitride $Ti_2C_{1-y}\eta_yN_{1-x}\eta_x$, where η_{δ} and η_y are the concentrations of structural vacancies η in the nitrogen and carbon sublattices respectively.

The results obtained reflect anomalies in the temperature behavior of the lattice parameters of microinclusions of the foreign phases in the temperature range $\Delta T_{tr} = 200 – 500$°C, which may be associated with reversible (and almost hysteresis-free) changes in the long-range-ordering parameters under the structural and phase transformations in the sublattices of the corresponding microphases.

It follows from the theoretical analysis made in [3 – 5] that variation of the temperature should yield in the nonstoichiometric cubic titanium nitride $TiN_{1-x}\eta_x$ only one type of superstructure and one parameter of long-range ordering corresponding to a unique structural and phase transformation in the nitrogen sublattice. On the contrary, the nonstoichiometric titanium carbonitride $Ti_2C_{1-y}\eta_yN_{1-x}\eta_x$ is characterized by two types of superstructure, two parameters of long-range ordering and two structural transformations in the nitrogen and carbon sublattices. However, in all the cases, the interstitial atoms are redistributed under such transitions between the geometrically and energetically single-type octahedral interstices in an elementary cell of the hcp-sublattice of titanium. Therefore, we may assume that the structural transformations of the kind mentioned should not make a noticeable contribution into the emission of energy in the respective DSC curves of the hcp-microphases detected in α-titanium, because they are smeared phase transitions close to hysteresis-free transitions of the second kind [4, 20].

It should be noted that in the case in question, the results of the x-ray diffraction analysis cannot bear information on the presence of superstructural lines in the respective diffraction patterns of the system, because the concentration of the mentioned microphases in α-titanium is quite low and the

values of the x-ray atomic factors of titanium and of the impurity atoms differ substantially [21]. Therefore, the inference on the existence of superstructural transitions in α-titanium and on the concomitant microstructural inclusions of foreign phases is based in our case on indirect evidences. A direct and reliable detection of structural and phase transformations in α-titanium containing microimpurities and of foreign microphase inclusions awaits a temperature neutron diffraction investigation.

CONCLUSIONS

1. Results of the thermoanalytical and x-ray diffraction studies of α-titanium with microimpurities have been used to determine the temperature ranges $\Delta T_{tr} = 200 – 500°C$ of superstructural "ordering ↔ disordering" phase transitions in the microphases contained in the α-titanium under thermocycling.

2. The long-range ordering parameters characterizing the distribution of interstitial atoms and vacancies in the O- and T-sublattices of the respective microphases have been determined.

3. Estimates have been obtained for the energies of interatomic interaction of impurity atoms incorporated into the O- and T-sublattices, i.e., $\overline{U_{ii}^{OO}} \approx 0.5\overline{U_{ii}^{TT}} \approx –0.02 \div –0.03$ eV.

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