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Polymorphic transformations in iodine titanium

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Based on the analysis of differential scanning calorimetry data, the possibility of classifying the observed endothermic or exothermic transformations as phase transformations of the first oder is considered. Two approaches have been implemented. The first is based on the correspondence between the temperatures of the maximum conversion rate and the temperatures of the extrema on the second derivative of the differential scanning calorimetry signal with respect to temperature.

In the second approach, the phase transformation is considered as a kind of kinetic reaction of a chemical process with the determination of some parameters included in the kinetic equations. In this case, the order parameter of such reaction n is obtained from the analysis of the differential scanning calorimetry signal shape in the region of phase transformation registration temperatures.

Using the example of experiments carried out during thermal cycling of titanium iodide samples, it is shown that both the first and second approaches make it possible to fairly adequately attribute the processes that cause calorimetric effects on the dependences of differential scanning calorimetry to first-order phase transitions.

In particular, the obtained results of differential scanning calorimetry during heating and cooling of iodide titanium show that polymorphic transformations in it are realized by various mechanisms depending on the rate of thermal cycling and the thermal history of the metal.

Keywords: activation energy, titanium, calorimetry, polymorphism, structure, approximation.

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1. Introduction

Polymorphous transformations when heating metals are considered (see, for example, [1–3]) as phase transformations of the first kind (PT-I). However, the information obtained by differential scanning calorimetry (DSC) for these transformations to Co, Ti, Zr (see [4–6]) does not allow for classifying such transformations as this PT type so unambiguously. The point is what criteria of DSC data analysis can be a sufficient basis to consider one or another calorimetric effects at DSC as caused exactly by a PT-I.

As early as in [7] it was shown for such a classic example of PT-I as crystallization, that „total crystallization rate achieves its maximum almost exactly at the moment when crystallized volume achieves a half of the initial volume“. This dependence of crystallization rate versus time passes through its maximum and is characterized by a median value.

For the solid state–solid state transformation implemented through emergence and growth of new phase nuclei, the Avrami–Erofeev equation is often used[8,9]:

$$[-\lg(1-\alpha)]^{1/m} = \kappa t, \tag{1}$$

where α — percentage of transformed substance, κ — Avrami constant, t — time, m — characteristic of leading mechanism of the transformation process (Avrami index).

Presuming that the thermal effect of transformation is proportional to the quantity of substance transforming to the new phase (see [9]), an extreme point should (and is) observed on the dependence of DSC signal in the region of phase transformation temperatures.

And in the special cases, when the endothermic peak while heating in the region of phase transformation temperatures can be approximated by the Gaussian function (standard distribution), the maximum of this function corresponds to the extreme point of its second derivative.

When the difference between temperatures of extreme points of DSC signal and its second derivative (DDDSC) is out of allowed errors of the experiment, a basis appears for considering that these features of the DSC signal are either attributable to phase transformations realized not by one, as it was in the previous case, but two or more mechanisms, or no any PT-I takes place at all in this temperature interval.

On the other hand, solid state → solid state, solid state → solid state + gas, or solid state → liquid phase transitions while heating from the kinetic point of view can be considered as an analog of a chemical reaction [10–12], which general kinetic equation for solid-phase reactions can be written as follows

$$\frac{d\alpha}{dt} = F(T) f(\alpha), \tag{2}$$

where $\frac{d\alpha}{dt}$ — reaction rate; $f(\alpha)$ — reaction function; $F(T)$ — function of temperature effect on the reaction rate.

It is known, that the same kinetic dependence $f(\alpha)$ can be described by different equations, depending on the implementation mechanism proposed for the given process. Thus, for example, Kissinger (see [13,14]) used the following equation to describe the process solid state → solid state + gas dissociation

$$\frac{d\alpha}{dt} = A(1-\alpha)^n \exp\left(-\frac{E}{RT}\right), \tag{3}$$

where A — normalization constant; n — empirical parameter of reaction; R — gas constant; E — energy of activation.

As a result he proposed an equation to determine the energy of activation, E, in the following form

$$E = -R\,\frac{dln\left(\frac{\beta}{T^2}\right)}{d\left(\frac{1}{T}\right)}, \tag{4}$$

where β — rate of heating, T — temperature of the endothermic peak maximum.

It is essential, that this equation appeared to be independent from the n order parameter in equation (3). It seems that it is this fact that is responsible for the frequent use of this relationship to determine the energy of activation for the processes implemented by mechanisms other than those of [13]. Incidentally, other proposed methods to determine the energy of process activation from the data of differential thermal analysis (DTA) and DSC in the vast majority of cases also use the above-mentioned relationship for the rate of a chemical reaction (see [9]). The order of reaction n can be determined from the relationship presented in [13]

$$n = 1.26\sqrt{S}. \tag{5}$$

Here S — form-factor of the DSC curve in the region of temperatures of endothermic process recording: a ratio of tangents between the tangent lines in tripping points of the thermal effect experimental dependence.

Shapes of DTA [10] and DSC [11,12] curves were theoretically calculated for different mechanisms of phase transformation: diffusion, reaction at the phase interface, nuclei growth process. For the first two mechanisms of them the order of reaction is $n < 1$ taking into account the form factor. For the process controlled by nucleus growth ($m = 4$). $n > 1$. In this case the $\frac{d\alpha}{dT}(T)$ dependence undergoes a maximum and is a symmetrical curve ($S = 1$).

In this work an attempt is made to compare these two approaches to the selection of PT-I criterion in respect to the DSC data obtained for one of the above-listed metals — titanium.

2. Research procedure

The research target were samples cut from a rod of coarse-cristalline iodide titanium of TI-1 grade (99.99% Ti). The differential scanning calorimetry measurements were performed using the STA „Jupiter“ 449 device by Netzsch. Heating and cooling were performed in argon (99.9995% Ar) atmosphere. The gas flow rate was 25−30 ml/min. The titanium sample mass varied within the range of 180−210 mg. The experimental DSC data were processed using the Proteus Analyses software and the Fityk package. In order to avoid the emergence of artifacts related to the specifics of experimental examination of phase transformations, the obtained data were smoothed with a polynomial of order 6−8.

Each heating was started with the same initial state of the metal — recrystallization annealing.

In the first variant of experiments as-received samples were heated at a rate of 40 °/min up to 750°C and soaked at this temperature for 5 min. After that, each sample was heated and cooled at a rate of 5, or 10, or 20, or 40 °/min. The effect of the number of such thermal cycles (750 ↔ 1000°C) on the parameters of polymorphic transformations was studied in the process.

In the second variant of experiments a sample in its initial state was heated at a rate of 40 °/min up to 750°C and soaked at this temperature for 5 min. After that, the same sample was subjected to a sequence of thermal cycles (750−1000°C) at heating and cooling rates of 5, 10, 20, and 40 °/min.

3. Experimental results and discussion

Fig. 1 shows the influence of the number of heating-cooling cycles on the DSC signal in the region of temperatures of endothermic effect while heating the samples of iodide titanium.

At a rate of thermal cycling of 5 °/min the maximum of endothermic peak shifts towards higher temperatures (851 → 894°C) with an increase in number of thermal cycles, the temperature interval of transformation, ΔT, increases from 22 to 64°. The thermal effect decreases from 40 down to 32 J/g. The temperature of transformation start and the temperature of endothermic process end shift towards slightly higher temperatures with an increase in the number of cycles.

For thermal cycling with high rates, in particular with a rate of 40 °/min, the above-noted trends, in general, are maintained (Fig. 1, *b*). With an increase in the number of thermal cycles the temperatures of transformation start and end shift insignificantly towards higher temperatures (763 → 872°C and 928 → 960°C, respectively), the temperature of maximum becomes slightly higher (898 → 903°C). The thermal effect decreases (33 → 30 J/g) and the intervals of phase transition realization, ΔT, increase (65 → 88°).

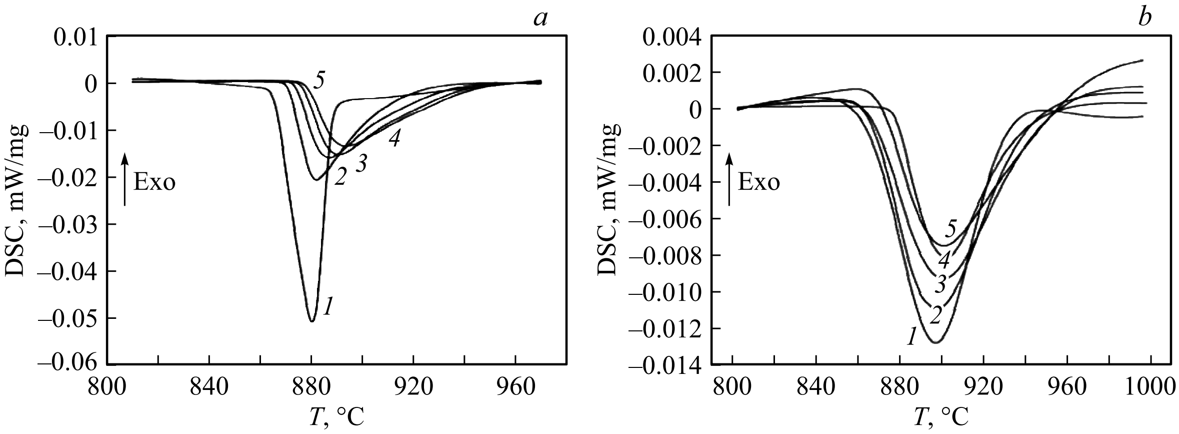

Figure 1. Influence of the number of heating cycles on DSC signal variation. *a* — heating rate of 5 °/min; *b* — heating rate of 40 °/min. *1, 2, 3, 4, 5* — heating cycles.

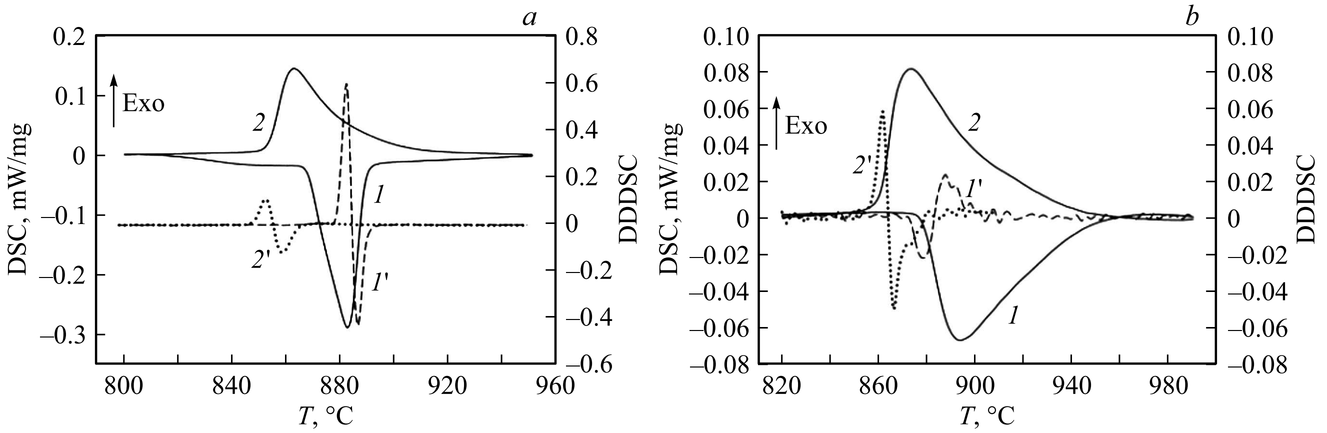

Figure 2. Variation of the DSC signal and its second derivative (DDDSC) while heating (*1*, *1'*) and cooling (*2*, *2''*) of titanium. The rate of thermal cycling of 5 °/min. *a* — the first cycle; *b* — the fifth cycle.

In connection with the noted features of the influence of the number of heating and cooling cycles on the shape and characteristics of DSC signal, Fig. 2, 3 show variations of the DSC signal and its second derivative with respect to temperature, DDDSC, for thermal cycling at different rates.

At a rate of thermal cycling of 5 °/min (Fig. 2) in the region of polymorphous transformation $\alpha \leftrightarrow \beta$. an asymmetry in the variation of the DSC signal while heating and cooling is observed. There are no maxima (minima) on the DDDSC in the region of calorimetric effects observed on the DSC dependencies. Thermal effects while heating and cooling are slightly different as well: 41 and 38 J/g. Transformation while heating starts at 867°C and ends up at 889°C. $\Delta T = 22°$. Start and end while cooling are, respectively, at 884.7 and 853.1°C $\Delta T = 32°$.

As can be seen from the presented data, the transformation while cooling starts at temperatures close to the temperatures of the end of endothermic effect. However, the transformation while cooling ends up at temperatures that are considerably lower than those of the start of endothermic process while heating. The difference in the interval of temperatures of exothermic and endothermic processes realization are not greater than 10–12°. The transformation itself while heating ends up within 20–22°. Thermal effects of the transformation while heating and cooling slightly differ from each other, 42 and 38 J/g.

Fig. 2, *b* shows variations of the DSC signal and DDDSC obtained at the fifth thermal cycle. In a manner exactly the same as that for the first thermal cycle, no DDDSC maximum is observed in the temperature interval of realization of endothermic or exothermic effects.

Thermal effects while heating and cooling are almost the same: 30 and 31 J/g. Transformation while heating starts at 872°C and ends up at 941°C. $\Delta T = 70°$. Start and end while cooling are, respectively, at 912 and 861°C. $\Delta T = 51°$.

In the case of thermal cycling at a rate of 40 °/min (see Fig. 3, *a*) extreme points on the DSC and DDDSC curves are observed for the first cycle in the region of endothermic and exothermic effects. Extremes while

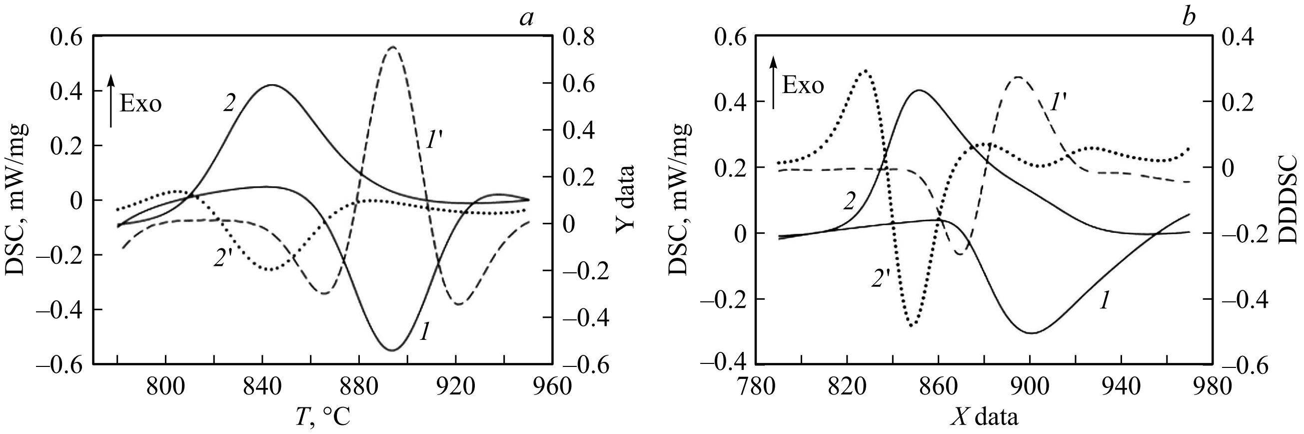

Figure 3. Variation of the DSC signal and its second derivative (DDDSC) while heating (*1*, *1'*) and cooling (*2*, *2''*) of titanium. The rate of thermal cycling of 40 °/min. *a* — the first cycle; *b* — the fifth cycle.

heating are, respectively, at 893.5 and 893.9°C. $\Delta T = 65°$. Thermal effect is 34 J/g. extremes while cooling are at 843.7 and 842.7°C. $\Delta T = 78°$. Thermal effect is 37 J/g.

For the fifth cycle of thermal cycling at a rate of 40 °/min (see Fig. 3, *b*), in the region of endothermic and exothermic effects extreme points on corresponding DDDSC curves are observed with a significant difference in temperatures of corresponding extreme points on DSC and DDDSC curves. While heating, respectively, at 901.7 and 894.3°C. $\Delta T = 91°$. Thermal effect is 31 J/g. While cooling at 851.5 and 848.8°C. $\Delta T = 78°$. Thermal effect is 35 J/g.

In the case of thermal cycling at a rate of 40 °/min transformations while cooling also start at temperatures close to the temperatures of endothermic process end. An in this case it ends up at lower temperatures than the start of endothermic transformation while heating. If in the case of heating $\Delta T = 68°$, then in the case of cooling $\Delta T = 74°$. The values of the thermal effect can be considered almost the same, 33 ± 1 J/g.

With an increase in the number of cycles some transformation of the structure of endothermic and exothermic effects takes place (see Fig. 4–7).

For the rate of thermal cycling equal to 5 °/min endothermic and exothermic effects (see Fig. 4–5) can be represented as a superposition of two subpeaks, one of which is attributable to the processes running over the entire temperature interval of transformation, while another one takes place while heating, at the beginning of the endothermic process development. In the case of cooling at the final stage this feature is manifested as well. It seems that the observed specifics of endothermic and exothermic peaks structure is attributable to the mechanisms of phase recrystallization with close realization temperatures at this temperature interval of new structure formation.

For the rate of thermal cycling equal to 40 °/min the endothermic effect at the first heating (Fig. 6, *a*) can be approximated by one Gaussian peak, while in the case of cooling it is a superposition of two subpeaks. The position of subpeaks itself at the first cycle is similar to that observed when thermal-cycling at a rate of 5 °/min.

At the fifth cycle of thermal cycling (Fig. 7) at a rate of 40 °/min, in the case of heating and cooling, endothermic and exothermic peaks can be represented as a superposition of two subpeaks with their mutual positioning coinciding with that previously established for the heating rate of 5 °/min.

Thus, there is unambiguous correspondence between the structure of endothermic and exothermic peaks on DSC signal curves in the region of phase transformations and the character of variation of the second derivative of the DSC signal with respect to temperature in this temperature interval.

As it was noted before, phase transitions while heating can be considered from the kinetic point of view as an analog of a chemical reaction, where the value of the parameter n characterizes the mechanism of this phase transformation (see [10–12]). The procedure to determine n in this study was performed on the basis of analysis of experimental data for the parameter of shape of endothermic and exothermic effect maxima. Thus, for example, at a rate of thermal control of 5 °/min while heating, $n < 1$ for the first heating ($n = 0.36$), and n is greater than unit for 2–5 cycles. For a heating rate of 10 °/min, $n < 1$ ($n = 0.48$). For 2–5 cycles $n \gg 1$. For a thermal cycling rate of 20 °/min $n < 1$ ($n = 0.56$) for the first cycle and $n \gg 1$ for subsequent heating. The situation is similar for thermal cycling at a rate of 40 °/min as well. Thus, for the first heating, always $n < 1$. For subsequent heating cycles $n \gg 1$.

In theory, the DTA (see [10]) or DSC (see [11–12]) signal for the mechanism of new phase nucleation and growth can be approximated by a function with a maximum, that is characterized by the presence of a median value. In particular, it can be a Gaussian function. In this case the form factor is $S = 1$ and then $n = 1.26$. In the presented data this is only observed at the first heating of titanium samples at a rate of 40 °/min.

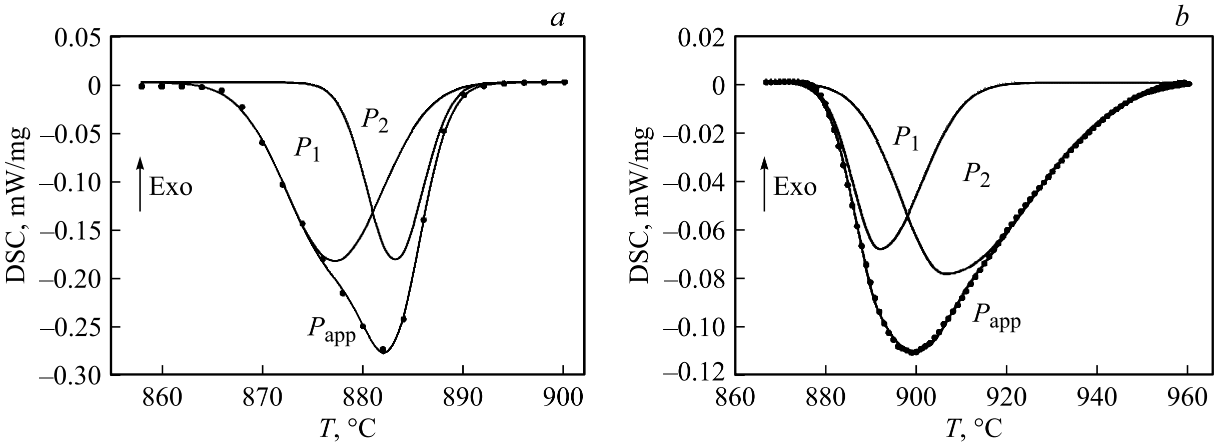

Figure 4. Structure of endothermic peaks while heating titanium at rates of 5 °/min. Dots — experimental data; P_{app} — result of approximation; P_1 and P_2 — subpeaks. *a* — the first cycle; *b* — the fifth cycle.

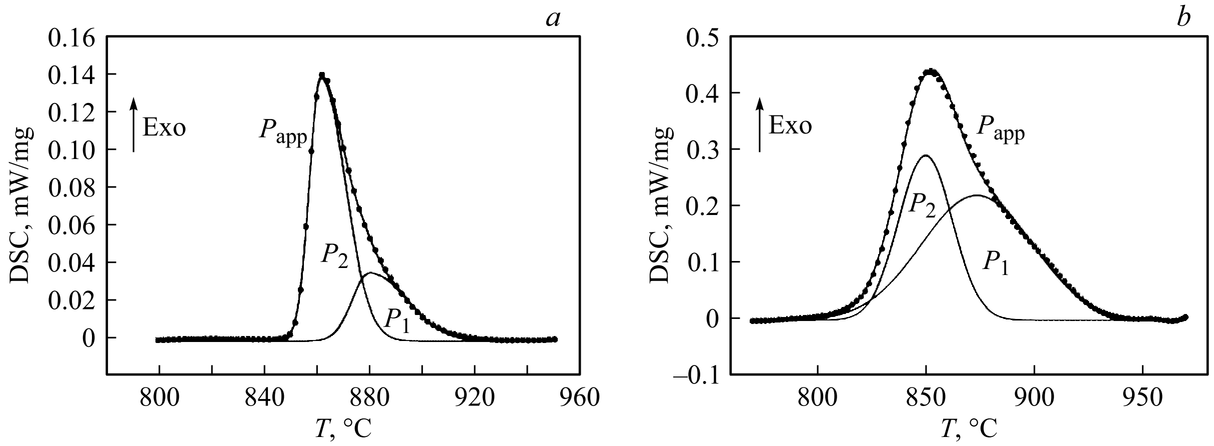

Figure 5. Structure of exothermic peaks while cooling titanium at rates of 5 °/min. Dots — experimental data; P_{app} — result of approximation; P_1 and P_2 — subpeaks. *a* — the first cycle; *b* — the fifth cycle.

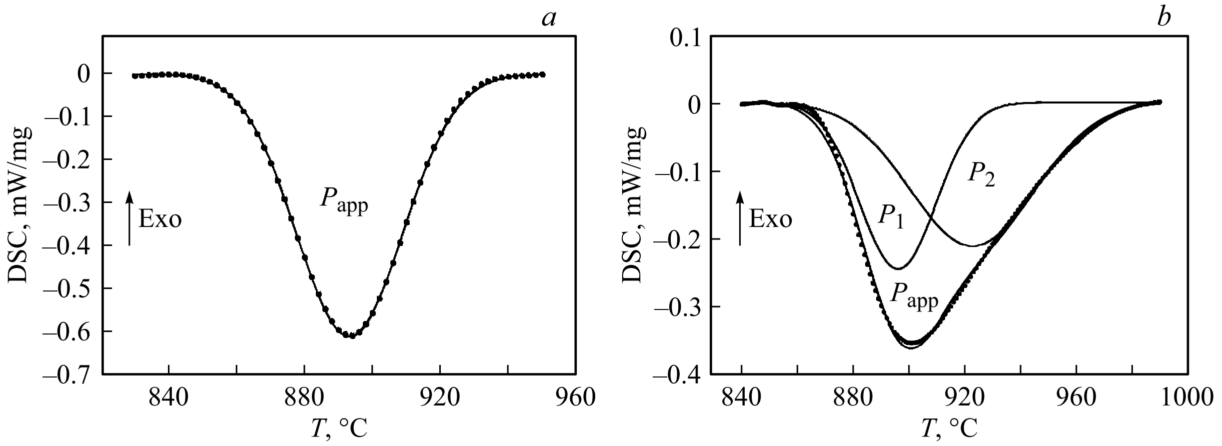

Figure 6. Structure of endothermic peaks while heating titanium at rates of 40 °/min. Dots — experimental data; P_{app} — result of approximation; P_1 and P_2 — subpeaks. *a* — the first cycle; *b* — the fifth cycle.

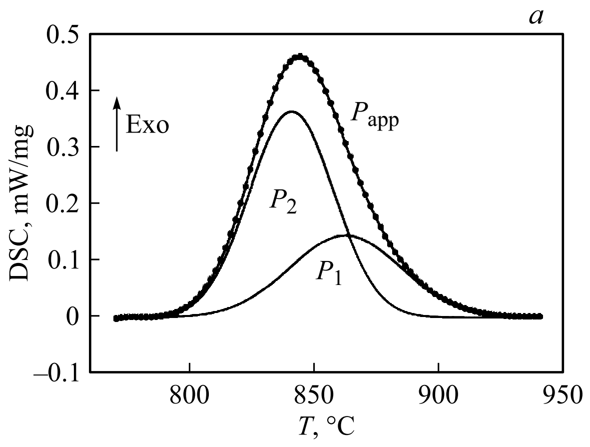

Figure 7. Structure of exothermic peaks while cooling titanium at rates of 40 °/min. Dots — experimental data; P_{app} — result of approximation; P_1 and P_2 — subpeaks. *a* — the first cycle; *b* — the fifth cycle.

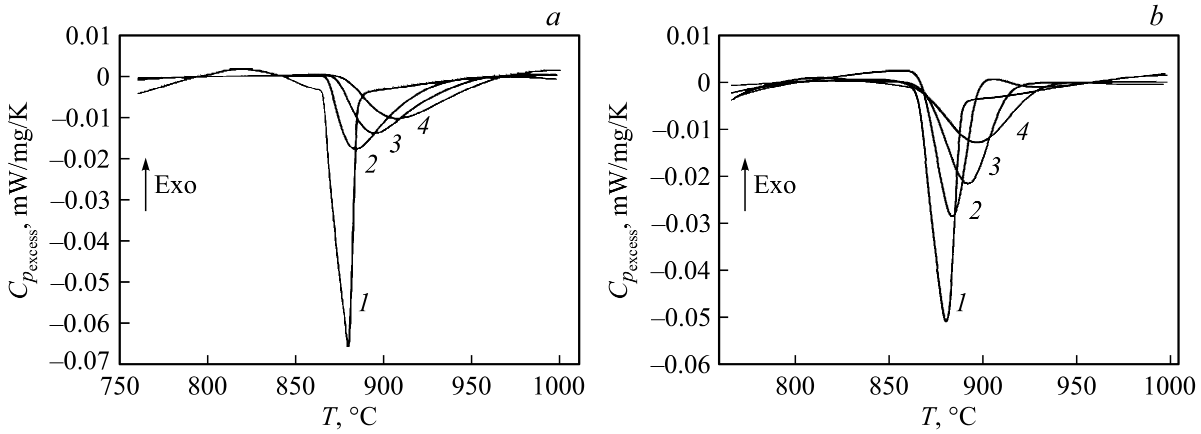

Figure 8. Influence of heating rate on the shape and positions of endothermic peaks at $\alpha \rightarrow \beta$ transformation in titanium. *1* — 5 K/min; *2* — 10 K/min; *3* — 20 K/min; *4* — 40 K/min. Successive heating of the same sample (*a*). Individual heating of samples (*b*).

For other thermal cycling conditions endothermic (exothermic) peaks can be represented as a superposition of two subpeaks, that can be described in almost all cases by a Gaussian (Split Gaussian) function. For each individual subpeak this condition ($n = 1.26$) is met quite correctly. Naturally, for the sum peak this correspondence is not observed. Thus, from the analysis of shape of endothermic (exothermic) peak the values of S ($= 1$) or n ($= 1.26$) can be used as criteria for classifying such transformation as a phase transformation of the first kind.

In case of successive heating of the same sample, if for the first heating at a rate of 5°/min $n = 0.5$, then for further heating cycles at rates of 10–20–40 °/min n it is much greater than unit. However, all peaks while heating and cooling can be approximated by two subpeaks of the Gaussian type

With an increase in the number of cycles an increase in temperature interval of phase transformations realization (20 → 71°) is observed while heating and a trend is observed to a decrease of the thermal effect (38 → 33 J/g). When cooling, ΔT changes from 23 to 73°, and the thermal effect increases from 35 to 38 J/g.

The above-noted features of the $\alpha \leftrightarrow \beta$-transformation in titanium suggest that mechanisms of recrystallization while heating are different from those while cooling.

It is essential, that in all studied situations no formal evidence is observed that in the case of phase recrystallization in titanium the process is described by PT-1 only. The exception is the case of the first heating at a rate of 40 °/min.

According to Gibbs, polymorphous transformations in metals, in particular in titanium, are phase transformations with zero degree of freedom, so-called nonvariant equilibrium. In the experiments related to DSC this should be correspondent to the maximum coincidence of extreme point temperatures on DSC and DDDSC curves. If we consider the data of studying polymorphous transformations in other metals, in particular, iron, by the DSC method (see [4]), such a coincidence to an accuracy of 0.1–0.2° is really observed.

However, in our case in all conducted experiments with TI-1 titanium, with transformations while heating ($\alpha \to \beta$), and cooling ($\beta \to \alpha$), a considerable difference (several degrees) between temperatures of such extreme points is observed in the case, when the extreme points of DDDSC curve are within the temperature interval of thermal effects.

The cause of this difference, probably, consists in the following. It is recognized that a polymorphous transformation in iron is realized by a diffusionless mechanism, so-called massive transformation [1–3]. But in the case of titanium recrystallization the $\alpha \leftrightarrow \beta$ transition is realized following another scenario: nucleation of recrystallization centers and their growth. That is, a combination of two mechanisms takes place: diffusionless (see [15]) and diffusion mechanisms are realized in overlapped temperature intervals. The structure of endothermic and exothermic maxima of DSC curves can serve as a sort of proof that this assumption is true.

A more detailed study of the influence of thermal cycling rate on the shape of DSC curves while heating and cooling was carried out in two experimental settings.

In one of them the same sample was successively thermal cycled in the same temperature interval at rates of 5, 10, 20, 40 °/min. In this case the dependencies shown in Fig. 8,*a* were recorded while heating. On the ordinate axis the so-called reduced heat capacity $C_{p_{\text{excess}}}$ is plotted, which is the data of the DSC analysis normalized to the rate of heating (β) and weight (m_s) of samples (see [16]):

$$C_{p_{\text{excess}}} = \frac{\dot{Q}_S - \dot{Q}_{Bl}}{m_s \beta}\,(\text{Jg}^{-1}\cdot\text{K}^{-1}). \tag{6}$$

Here: $\dot{Q}_S$ and $\dot{Q}_{Bl}$ — heat flow rates during heating with sample and basic heat flow rates, respectively.

As can be seen from Fig. 8,*a*, with an increase in the heating rate, the maximum of the heat energy absorption rate shifts towards higher temperatures (865 → 875 °C) and the temperature interval of phase transformation ΔT increases (29 → 88°). The thermal effect of transformation slightly decreases (43 → 36 J/g).

The shift of the endothermic process rate maximum towards higher temperatures allows estimating by the Kissinger method (see equation 4) the energy of activation of phase recrystallization at $\alpha \to \beta$-transformation: solving six paired equations (four heating rates) gave $E = 590 \pm 110$ kJ/mol.

In the second experiment variant an individual titanium sample in the initial state was used for each rate of thermal cycling. Fig. 8,*b* shows the influence of the heating rate on the shape and positioning of endothermic effects at individual heating of each sample in the initial state (the first heating). And in this case, with an increase in the heating rate the temperature of transformation start and the temperature of endothermic effect minimum shift towards higher temperatures (867 → 875°C). The temperature interval of the transformation increases (28 → 65°). The thermal effect of the transformation changes as well (31 → 33 kJ/mol). The mean value of phase recrystallization energy is determined as 1700 ± 250 kJ/mol.

For the fifth heating the temperature of transformation start is weakly dependent on the rate of heating. The temperature interval of the transformation increases (71 → 88°). The thermal effect of the transformation changes as well (26 → 30 kJ/mol.). The mean value of phase recrystallization energy for this case is determined as 2100 ± 500 kJ/mol.

Such big difference in values of activation energy for the first and the second experiment schemes can be explained by an assumption that at thermal cycling of the same sample a certain heredity is realized in the emergence of phase recrystallization centers and their further growth. Also, the data on the influence of the number of thermal cycles on the results of determining the activation energy of $\alpha \to \beta$-transformation may be indicative of this.

When comparing the obtained results of determining the activation energy of $\alpha \to \beta$ transformation for TI-1 and VT1-00 (see [5]), the difference for the successive mode of thermal cycling taking into account the dispersion of experimental data is insignificant. For the individual scheme of thermal cycling this difference is significant and beyond the errors of determining this value, 1700 and 1100 kJ/g, respectively. The difference is especially large for the fifth cycle of heating (2100 ± 500 kJ/mol). It is worth noting, that in both cases this is indicative that the rate of heating has little impact on the shift of maximum of the phase transformation endothermic effect. The last fact can serve as a basis for the assumption that in this case the transformation has features of the shear mechanism of phase transformation.

4. Conclusion

It is shown, that phase recrystallization while heating and cooling of TI-1 titanium in most cases is realized by only one mechanism of phase transition of the first kind.

With an increase in the number of heating–cooling thermal cycles in the region of temperatures of polymorphous transformation the energy cost of the transition from one space configuration of titanium atoms to another demonstrates a trend to decrease.

With an increase in the rate of heating the temperature interval of phase transformation becomes wider, although the temperature of transformation start shifts towards higher temperatures to a noticeably less extent.

When cooling, the process of phase recrystallization completion does not depend on the number of thermal cycles for a fixed process rate in the temperature interval of recrystallization. At the same time the temperature of transformation start slightly shifts towards lower temperatures with an increase in the cooling rate.

Based on the DSC data, it was suggested that phase recrystallization at a polymorphous transformation in titanium is realized by diffusionless (nucleation) and diffusion (growth) mechanisms running in overlapped temperature intervals.

Criteria, that can be used to reasonably classify calorimetric effects on DSC curves as phase transformations of the first kind are: analysis of shape of endothermic (exothermic) peak or comparison of extreme points on DSC and DDDSC curves.

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Conflict of interest

The authors declare that they have no conflict of interest.

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