

TITANIUM AND ITS ALLOYS

MECHANISMS OF THE ISOTHERMAL DECOMPOSITION OF β -SOLID SOLUTION IN TWO-PHASE MARTENSITIC TITANIUM ALLOYS

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A study of processes occurring during undercooling and isothermal exposure of titanium alloys and plotting isothermal decomposition diagrams for undercooled β -solid solution, similar to diagrams for the decomposition of an undercooled austenitic steel, makes it possible not only to reveal the mechanisms of phase and structural transformations in titanium alloys, but it has considerable practical application. It is necessary for determining rational heat-treatment schedules for titanium alloys and determining their thermal stability at different temperatures. The latter is particularly important since many titanium alloys operate at quite high temperatures, and they should not undergo phase transformations which lead to a reduction in mechanical properties.

Very many studies of the thermal stability of titanium alloys have been carried out, although the majority of them are devoted to highly alloyed titanium. Isothermal decomposition of metastable β -solid solution proceeds by two mechanisms: $\beta_{\text{met}} \rightarrow \alpha + \beta$ -transformation during exposure at high temperature and $\beta_{\text{met}} \rightarrow \beta + \omega$ -transformation at low temperature. Isothermal decomposition of undercooled β -solid solution in medium-alloy two-phase martensitic titanium has been studied much less. Diagrams plotted [1-5] indicate decomposition of undercooled β -solid solution with precipitation of α -phase at temperatures above M_s and decomposition of α'' -martensite ($\alpha'' \rightarrow \alpha + \beta$ -transformation) at temperatures below M_s . Consideration was given in [6] to processes occurring in undercooled alloys Ti-10% V and Ti-10% V-3% Al from 900°C to a temperature corresponding to the martensitic $\beta \rightarrow \alpha''$ -transformation range. Almost all of the alloys studied were heated to a β -region temperature, whereas in practice during heat-treatment titanium alloys are often heated to a temperature in the two-phase $\alpha + \beta$ -region.

The present work concerns a study of transformations occurring during isothermal exposure of two-phase martensitic alloys VT3-1, VT6, VT8, VT9, and VT23 undercooled from different temperatures of the $\alpha + \beta$ - and β -regions. Chemical composition of the alloys is given in Table 1.

In each of these alloys during quenching from certain temperatures there is a martensitic $\beta \rightarrow \alpha''$ -transformation. The minimum temperature from which on quenching orthorhombic α'' -martensite forms is called the critical temperature. Quenching from the critical temperature leads to formation of the maximum amount of α'' -martensite for a given alloy composition and the greatest amount of residual β -phase [7]. With quenching from a temperature below the critical level, polymorphic transformation does not occur; in this case the high-temperature $\alpha + \beta$ -structure is retained. Quenching from a temperature above the critical level leads to an increase in the amount of α'' -martensite in the structure, a reduction in the amount of residual β -phase, and impoverishment of β -stabilizing elements in them [7].

Phase transformation kinetics were studied by x-ray structural analysis in a DRON-1.5 diffractometer in copper K_α -radiation, and the modulus of normal elasticity, hardness, and mechanical properties were determined after heat treatment under different conditions. Tensile tests were performed on standard specimens (GOST 1497-73), and impact strength was determined on specimens with a U-shaped notch. Specimens used to measure elasticity modulus were 8 mm in diameter and 180 mm long, and for x-ray structural analysis they were 20 mm in diameter and 3 mm thick. All of the specimens were furnace heated to a specific temperature, soaked for 1 h, transferred to a salt bath with a temperature from 100 to 700°C, held at this temperature for different periods, and then water-cooled.

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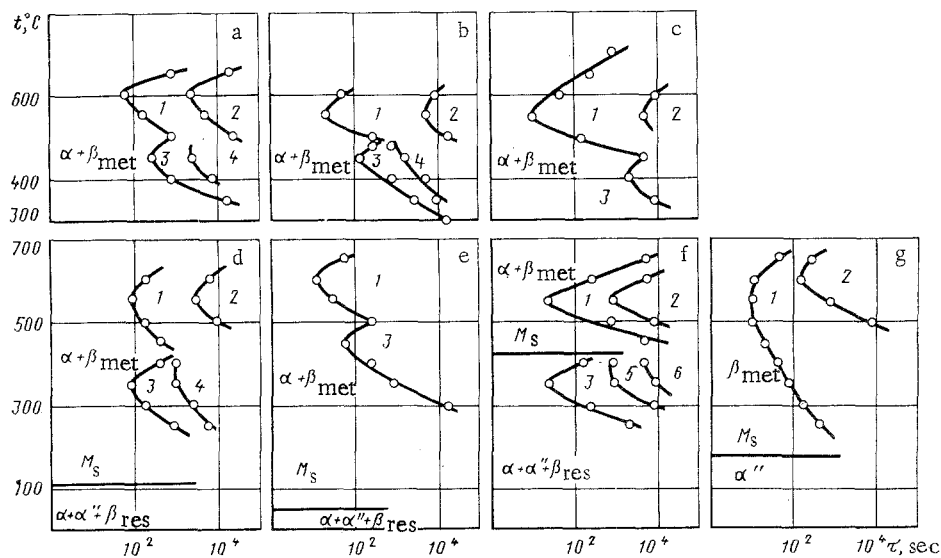


Fig. 1. Diagrams for isothermal decomposition of β -solid solution of alloys VT-8 (a, f), VT23 (b, c, e, g) and VT3-1 (d) undercooled from 820°C (a, c), 780°C (b), 900°C (d), 840°C (e), and 940°C (f, g): 1) $\beta_{\text{met}} \rightarrow \alpha + \beta_{\text{enr}}$; 2) $\alpha + \beta_{\text{enr}}$; 3) $\beta_{\text{met}} \rightarrow \alpha''$; 4) $\alpha'' \rightarrow \beta_{\text{enr}} + \alpha''_{\text{imp}}$; 5) $\alpha'' \rightarrow \alpha + \alpha''_{\text{enr}}$; 6) $\alpha''_{\text{enr}} \rightarrow \beta_{\text{enr}} + \alpha$.

TABLE 1

Alloy	Content of elements, wt. %			
	Al	Mo	Fe	Si
VT6	6.3	—	0.32	0.05
VT8	6.8	2.9	0.16	0.30
VT9	6.8	3.1	0.13	0.32
VT3-1	6.4	2.7	0.37	0.26
VT23	6.3	2.6	0.74	0.25

Note. In addition, alloys VT6 and VT23 contained 4.2 and 4.3% V, respectively, alloys VT3-1 and VT23 contained 1.6 and 1.2% Cr, respectively, and alloy VT9 contained 1.6% Zr.

Diagrams for isothermal decomposition of undercooled β -solid solution for the test alloys were built up on the basis of x-ray structural analysis results, i.e., from the data for the change in crystal lattice parameters for α -, β -, and α'' -phases and the relative intensity of lines for these phases in proportion to their amount.

An increase in heating temperature up to the two-phase region leads to a change in the degree of alloying for high-temperature β -solid solution, and this has an effect on its isothermal decomposition. By varying alloy heating temperature in the two-phase region, it is possible to obtain different types of isothermal decomposition diagram for undercooled β -solid solution. For two-phase martensitic alloys it is possible to obtain three types of diagram.

Isothermal decomposition diagrams for high-temperature β -solid solution of the first type are typical for alloys heated to a temperature in the two-phase region from which during quenching the $\alpha + \beta$ -structure is retained, i.e., the β -solid solution content corresponding to this heating temperature has a temperature for the start of the martensitic $\beta \rightarrow \alpha''$ -transformation below room temperature (Figs. 1a-c). The process of isothermal decomposition of undercooled β -phase alloys heated to these temperatures proceeds in two clearly defined stages having the form of C-shaped curves.

The low temperature stage of decomposition is intermediate transformation of undercooled β -solid solution with formation of orthorhombic martensite. Appearance of α'' -mar-

tensite precedes layering of the β -solid solution into impoverished and enriched areas. Decomposition of β -solid solution of the intermediate transformation type is also observed with continuous heating and tempering of quenched alloys [7, 8]. With quite prolonged exposure α'' -phase, being a product of intermediate transformation, decomposes with precipitation of β -phase enriched in alloying elements (Figs. 1a-c).

At higher isothermal exposure temperatures there is decomposition of β -solid solution with precipitation of α -phase whose particles originate and grow in impoverished areas formed during layering. Decomposition of β -solid solution by a diffusion mechanism with quite prolonged exposure is completed with formation of an $\alpha + \beta$ -structure close to the equilibrium situation. A diagram of this type is given schematically in [9].

By comparing diagrams for alloy VT23 heated to 780 and 820°C (Figs. 1b and c) it can be seen that with increasing heating temperature, i.e., a reduced level of alloying for high-temperature β -solid solution with transitional elements, C-shaped curves characterizing its decomposition kinetics are displaced in the direction of lower and shorter exposures. Consequently, an increase in heating temperature provides acceleration of undercooled β -solid solution decomposition.

The second type of diagram for isothermal decomposition of β -solid solution in two-phase alloys is typical for the case of heating to the critical temperature or close to it. Isothermal decomposition of undercooled β -solid solution in this case occurs in two stages at temperatures above M_s (Figs. 1d and e). At relatively low temperatures there is intermediate transformation of high-temperature β -phase with formation of α'' -martensite: $\beta_{met} \rightarrow \beta_{imp} + \beta_{enr} \rightarrow \alpha'' + \beta_{enr}$. With increasing exposure α'' -phase decomposes with precipitation of β -phase enriched in alloying elements. By comparing the diagrams presented in Figs. 1b, c, and e it can be seen that the curve describing the kinetics of intermediate transformation in alloy VT23 undercooled from 840°C is moved in the direction of shorter exposures in comparison with curves for the alloy undercooled from 780 and 820°C, i.e., an increase in heating temperature in this case accelerates decomposition of undercooled β -solid solution.

At high isothermal temperatures, decomposition of β -solid solution proceeds by a diffusion mechanism with precipitation of α -phase. This process precedes layering of the solid solution with formation of impoverished and enriched areas. Particles of α -phase originate and grow in impoverished areas. The diffusion arm of the isothermal diagram for undercooled β -solid solution decomposition in alloy VT23 heated to 840°C is the same as in the intermediate arm, and it is moved into the region of shorter exposures by comparison with alloy undercooled from a lower temperature.

With alloy undercooling to a temperature below that for the start of the martensite $\beta \rightarrow \alpha''$ -transformation, a structure of $\alpha + \alpha'' + \beta_{res}$ is formed. An increase in exposure in the martensitic range leads to an increase in the amount of α'' -martensite and a reduction in the amount of β -phase without changing crystal lattice parameters, i.e., without changing their composition. This indicates development of an isothermal martensitic $\beta \rightarrow \alpha''$ -transformation [10]. With certain exposure periods the isothermal martensite transformation dies out.

Comparison of diffraction pictures for specimens of alloy VT3-1 undercooled from 900°C after exposure for 30 sec at different temperatures showed that with increasing isothermal temperature the amount of β -phase retained in the alloy after water cooling increases significantly, and the amount of α'' -martensite decreases (Fig. 2). Apparently, short periods of exposure with alloy undercooled to a temperature above M_s causes thermal stabilization of high-temperature β -solid solution, as a result of which during subsequent water cooling the amount of α'' -martensite formed decreases in comparison with its amount after direct quenching from the heating temperature. With increased isothermal temperature the effect of β -solid solution stabilization is strengthened; isothermal exposure of the alloy for 30 sec at 500, 550, and 600°C completely stabilizes β -solid solution in relation to the martensitic $\beta \rightarrow \alpha''$ -transformation. With water cooling after this treatment α'' -martensite does not form, and the $\alpha + \beta$ -structure is retained. The possibility of thermal stabilization for high-temperature β -solid solution should be considered in selecting heat-treatment schedules for titanium alloys since the presence of metastable β -phase in the structure leads to phase transformations during operation of an article, and as a result of this the properties are unstable.

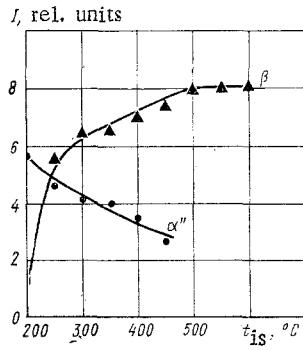


Fig. 2. Change in relative intensity of diffraction lines for β - and α'' -phases in alloy VT3-1 undercooled from $900^\circ C$ in relation to isothermal exposure temperature. Exposure time is 30 sec.

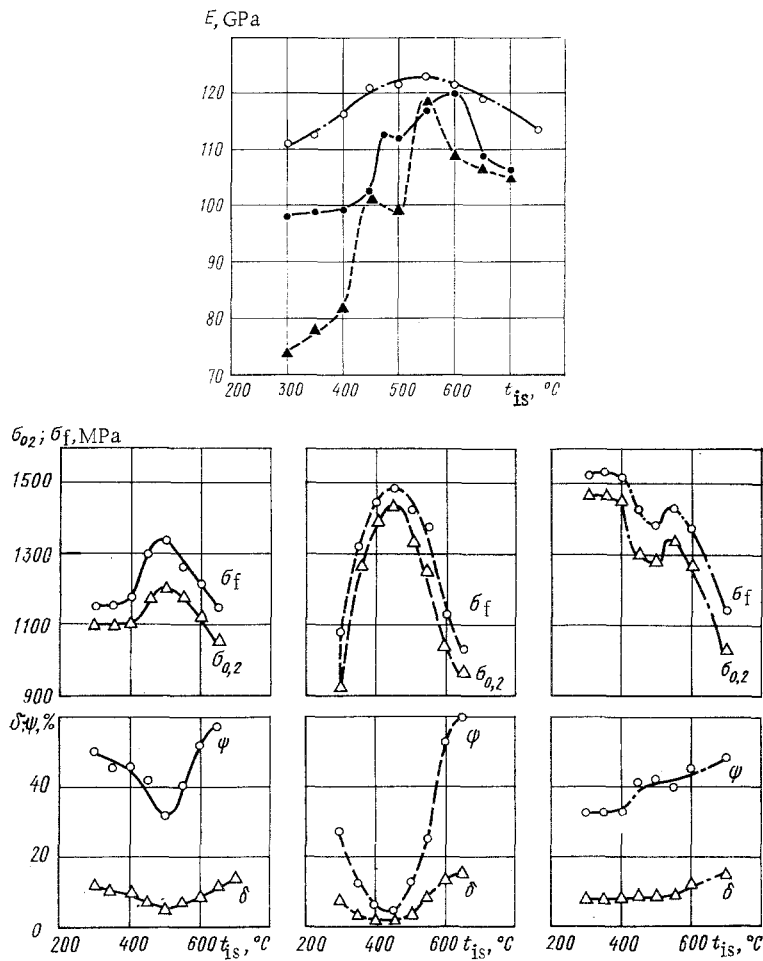


Fig. 3. Effect of isothermal exposure temperature on the mechanical properties and modulus of normal elasticity for alloy VT23 undercooled from $780^\circ C$ (solid lines) and from $820^\circ C$ (broken lines) and for alloy VT3-1 undercooled from $900^\circ C$ (dotted broken lines). Exposure time is 4 h.

Isothermal decomposition of undercooled β -solid solution of the third type, which is typical for alloys heated either to a temperature in the two-phase region close to the $(\alpha + \beta)/\beta$ boundary, or in the single-phase β -region, and having a quite high temperature for the start of the $\beta \rightarrow \alpha''$ -transformation, only occurs by a diffusion mechanism (see Figs. 1f and g). Two kinds of diagram of the third type are encountered depending on the position of the M_s point. For alloy VT8 which has a high martensite point M_s (in the range 400-450°C), with isothermal exposure in the martensite range after undercooling from 940°C there is intermediate transformation of residual β -phase, and then decomposition of α'' -martensite. The α'' -martensite formed in alloy VT8 during cooling from 940°C has a small degree of alloying, and its decomposition is accompanied by precipitation of α -phase and not β -phase as is observed in alloys heated to much lower temperatures [7]. Such diagrams for isothermal decomposition of undercooled β -solid solution have also been obtained for alloys VT6 and VT9 [11, 12]. For alloy VT23, which contains the most transitional elements (see Table 1) and even after heating to a temperature in the β -region (above 900°C) has an M_s point in the range 150-180°C, during isothermal exposure in this range there is no α'' -martensite decomposition (see Fig. 1g), but the isothermal martensitic $\beta \rightarrow \alpha''$ -transformation develops. In the same way as in alloy VT3-1 undercooled from 900°C, for alloys VT8, VT23, VT6, and VT9 during short-term isothermal exposure above M_s there is thermal stabilization of high-temperature β -phase. For example, an increase in exposure up to 1 min at 200°C for alloy VT23 undercooled from 940°C leads to the appearance of a small amount of residual β -phase in the structure, whereas with direct quenching from 940°C the alloy structure is only α'' -martensite. As a result of exposure at 200°C for 30 min or more the degree of β -solid solution stabilization achieved is such that the martensite transformation during subsequent water cooling is completely suppressed, and only high-temperature β -phase is retained in the alloy structure.

For alloy VT8 heated to 940°C exposure at any temperature above M_s in the region of β -solid solution stability causes its complete stabilization in relation to the martensitic $\beta \rightarrow \alpha''$ -transformation. Similar mechanisms are typical for alloys VT6 and VT9 [11, 12].

A schematic diagram for isothermal decomposition of β -solid solution similar to that presented in Fig. 1f was described in [9], but in this diagram a region of α'' -martensite decomposition occurring with undercooling below M_s comes before the region for residual β -phase decomposition. Results of our studies make it possible to correct the scheme proposed by the author of [9]; if apart from α'' -martensite there is high-temperature β -phase in the alloy it will decompose sooner than the α'' -martensite under any conditions, i.e., during tempering after quenching, during continuous heating, and during isothermal exposure of undercooled alloy [7, 8, 11, 12].

The decomposition process for undercooled β -solid solution has a marked effect on alloy properties. Development of intermediate transformation of metastable β -phase with formation of α'' -martensite followed by decomposition of martensite with separation of enriched β - or α -phase (depending on the degree of alloying for α'' -martensite) leads to marked strengthening, an increase in the modulus of normal elasticity, an increase in hardness, and a sharp reduction in alloy ductility characteristics (Fig. 3). Diffusion decomposition of high-temperature β -phase for the first stage and formation of an $\alpha + \beta$ -structure close to an equilibrium situation caused less alloy strengthening, but increased ductility. Maximum values for normal elasticity modulus are obtained after isothermal exposure at a temperature at which decomposition of high-temperature β -solid solution in the first stage proceeds at the maximum rate and is entirely complete (Fig. 3). This is explained by the formation during decomposition of β -solid solution of a large amount of α -phase for which a high elasticity modulus is typical. At lower and higher undercooling temperatures decomposition of metastable β -solid solution occurs more slowly and is often incomplete; less α -phase is formed in this way and as a result the E value is reduced.

Results of mechanical property determination for the test alloys showed that the properties of alloys undercooled to a temperature at which the rate for β -solid solution decomposition by the first stage is at a maximum are distinguished by considerable stability; an alloy after this treatment has a high strength as well as good ductility and impact strength. This is due apparently to formation of a large amount of dispersed α -phase particles uniformly distributed in the β -matrix. Isothermal treatment of undercooled alloys has an undoubted advantage compared with tempering quenched alloys since during tempering the acicular structure of α'' -martensite is retained to higher temperatures and this gives rise to

formation of orientated precipitates during tempering, which leads to a marked reduction in impact strength and ductility, as well as worse property stability. As the studies carried out have shown, the optimum combination of strength, impact strength, and ductility is obtained after heating alloys to a temperature close to the critical value at which the decomposition rate for high-temperature β -solid solution in the first stage is at a maximum. For example, alloy VT3-1 after heating to 900°C and exposure for 1 h, undercooling to 550°C with exposure for 2 h and air cooling has the following properties: $\sigma_f = 1060-1070$ MPa, $\sigma_{0.2} = 1040-1050$ MPa, $\delta = 18-20\%$, $\psi = 51-57\%$, $a_1 = 0.56-0.65$ MJ/m², $a_c = 0.27-0.33$ MJ/m².

CONCLUSIONS

1. The kinetics of isothermal decomposition of high-temperature β -phase for two-phase martensitic titanium alloys after undercooling from different temperatures are described by typical C-shaped curves; this decomposition may have one or two stages above the M_s point. The type of isothermal decomposition diagram for this phase is governed by the alloy heating temperature and the temperature for the start of the martensite $\beta \rightarrow \alpha''$ -transformation.

2. An increase in alloy heating temperature into the two-phase region leads to a shift in C-shaped curves in the direction of higher temperatures and shorter exposures, i.e., the decomposition process is accelerated.

3. With isothermal exposure for undercooled alloys in the martensite range it is possible for the martensitic $\beta \rightarrow \alpha''$ -transformation to occur. With undercooling to a temperature above M_s high-temperature β -solid solution is stabilized and the martensitic $\beta \rightarrow \alpha''$ -transformation does not occur during subsequent cooling.

4. Mechanical properties of the alloys are governed by the mechanism of high-temperature β -phase decomposition. Decomposition by an intermediate mechanism provides high alloy strength, although the ductility is lower. As a result of β -solid solution decomposition by a diffusion mechanism, an alloy has higher ductility with quite high strength. The optimum combination of strength and ductility as well as high property stability is obtained as a result of isothermal exposure for an alloy undercooled from the two-phase region to a temperature corresponding to the maximum rate for β -solid solution decomposition in the first stage.

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