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## Abstract

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# INVESTIGATION OF PHASE EQUILIBRIUM IN THE TERNARY SYSTEM TITANIUM–ALUMINUM–OXYGEN

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Aluminum is the most important alloying element of titanium in the creation of alloys suitable for service under high-temperature conditions. Alloying binary titanium—aluminum alloys with oxygen leads to a significant increase in the temperature of the allotropic transformation ([1]-[3]). Aluminum and oxygen lead to an increase in the strength of the chemical bond when titanium is alloyed within the limits of existence of solid solutions based on $\alpha$-titanium ([4], [5]), and both reduce the rate of plastic deformation at elevated temperatures ([6], [7]).

The study of the interaction of titanium during simultaneous alloying with aluminum and oxygen is of great practical importance in connection with questions concerning the prospects for the use of alloys based on transition metals alloyed with refractory oxides. Such materials are finding ever broader application, since they prove to be stable up to very high temperatures. As examples one may mention alloys based on nickel alloyed with thorium oxide, chromium alloys alloyed with aluminum oxide, and, finally, alloys of the SAP type ([8]-[10]).

The interaction of titanium with aluminum and oxygen has a number of special features. Titanium, as one of the metals of the transition groups with the maximum number of unfilled levels in the *d*-shell, is capable of forming, over wide concentration ranges, solid solutions with other elements and, in particular, with aluminum and oxygen. At the same time, aluminum and oxygen, along with the formation of limited solid solutions in $\alpha$-titanium, are capable of forming with it a number of metalloids.

One of the stages in the investigation of phase equilibrium in the titanium—aluminum—oxygen system was the development of a method for the simultaneous introduction of aluminum and oxygen into titanium. Several procedures were tested, including the introduction of aluminum and oxygen in the form of aluminum oxide, in the form of a titanium—oxygen master alloy and pure aluminum, and also in the form of two master alloys, titanium—oxygen and titanium—aluminum.

As a result of microstructural and chemical analysis of the alloys obtained, carried out in order to check the homogeneity and the amount of alloying elements introduced, it was concluded that the most expedient procedure is the introduction of oxygen and aluminum in the form of two binary master alloys. In this case melting proceeded smoothly, and the alloys obtained were homogeneous in chemical composition.

The alloys were prepared by melting in an arc furnace with a nonconsumable tungsten electrode in an atmosphere of purified helium.

The starting materials for preparing the alloys were iodide titanium (99.9%) and titanium master alloys with 15.8 wt.% $O_2$, as well as a titanium master alloy with 35.8 wt.% aluminum.

Among the alloys prepared by the indicated method, some proved to contain cracks, and many disintegrated into pieces during crystallization from the liquid state. A practically important group of alloys rich in titanium and

possessing sufficient plasticity at room temperature. These composition regions are limited to 2-3 wt.% oxygen and up to 15 wt.% aluminum.

The alloys were prepared along sections parallel to the titanium-aluminum side with a constant oxygen content of 1; 5; 10; 14.5 and 25 at.%, and also along sections passing through pure titanium and the compound $Al_2O_3$, through the compounds $Ti_3Al$ and $Ti_3O$, and also through the compounds $Ti_6Al$ and $Ti_6O$. In all, alloys of 120 different compositions were prepared.

Examination of the structure of the cast alloys showed that, on the $Ti—Al_2O_3$ section, within the limits studied, only two phases are present, which indicates the existence of a quasi-binary section. One of the stages in solving the problem of triangulation of the ternary constitution diagram was to establish the character of the phase equilibrium in the $Ti—Al_2O_3$ system.

There are no data in the literature on the character of phase equilibrium in the $Ti—Al_2O_3$ system, nor in the titanium—aluminum—oxygen system.

Attaching great importance to the question of the interaction of titanium with aluminum and oxygen in the ratio corresponding to the compound $Al_2O_3$, an investigation was carried out of alloys of the titanium—aluminum—oxygen system along the $Ti—Al_2O_3$ section in the concentration range from 0.5 to 30 wt.% (16.8 mol.%) $Al_2O_3$.

The alloys lying on the $Ti—Al_2O_3$ section, after casting, were subjected to homogenizing annealing and additionally to annealing at 600, 800, 1000 and 1200° for 400, 300, 100 and 2 hours, respectively, followed by quenching in ice water. The homogenizing annealing was carried out in a vacuum of $10^{-3}$—$10^{-4}$ mm Hg according to the following schedule: 1300°—10 h, 1200°—100 h, 1100°—50 h, 800° —50 h, followed by slow cooling to room temperature over 48 h.

In the work, methods of thermal and microscopic analysis were used, as well as measurements of microhardness, electrical resistivity, and thermo-e.m.f.

The temperature at the onset of melting was determined with an optical pyrometer on specimens with a hole of internal diameter 1 mm and depth 2-3 mm after prolonged homogenizing annealing at 1400°.

The results of studying the solidus temperature of alloys of the $Ti{-}Al_2O_3$ system showed that the temperature at which titanium begins to melt increases when it is alloyed with aluminum oxide from 1675 to 1880° for an alloy with 4 wt.% $Al_2O_3$. Further alloying of titanium with aluminum oxide does not lead to a change in the temperature at the onset of melting and remains at the level of $1880 \pm 20°$.

Microscopic analysis of alloys quenched from 600 and 800° showed that alloys containing up to 3 wt.% $Al_2O_3$ are single-phase. In the structure of alloys with 5 wt.% $Al_2O_3$, a second phase appears, $Ti_x(Al_2O_3)_y$, the amount of which increases with increasing $Al_2O_3$ content. In polarized light the second phase appears luminous and can easily be identified in the alloy structure.

Alloys of compositions up to 3 wt.% $Al_2O_3$ can be forged at a temperature of 1200° without forming cracks.

The results of studying the microhardness of alloys of the $Ti{-}Al_2O_3$ system quenched from 600; 800; 1000 and 1200° showed that, within the limits of the single-phase region, the microhardness increases, and upon transition into the two-phase region remains practically constant, which indicates the solubility of aluminum oxide in $\alpha$-titanium at 600° of about 3 wt.%, at 800° 4, at 1000° 4.5, and at 1200° 6 wt.%.

Analysis of the change in electrical resistivity of alloys of the $Ti{-}Al_2O_3$ system quenched after annealing at 800° shows that alloying titanium with aluminum oxide up to 3 wt.% leads to a smooth increase in the electrical resistivity of the alloys; when aluminum oxide is introduced in an amount

with 5% the electrical resistivity increases by more than a factor of two compared with the alloy containing 3 wt.% $Al_2O_3$. Further alloying of titanium with aluminum oxide leads to an even greater increase in electrical resistivity, which reaches a value of 520 $\mu$ohm · cm at 7% $Al_2O_3$. Thus, the change in electrical resistivity as a function of the composition of alloys of the $Ti{-}Al_2O_3$ section confirms the data from measurements of the microstructure and microhardness ([11]).

Figure 1 shows the phase diagram of the $Ti{-}Al_2O_3$ system. The equilibrium diagram of the quasibinary $Ti{-}Al_2O_3$ system reveals a peritectic and peritectoid character of interaction. Alloying titanium with aluminum oxide raises the allotropic transformation and melting temperatures of titanium. The temperature of the peritectic horizontal is $1880 \pm 20°$, and the temperature of the peritectoid horizontal is about 1300°. Aluminum oxide dissolves in $\alpha$-titanium at 600° in an amount of 3 wt.%, and at the temperature of the peritectoid horizontal in an amount of about 7 wt.%. Microscopic analysis of alloys quenched from 800° showed the following picture of phase equilibrium in the ternary system

Fig. 1. Phase diagram of the Ti—$Al_2O_3$ system

Figure 1: Fig. 1. Phase diagram of the Ti—$Al_2O_3$ system

Fig. 2. Isothermal section of the titanium—aluminum—oxygen system at 800°

Figure 2: Fig. 2. Isothermal section of the titanium—aluminum—oxygen system at 800°

titanium—aluminum—oxygen.

**Fig. 1. Phase diagram of the Ti—$Al_2O_3$ system**

Figure 2 shows an isothermal section of this system at a temperature of 800°, i.e., below the temperature of the allotropic transformation of titanium. From consideration of this figure it follows that at this temperature the section contains five single-phase regions. The extent of the $\alpha$-solid solution is limited on the titanium—aluminum side to 8 at.% and on the titanium—oxygen side to 8 at.%. There is also a limited region of solid solutions based on the compound $Ti_6O$, as well as regions based on the compounds $Ti_6Al$, $Ti_3Al$, and $Ti_2Al$. The solid-solution region based on $\alpha$-titanium is separated by the two-phase region $\alpha + Ti_x(Al_2O_3)_y$ from regions alloyed mainly with aluminum and oxygen.

**Fig. 2. Isothermal section of the titanium—aluminum—oxygen system at** 800°

In addition, the section contains two-phase regions $\alpha + Ti_6Al$ and $\alpha + Ti_6O$, which separate the single-phase regions based on the compounds $Ti_6Al$ and $Ti_6O$ from the neighboring solid solution based on $\alpha$-titanium, as well as the region $\alpha + Ti_x(Al_2O_3)_y$.

Figure 3 presents the isothermal section of the ternary system at a temperature of 1000°.

It follows from consideration of this figure that at this temperature there are three single-phase regions: the $\alpha$-solid solution, the $\beta$-solid solution, and the solution based on the compound $Ti_3Al$. It should be noted that the two-phase region $\alpha + Ti_x(Al_2O_3)_y$ expands considerably in comparison with the section at 800°. In this section there is one more two-phase region, $\alpha + \beta$. In addition, it should be noted that in this section, in comparison with the preceding section, the two-phase regions that had previously separated the solid solutions based on the compounds $Ti_6Al$ and $Ti_6O$ from the adjacent single-phase region of the $\alpha$-solid solution have disappeared.

Fig. 3. Isothermal section of the titanium—aluminum—oxygen system at 1000°

Figure 3: Fig. 3. Isothermal section of the titanium—aluminum—oxygen system at 1000°

**Fig. 3. Isothermal section of the titanium—aluminum—oxygen system at** 1000°

The section at 1200° differs practically in no way from the section at 1000°.

From consideration and comparison of the isothermal sections presented in Figs. 2 and 3, it may be concluded that alloying titanium—aluminum alloys with oxygen, already in an amount of 1-2 at.% , leads to the disappearance in the ternary titanium—aluminum—oxygen system of the compound $Ti_6Al$. Thus, the influence of the third element, in the present case oxygen, leads not to stabilization of this compound but, on the contrary, to its disappearance in the system.

The same may be said of the influence of oxygen on the stability of the compound $Ti_3Al$. It also disappears at a temperature of 800° when alloyed with 3-4 at.% oxygen. This fact is of great importance for explaining the discrepancies in data on the character of phase equilibrium in the titanium—aluminum system in various works.

At present, in the literature on the titanium—aluminum system there are five fundamentally different variants of the phase diagram in this system. It is possible that the differences in the character of the interaction between titanium and aluminum are explained by the different purity of the starting materials, as well as by the possibility of introducing additional impurities during melting and heat treatment. In this connection it is interesting to note that the first variant of the phase diagram of the titanium—aluminum system assumed the presence of neither the compound $Ti_6Al$ nor $Ti_3Al$. Investigations of later years on purer starting materials led to a complete alteration of the earlier variant of the diagram. However, even up to the present time this question has not been finally resolved.

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