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1963

SovietRxiv

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Abstract

Full Text

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ON THE FORMATION OF THE COMPOUNDS Ti_6O AND Ti_3O IN THE TITANIUM-OXYGEN SYSTEM

(Presented by Academician A. A. Bochvar, January 16, 1963)

The equilibrium diagram in the titanium-oxygen system is characterized (1–3) by a wide region of formation of solid solutions based on α-titanium and by the existence of the compounds TiO, Ti_2O_3, and TiO_2.

In the study of alloys of titanium with oxygen by the method of X-ray structural analysis (4,5), and also by the electrical-resistivity method (6), an anomalous change in the properties of the alloy was noted at a content in it of about 25 at.% oxygen; on this basis, suggestions were made concerning the possible formation of an ordered state of the alloy corresponding to the composition Ti_3O. It was noted at the same time that the ordered state is unstable at temperatures not above 400° (4). However, in work (7), the continuous character of the change in the crystal structure of a chemical compound of variable composition, of the α-phase type of the titanium-oxygen system, was again confirmed.

It should be noted that, on the basis of an analysis of data on the interaction of metals of Group IV of the periodic system with oxygen (8), one of the authors of the present article proposed the possible existence of the compound Ti_3O in this system. The considerations advanced concerning suboxide compounds of titanium with a metallic character of bonding follow from an analysis of the properties of titanium (9) and its tendency to form metallic compounds with electronegative elements. A clear example in this respect is the formation, from an α-solid solution of aluminum in titanium, of the compounds Ti_3Al and Ti_6Al (10).

Fig. 1. Phase diagram of the titanium-oxygen system (according to data of (1))

In subsequent experimental investigations, on the basis of very incomplete studies of the structure of scale (11) and of the dependence of the electrical resistance

Figure 3

Figure 2: Figure 3

of cast alloys on composition ([12]), suggestions were also made concerning the possible existence of the compounds Ti_6O and Ti_3O. On the basis of the foregoing, it may be concluded that the character of the chemical interaction of titanium with oxygen is far from as simple as follows from the phase diagram shown in Fig. 1.

We carried out a detailed investigation of alloys of the titanium-oxygen system in the range from 0 to 35 at.% oxygen.

The alloys were prepared by melting in an arc furnace with a nonconsumable electrode in an atmosphere of argon. The starting material for preparing the alloys was iodide titanium (99.9% Ti), the principal impurities of which were:

Mg 0.01%; Si 0.01%; Al 0.02%; Fe and Ni less than 0.01%; Cr 0.01%; C 0.015%; O_2 0.02%; N_2 0.02. Oxygen was introduced into the alloys in the form of a titanium—oxygen master alloy with a content of the latter of 15.8 wt. %. The master alloy was prepared by melting in an arc furnace compacts pressed from titanium and titanium dioxide of chemically pure grade, containing 99.93% TiO_2. In the manner described above, alloys were prepared with contents of 0, 1, 3, 5, 7 at. % oxygen, and thereafter at intervals of one percent up to 35 at. %. Alloys of 10 compositions were analyzed by the vacuum-melting method. In this, good agreement was obtained between the oxygen content calculated from the charge and the data of chemical analysis.

Fig. 3. Change in microhardness (*a*), electrical resistivity (*b*), and thermoelectric power (*c*) as a function of the composition of titanium—oxygen alloys after quenching from various temperatures.

The cast alloys were subjected to a homogenizing anneal in vacuum at 800° for 1000 h. After annealing at 800°, the alloys were annealed at 400, 600, 800, 850, 1000, and 1400° for 600, 400, 1000, 100, 100, and 2 h, respectively, followed by quenching in ice water. To study the chemical interaction, the following methods were used: the physicochemical analysis method developed in the works of N. S. Kurnakov, involving the construction of chemical composition—property diagrams[13,14]; microscopic and qualitative X-ray structural analyses; measurement of microhardness, electrical resistivity, and thermoelectric power. The microhardness was measured on a PMT-3 instrument under a load of 200 g, according to the procedure given in Ref. [15]. As an etchant for revealing the microstructure of the alloys, a mixture consisting of 20 parts HF, 20 parts HNO_3, the remainder glycerin (by volume), was used. The electrical resistivity of the alloys was measured by the probe method, since alloys containing more than 10 at. % oxygen proved brittle and did not lend themselves to any mechanical treatment. Specimens for measuring electrical resistivity were prepared by casting the alloys into molds 6 mm in diameter. The electrical resistivity was

Microstructures of titanium alloys with oxygen: a –5% oxygen, quenched after annealing at 600°, 500×; b –10%, quenched after annealing at 600°, 500×; c –30%, quenched after annealing at 800°, 200×

Figure 3: Microstructures of titanium alloys with oxygen: a –5% oxygen, quenched after annealing at 600°, 500×; b –10%, quenched after annealing at 600°, 500×; c –30%, quenched after annealing at 800°, 200×

Fig. 4. Phase diagram of the titanium–oxygen system (according to the data of the present work)

Figure 4: Fig. 4. Phase diagram of the titanium–oxygen system (according to the data of the present work)

measured on specimens 25-30 mm high. The thermoelectric power was measured on specimens previously used for studying electrical resistivity, in contact with copper.

Fig. 2. Microstructures of titanium alloys with oxygen:
a –5% oxygen, quenched after annealing at 600°, 500×;
b –10%, quenched after annealing at 600°, 500×;
c –30%, quenched after annealing at 800°, 200×.

X-ray structural analysis was carried out on powders prepared from specimens for microstructural analysis and heat-treated at 400, 600, 800, and 1000°. The radiographs were taken in copper radiation with a nickel filter, on two films. Investigation of titanium–oxygen alloys by the methods indicated above led to the following results.

Microscopic analysis of alloys quenched after annealing at 400° showed that alloys containing less than 10 and more than 22 at. % oxygen were single-phase. In the structure of alloys with contents of 10, 11, 12, and 13%, and also from 16 to 21% oxygen, a second phase appeared; alloys with 14 and 15% oxygen were single-phase. Alloys quenched from 600° have approximately the same structure as after quenching from 400°.

Fig. 4. Phase diagram of the titanium–oxygen system
(according to the data of the present work)

In Fig. 2*a*, *b* is shown the microstructure of titanium alloys with oxygen, with contents of the latter of 5 and 10 at. % after quenching from 600°; the alloy with 5% oxygen has a polyhedral structure, and that with 10% has a two-phase structure. An alloy with 25% (up to 30 at. %) oxygen is characterized by the presence of slip lines in the structure. Microscopic analysis of alloys quenched from 800° showed that only alloys with 13, 14, and 16% oxygen were two-phase; the remaining alloys had a polyhedral structure. It should be noted that alloys containing more than 10 at. % oxygen are all covered with cracks and pores, the number of which increases with increasing oxygen content. Alloys quenched from 850° had a single-phase structure, with the exception of the alloy with 25% oxygen, which at all quenching temperatures retains slip lines.

In Fig. 3, the results of measurements of microhardness (*a*), electrical resistivity (*b*), and thermoelectromotive force of the alloys (*c*) quenched from various temperatures are presented in the form of composition—property diagrams. Analysis of the microhardness curves of titanium alloys with oxygen quenched from 400 and 600° shows that on the microhardness—composition curves two singular minima are observed, corresponding to compositions of 14.5 and 25% oxygen.

The isotherm at 800° has, at the composition 14.5%, a noticeable bend in the curve and a clearly expressed minimum at the composition 25 at.% oxygen. On the isotherms at 1000 and 1400° the microhardness-composition curves have singular minima only at the composition with 25% oxygen.

Figure 3b presents the dependence of electrical resistivity on the composition of alloys quenched after holding at 800, 1000, and 1400°. Examination of these dependences for alloys quenched from 800° shows that the electrical resistivity rises sharply from 45.8 $\mu\Omega$/cm for pure titanium to 168 $\mu\Omega$/cm for the alloy with 10% oxygen. At 15% the electrical-resistivity curve rises sharply upward, reaching 466 $\mu\Omega$/cm; it is followed by a rise to 500 $\mu\Omega$/cm for the alloy with 22% oxygen. The alloy with 25% has a resistivity of 150 $\mu\Omega$/cm.

Analysis of the curve for the dependence of the electrical resistivity of alloys quenched from 1000 and 1400° on composition shows the presence of a singular minimum at 25% oxygen. Figure 3 presents the dependence of the thermoe.m.f. of titanium alloys on the oxygen content in a couple with copper after quenching from 800, 1000, and 1400°. Examination of this dependence for alloys quenched from 800° shows that the thermoe.m.f. decreases sharply from pure titanium (30 mV/deg) to the composition with 14% oxygen (−78 mV/deg). It should be noted that at 5 at.% oxygen the thermoe.m.f. changes sign, which indicates a change in the type of conductivity from hole to electronic. On the isotherms at 1000 and 1400° the minimum is retained only for the composition with 25% oxygen. Preliminary X-ray structural-analysis data show that the alloy of composition 25 at.% oxygen at temperatures up to 1000° has one superstructural line, while no superstructural lines were found on the alloy of composition 14.5% oxygen.

Thus, on the basis of the results of microstructural analysis and analysis of the composition-property diagrams in the investigated concentration range, the presence has been established of two special points corresponding to the compositions of the compounds Ti_6O and Ti_3O. Judging from the character of the chemical composition-property diagrams at 800°, and also on the basis of microscopic-analysis data, it may be concluded that the compound Ti_6O is stable up to a temperature of 820-830°. The compound Ti_3O with an ordered structure is apparently stable above 1400°, since the singular character of the composition-property diagrams at this temperature remains unchanged.

In accordance with the results of the present investigation, Fig. 4 gives a new equilibrium phase diagram for the titanium-oxygen system. Examination of this diagram shows that in the titanium-oxygen system two compounds, Ti_6O and Ti_3O, are formed from α-solid solutions.

The new compounds Ti_6O and Ti_3O established in the present work are of great importance for studying equilibria in complex titanium systems with oxygen and for clarifying the influence of oxygen on the properties of titanium and its alloys.

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Received
9 I 1963

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