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Abstract

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CHEMISTRY

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INVESTIGATION OF CERTAIN STRENGTH CHARACTERISTICS OF THE CHEMICAL BOND IN THE COMPOUNDS Ti_6O AND Ti_3O FORMED FROM α-SOLID SOLUTIONS OF THE TITANIUM-OXYGEN SYSTEM

(Presented by Academician I. I. Chernyaev, 4 VII 1963)

The authors have carried out a detailed investigation of the nature of the phase equilibrium of alloys of the titanium-oxygen system in the concentration range from 0 to 35 at.% (^{1}), which showed that the earlier existing views (^{2}) concerning the presence of a broad region of α-solid solutions are incorrect. It proved that in this system the compounds Ti_6O and Ti_3O are formed from α-solid solutions during prolonged annealing (see Fig. 1a). The compound Ti_6O is stable up to 820–830°, and the stability of the compound Ti_3O is presumably above 1400° (^{1}).

We have studied certain strength characteristics of the chemical bond of titanium alloys with oxygen in the region of solid solutions based on α-titanium.

The thermal expansion of Ti—O alloys was investigated in the temperature range up to 800° and over a wide concentration range. This property is important in assessing the strength of solids under conditions of elevated temperatures, and also makes it possible to estimate such important properties as the elastic modulus, the characteristic temperature, and the mean-square displacements of atoms from the equilibrium position, which are directly related to the strength characteristic of the chemical bond in metallic alloys (^{3}, ^{4}). The alloys were prepared by melting in an arc furnace with a nonconsumable electrode in an argon atmosphere. The starting materials for preparing the alloys were iodide titanium (99.9% Ti), the main impurities of which were: Mg 0.01%; Si 0.01%; Al 0.01%; Fe and Ni less than 0.01%; Cr 0.015%; O_2 0.01%; N_2 0.01%, and titanium dioxide with a content of 99.93% TiO_2.

(Figure: Figure 1)

Fig. 1. Change in thermal expansion (b) as a function of the composition of alloys of the titanium-oxygen system, the coefficient of linear expansion and the elastic modulus (c), in comparison with the equilibrium state diagram (a)

Oxygen was introduced into the alloys in the form of a master alloy with an oxygen content of 15.8 wt.%. The master alloys were prepared by melting in an arc furnace rods pressed from titanium and titanium dioxide.

By the method described above, alloys were prepared with oxygen contents of 0, 3, 5, 10, 15, 18, 20, 23, 24, 25, 26, 28, and 32 at.%. The resulting alloys—

were subjected to chemical analysis by the vacuum-fusion method. The analytical results showed good agreement between the oxygen content in the charge and the chemical-analysis data. The cast alloys were subjected to prolonged annealing for 1000 h at 800° and quenched from this temperature into ice water.

Thermal expansion of the alloys was studied on specimens 6 mm in diameter and 25–30 mm high, using an indicator dilatometer with a scale division of 1 μ (^{5}), in the temperature interval from room temperature to 800°. Heating was carried out at a rate of 4 deg/min.

In comparison with the equilibrium phase diagram of titanium—oxygen (Fig. 1a), Fig. 1b shows the isotherms $\Delta l/l$ as a function of composition at 100, 200, 300, 400, 500, 600, 700, and 800°.

From consideration of this graph it follows that all isotherms have a qualitatively similar character. Initially, upon alloying titanium with oxygen, a certain decrease in thermal expansion is observed at each given temperature. The composition Ti_6O (14.5 at. %) corresponds to a relatively weakly expressed minimum. A further increase in oxygen content leads to an increase in thermal expansion up to 23 at. % oxygen, after which there is a sharp drop. The composition Ti_3O (25 at. %) corresponds to a sharply expressed singular minimum of $\Delta l/l$.

(Figure: Fig. 2. Dependence of the value of the elastic modulus, determined by Frenkel' s formula, on the oxygen concentration in the solid solution)

Fig. 2. Dependence of the value of the elastic modulus, determined by Frenkel' s formula, on the oxygen concentration in the solid solution

From these data the values of the coefficient of thermal expansion α were calculated; its dependence on composition for the temperature interval 20–100° is shown in Fig. 1c. It follows from this figure that the character of the concentration dependence of α is qualitatively analogous to the dependence of $\Delta l/l$ on composition shown in Fig. 1b. The data obtained on the thermal expansion of alloys of the titanium—oxygen system make it possible to estimate the elastic modulus over a wide concentration interval. Such an estimate is very useful, since experimental determination of the elastic modulus of brittle alloys with high oxygen content is a difficult experimental problem.

As was shown by Frenkel (^{6}), the coefficient of thermal expansion is related to the elastic modulus by the following relation:

$$E = \frac{k}{\alpha a^3}, \tag{1}$$

where k is Boltzmann' s constant, α is the coefficient of thermal expansion, and a is the shortest interatomic distance in the crystal lattice of α-titanium. In

(7) it was noted that this formula gives the correct order of magnitude, but that, in order to obtain a quantitative dependence in each particular case, the introduction of an empirical proportionality coefficient is required.

On the basis of the values of α obtained in the present work and the results of (8) on determining α with the aid of Frenkel' s formula, calculations were made of the elastic modulus E_{calc} of Ti–O alloys of various compositions; these showed that in the concentration interval from 0 to $\sim$ 10 at. % oxygen the elastic modulus is a linear function of concentration (Fig. 2)*.

* In Fig. 2 the dependence of E_{calc} on composition is given only up to 3 at. % oxygen, because this graph is used as a working graph in determining the empirical coefficient in the concentration interval from 0 to 2 at. %.

The obtained values of E_{calc} for pure titanium proved to be lower than the experimentally found E_{exp} (9), which indicated the need to introduce an empirical coefficient.

To determine the magnitude of this coefficient we used the data of Graft' s work (10) on the effect of oxygen on the elastic modulus of titanium in the concentration interval from 0 to 1.7 at.%.

Table 1

No. in order	Oxygen content, at.%	E_{exp}	E_{calc}	$\frac{E_{\text{exp}}}{E_{\text{calc}}}$
		kg/cm^2 · 10^{-6}		
1	0.00	1.14	0.7716	1.475
2	0.10	1.15	0.7745	1.480
3	0.33	1.13*	0.7800	1.450
4	1.20	1.18	0.8020	1.475
5	1.48	1.19	0.8080	1.475
6	1.77	1.20	0.816	1.475

* Reduced titanium sponge.

Table 1 gives the values of E_{exp}, taken from (10), and E_{calc}, obtained for alloys of the same compositions from the graph shown in Fig. 2.

Comparison of these data showed that the ratio between E_{calc} and E_{exp} is a constant quantity:

$$\frac{E_{\text{exp}}}{E_{\text{calc}}} = \text{const} = 1.475. \tag{2}$$

The only exception for the alloy with 0.33% oxygen content can be explained by the fact that the specimen for measuring the modulus with the indicated content was obtained from reduced titanium sponge and could contain other impurities lowering E_{exp}.

In this connection, it may be considered with sufficient justification that the relation between E and a for alloys of the titanium–oxygen system can be expressed by the relation:

$$E = \frac{1.475\,k}{a\alpha^3}. \tag{3}$$

The values of E, calculated by formula (3) on the basis of the coefficients of thermal expansion obtained in the present work and the data on the interatomic distance obtained in work (^{8}), are given in Table 2, and the character of the concentration dependence of E is shown in Fig. 1b. The data obtained also made it possible to calculate the values of the characteristic temperature and the root-mean-square displacements of atoms from the equilibrium position.

Table 2*

No. in order	Composition, at.%	E, kg/cm^2 $\cdot\,10^{-6}$	d, g/cm^3	A_{av}	$\theta°$, K	$\sqrt{U^2_{293}}$	$\alpha \cdot 10^{-6}$/°C (100–250°)
1	0	1.14	4.5142	47.9	384	0.1315	7.11
2	3	1.2442	4.539	46.9	404.2	0.1279	6.46
3	5	1.2827	4.5504	46.3	413.1	0.1268	6.26
4	10	1.5867	4.6003	44.7	462.8	0.1177	5.04
5	14.5	1.6950	4.657	43.115	483.5	0.1161	4.54
6	18	1.4969	4.693	42.158	457.1	0.1233	5.31
7	20	1.2790	4.717	41.52	424.1	0.1331	6.20
8	23	1.1471	4.725	40.56	404.8	0.1405	6.90
9	25	0.9516	4.739	40.24	369.5	0.1525	8.31
10	25	2.4403	4.753	39.92	592.5	0.1039	3.24
11	26	0.9178	4.771	39.60	364.3	0.1554	8.60
12	28	1.285	4.816	38.97	432.7	0.1357	6.18
13	32	1.3834	4.892	37.89	452.0	0.1321	5.77

* Calculated data for E are given only at room temperature. Calculations at higher temperatures were not performed, since the dependence of a on temperature is unknown.

In the works of Koster (^{11}), and also of Frantsevich (^{12}), it was shown that, knowing the magnitude of the elastic modulus (E), the specific weight of the alloy (d), and the averaged atomic weight (A), one can calculate the characteristic temperature (θ):

$$\theta = \frac{1.6818 \cdot 10^{3} E}{A^{1/3} \cdot d^{1/6}} \tag{4}$$

and the root-mean-square displacements of atoms from the equilibrium position:

$$\overline{U}^{2}_{293} = \frac{4.3 \cdot 10^{-14} \left[\frac{D(\theta/T)}{\theta/T} + \frac{1}{4} \right]}{A\theta}. \tag{5}$$

Such calculations are valid if the values of the Poisson coefficient lie in the range from 0.25 to 0.45 (^{12}). For pure titanium the value of the Poisson coefficient is 0.36.

Table 2 gives the values of θ and $\sqrt{\overline{U^{2}_{293}}}$, calculated from formulas (4) and (5). The character of the concentration dependence of these quantities is shown in Fig. 3.

The validity of the calculations performed for titanium and its alloys is also proved by the fact that the value of θ found experimentally coincides with the value of θ calculated by formula (4) (Table 2). On the basis of analysis of the data obtained on the characteristics of interatomic interaction α, E, θ, and $\sqrt{\overline{U^{2}_{293}}}$, it may be concluded that, when titanium is alloyed with oxygen, the strength of the chemical bond between atoms increases as the oxygen concentration increases. On the composition-property diagrams (see Figs. 1b, c and 3), special points are revealed: minima of the coefficient of linear expansion α and of the root-mean-square displacement of atoms $\sqrt{\overline{U^{2}_{293}}}$, and maxima of the elastic modulus E and the characteristic temperature θ. These special points on the diagrams correspond to the compositions of the compounds Ti_6O and Ti_3O.

(Figure: Fig. 3. Dependences of Θ and $\sqrt{\overline{U^{2}_{293}}}$ on the composition of alloys of the titanium-oxygen system)

Fig. 3. Dependences of Θ and $\sqrt{\overline{U^{2}_{293}}}$ on the composition of alloys of the titanium-oxygen system

As a result of an experimental study of the thermal expansion of titanium-oxygen alloys over a wide range of temperatures and oxygen concentrations, an empirical dependence of the elastic modulus E on the coefficient of thermal expansion α of alloys of this system was established. Calculations were made of the elastic modulus, the characteristic temperature, and the root-mean-square displacements of atoms from their equilibrium positions in the crystal lattice of solid solutions and of the new compounds Ti_6O and Ti_3O, which form in this system from α-solid solutions of titanium. On the basis of analysis of the concentration dependence of the indicated characteristics, conclusions were drawn about an increase in the strength of the chemical bond between atoms in the crystal lattice of α-titanium when it is alloyed with oxygen up to 15 at. %. The compound Ti_3O is distinguished by the greatest strength of the chemical bond, and it is more thermally stable than the compound Ti_6O.

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