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CRYSTALLOGRAPHY

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CRYSTAL STRUCTURE OF THE SUBOXIDE Ti_2ZrO

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Titanium and zirconium form a continuous series of solid solutions with one another (^{1}). Studies in recent years have shown that, in the titanium–oxygen and zirconium–oxygen systems, compounds of the suboxide type with a nonvalent atomic ratio are formed ($^{2-5}$). Preliminary investigations carried out on the ternary titanium–zirconium–oxygen system by methods of physicochemical analysis showed that in this system there are no broad regions of solid solutions based on the low-temperature modifications of titanium and zirconium, and that the nature of the phase equilibrium proves to be rather complex.

In work (^{6}) it was established by x-ray diffraction that, as a result of annealing at a temperature of 800°, in an alloy Ti_2O_x with $x = 0.55$—0.9, along with an ordered solid solution of oxygen in α-titanium (the Ti_2O phase) and titanium monoxide TiO (NaCl-type structure), a tetragonal δ-oxide of titanium is formed, whose composition corresponds to $x = 0.5$, and whose unit-cell parameters of the crystal lattice are $a = 4.991$ Å and $c = 2.879$ Å. On the other hand, in works ($^{7-9}$) on titanium alloys with β-stabilizing elements (Cr, V, Mo, Mn, Nb, Ta), a hexagonal phase was found ($a = 4.60$ Å and $c = 2.82$ Å), which received the name ω-phase.

Hatt and Roberts (^{10}) were the first to note the presence of the ω-phase in Ti–Zr alloys. The authors of work (^{11}) observed the presence of ω-phase lines on x-ray diffraction patterns of Ti–Zr alloy specimens containing from 40 to 80 at.% Zr and cooled from temperatures above 1000° at a rate of 200–300 deg/sec. Like the δ-oxide of titanium, the ω-phase has not been isolated in pure form (^{9}).

There is a large crystallographic correspondence between these two phases. It is expressed in the fact that the structure of both phases can be obtained from the high-temperature b.c.c. structure of the corresponding alloys. In this case, one half of the space diagonal and the edge diagonal of the b.c.c. structure become, respectively, the periods a_g and c_g of the hexagonal lattice, while the

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

coordinates of two basal atoms become equal to $z = 1/2$ instead of $z = 1/3$ and 2/3 in the b.c.c. lattice (^{12}).

The present communication is devoted to a presentation of some results of a neutron- and x-ray-diffraction study of the crystal structure of the Ti_2ZrO phase, which we discovered in a general investigation of suboxide phases in the Ti—Zr—O system.

The investigations were carried out on cast specimens, melted in arc furnaces in an atmosphere of purified argon and quenched on a water-cooled copper hearth. Iodide titanium and zirconium of 99.9% purity were used as starting materials. Oxygen was introduced into the alloys in the form of a titanium—oxygen master alloy. The master alloy was prepared by melting in the same furnace, after first pressing rods of titanium dioxide of 99.93% purity with titanium. Analysis of the master alloy showed that it con—

contains 16.08 wt.% oxygen. Gas analysis of the alloys by the vacuum-melting method showed that the oxygen content in the alloys (by charge) differs only insignificantly from the amount of oxygen introduced. The alloys were melted in 150-g batches.

Neutron diffraction patterns of the samples studied were obtained on a large powder spectrometer at the VVR-Ts reactor. Ground

Fig. 1. Neutron diffraction pattern ($a, \lambda = 1.27$ Å) and X-ray diffraction pattern ($b, \lambda = 1.54$ Å) of the alloy Ti_2ZrO

samples were placed in a vanadium thin-walled container; during exposure the samples were rotated. In reducing the peak intensities to relative values, no correction for absorption was introduced. X-ray diffraction patterns of the samples were recorded on a URS-50I apparatus by the flat-sample method.

Figure 1 shows the neutron diffraction pattern and X-ray diffraction pattern of a sample of composition $(Ti_{0.62}Zr_{0.38})_3O$, corresponding to the formula Ti_2ZrO. Both diffraction patterns can be indexed on the basis of a hexagonal unit cell with periods $a = 4.788$ Å and $c = 3.043$ Å ($c/a = 0.636$), and with a shape close to the cells of the δ-oxide and ω-phase.

To determine the positions of the atoms in the unit cell, an analysis was carried out of the intensities of reflections for 14 different models of atomic arrangement.

Fig. 2. Unit cell of Ti_2ZrO

Fig. 3. Calculated (1) and measured (2) reflection intensities for the neutron diffraction pattern of Ti_2ZrO

Figure 3: Fig. 3. Calculated (1) and measured (2) reflection intensities for the neutron diffraction pattern of Ti_2ZrO

In view of the fact that the total amplitude of coherent neutron scattering by the disordered solid solution of composition $Ti_{0.62}Zr_{0.38}$ is equal to zero (zero matrix), it was assumed that, in contrast to X-ray diffraction patterns, the neutron diffraction patterns of suboxide phases of composition $(Ti_{0.62}Zr_{0.38})_nO$ should reflect only the ordered arrangement of oxygen atoms in the crystal lattice of the metal.

For all 7 variants of the structure, corresponding to a disordered arrangement of the metal atoms Ti and Zr and to various variants of ordered and disordered arrangements of oxygen atoms in the octahedral voids of the ω-phase-type structure, no satisfactory agreement was obtained between the calculated and measured intensities.

Taking into account the ordered arrangement of Ti and Zr atoms in the unit cell made it possible to establish that precisely such an ordered arrangement of the metal atoms occurs in the suboxide structure.

Fig. 3. Calculated (1) and measured (2) reflection intensities for the neutron diffraction pattern of Ti_2ZrO

The best agreement between the calculated and experimental intensities of the neutron diffraction pattern was obtained for the following structural variant (Fig. 2):

Space group $D_{6h}^1 - P6/mmm$.
Unit-cell parameters $a = 4.788$ Å, $c = 3.043$ Å.
The unit cell contains one formula unit Ti_2ZrO.
1 Zr atom in position 1 (a): $0, 0, 0$.
2 Ti atoms in position 2 (d): $\frac{1}{3}\ \frac{2}{3}\ \frac{1}{2};\ \frac{2}{3}\ \frac{1}{3}\ \frac{1}{2}$.
1 O atom statistically in position 3 (f): $\frac{1}{2}\ 0\ 0;\ 0\ \frac{1}{2}\ 0;\ \frac{1}{2}\ \frac{1}{2}\ 0$.

For this structural variant, using the values of the coherent neutron-scattering amplitudes [13]: $b_{\mathrm{Zr}} = 0.70 \cdot 10^{-12}$ cm, $b_{\mathrm{O}} = 0.58 \cdot 10^{-12}$ cm, $b_{\mathrm{Ti}} = 0.38 \cdot 10^{-12}$ cm, and taking into account the chemical composition of the sample and the temperature factor at $B = 0.6$, the reliability factor is $R = 0.068$. The resulting agreement between the calculated and experimental intensities of the neutron diffraction pattern is shown in Fig. 3.

A similar treatment of the X-ray data gives $R = 0.105$ and $R = 0.240$, respectively, for ordered and disordered arrangements of Ti and Zr atoms (without allowance for the thermal factor). It should be noted that the difference between the theoretically calculated models is substantially smaller than the same difference for neutrons, which confirms the preference for the neutron diffraction method in studying the structure of phases in the Ti—Zr—O system as compared with the X-ray diffraction method.

From Fig. 2 and Table 1 it is seen that each Zr atom has 2 nearest neighboring Zr atoms at a distance of 3.043 Å and 12 Ti atoms at a distance of 3.157 Å. Each Ti atom is located at the center of a trigonal prism of Zr atoms; in addition, it has 3 more neighboring atoms in adjacent prisms at a distance of 2.761 Å in the plane $z = \frac{1}{2}$, thus forming a hexagonal net analogous to the net of boron atoms in a structure of the AlB_2 type. This indicates very strong bonds in the plane $z = \frac{1}{2}$. All oxygen atoms are statistically located with weight $\frac{1}{3}$ in octahedral voids formed by 4 titanium atoms and 2 zirconium atoms. The coordination and interatomic distances of the Ti_2ZrO structure are given in Table 1.

Thus, the structure of Ti_2ZrO proved to be analogous to the structure of Mn_2TaO_3, found in the system Mn—Ta—O (^{14}). However, unlike Mn_2TaO_3 and δ-TiO_x, the Ti_2ZrO phase forms within the ternary Ti—Zr—O diagram in a concentration region with a significantly lower oxygen content than in Mn_2TaO_3 and in the δ phase of the Ti—O system. In particular, it was found by us in a sample of composition $(Ti_{0.62}Zr_{0.38})_6O$, and also of composition $(Ti_{0.5}Zr_{0.5})_3O$. The phase found is apparently stabilized by oxygen, since its existence does not seem natural in view of the presence of a continuous series of solid solutions in the titanium—zirconium system. Attention was drawn in (^{15}) to the stabilization of phases by oxygen in titanium- and zirconium-based systems.

Table 1

Interatomic distances and coordination in Ti_2ZrO

Atom	Coordination	Interatomic distances, Å
Zr in 1 (*a*)	2 Zr in 1 (*a*)	3.043
Zr in 1 (*a*)	12 Ti in 2 (*d*)	3.157
Zr in 1 (*a*)	6 O in 3 (*f*)	2.394
Ti in 2 (*d*)	6 Zr in 1 (*a*)	3.157
Ti in 2 (*d*)	3 Ti in 2 (*d*)	2.761
Ti in 2 (*d*)	2 Ti in 2 (*d*)	3.043
Ti in 2 (*d*)	6 O in 3 (*f*)	2.110
O in 3 (*f*)	4 Ti in 2 (*d*)	2.110
O in 3 (*f*)	2 Zr in 1 (*a*)	2.394

To establish the exact boundaries of existence of this phase in the ternary titanium—zirconium—oxygen system, additional studies are required.

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