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# Interactions in the $Al_2TiO_5$–$Ti_2O_3$ System

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**Abstract**—Interactions in the $Al_2TiO_5$–$Ti_2O_3$ system were studied and the regions of existence of $Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5$ solid solutions with a pseudobrookite structure were determined.

A distinguishing feature of ceramics based on aluminum titanate is their refractoriness and low overall coefficient of linear thermal expansion [1]. Owing to this property, it is expedient to use aluminum titanate, in processes that occur in nonstandard operation modes, as a material resistant to thermal shocks. Aluminum titanate is used as a heat insulator in propulsion engineering, material for crucibles in ferrous and nonferrous metallurgy, and support for catalysts [2, 3].

Aluminum titanate $Al_2TiO_5$ belongs to an isomorphous series of binary oxides $A_2BO_5$ with a pseudobrookite structure (also including $Fe_2TiO_5$, $Ti_3O_5$, and $Ti_2MgO_5$), in which A and B atoms may be isovalently substituted by various cations, with continuous series of solid solutions formed [4, 5]. Aluminum titanate has an orthorhombic lattice with a *Cmcm* space group, with the following lattice constants: $a = 0.3591$, $b = 0.9429$, and $c = 0.9636$ nm [4]. A characteristic feature of the representatives of the isomorphous $A_2BO_5$ series is the anomalously high anisotropy of thermal expansion, caused by distortion of $[MO_6]$ octahedra and different lengths of M–O bonds [6, 7].

Titanium pentoxide $Ti_3O_5$ has two, high- and low-temperature, modifications [8]. Crystals of anosovite (high-temperature modification of $Ti_2O_5$) [9, 10] belong to the rhombic crystal system, are characterized by the *Cmcm* space group, and have the following lattice constants: $a = 0.3747$, $b = 0.9465$, and $c = 0.9715$ nm. The crystal structure of the low-temperature modification of $Ti_3O_5$ belong to the monoclinic system, is characterized by the $C2/m$ space group, and has the following lattice constants: $a = 0.3808$, $b = 0.9442$, $c = 0.9752$ nm, and $\beta = 91.55°$.

The high- and low-temperature modifications of $Ti_3O_5$ are rather easily transformed one into the other at a temperature of about 120°C. At slightly higher temperatures [8], the structure $Ti_3O_5$ is similar to that of orthorhombic anosovite, but is slightly distorted (monoclinic), with lattice constants $a = 0.378$, $b = 0.997$, $c = 0.982$ nm, and $\beta = 91.0°$. At higher temperatures, the monoclinic angle gradually approaches 90°, and the lattice constants, those of anosovite. The crystal structure of the high-temperature modification can also remain stable at low (room) temperatures in the presence of a certain amount (several weight percent) of iron, magnesium, or aluminum. In the absence of admixtures, titanium pentoxide has at room temperature the structure of its low-temperature modification. According to the refined data [11], the lattice constants of the low-temperature modification of $Ti_3O_5$ are $a = 0.3801$, $b = 0.9441$, $c = 0.9748$ nm, and $\beta = 91.53°$.

The sinterability of aluminum titanate ceramics is commonly improved, and its thermal stability, raised, by introducing mineralizers into the stock [12–14]. The stability of the structure of the high-temperature modification of $Ti_3O_5$ at room temperature in the presence of a minor amount of $Al_2O_3$ admixture was confirmed in [13]: solutions of composition $[(Ti_{1-x}Al_x)_2O_3TiO_2]$ with $0 \le x \le 0.4$ have the structure of low-temperature $Ti_3O_5$, and compounds with $x \ge 0.08$ are structurally similar to high-temperature $Ti_3O_5$. A transition from the monoclinic crystal system, to which the crystal structure of compounds with $0 \le x \le 0.2$ belongs, to the rhombic crystal system characteristic of compounds with $0.3 < x < 1$ was found [13].

To perform a directed synthesis of ceramic materials, it is necessary to study in detail the structural

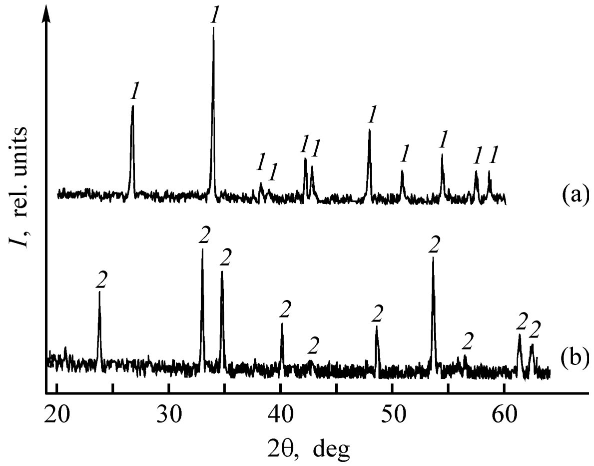

**Fig. 1.** X-ray diffraction patterns of the starting powders of (a) $Al_2TiO_5$ and (b) $Ti_2O_3$. (*1*) $Al_2TiO_5$ and (*2*) $Ti_2O_3$. (*I*) Intensity and (2θ) Bragg angle; the same for Fig. 3.

parameters of the forming samples and their correlation with the properties of the samples. A study of real structure of substances with all its defects makes it possible to search for new compounds with valuable properties and to improve processes of their synthesis by using various methods of control over their composition and the distortion of their structure. In this study, we examined the phase formation in the $Al_2TiO_5$–$Ti_2O_3$ system and the physicochemical properties of ceramic materials based on $Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5$ solid solutions with a pseudobrookite structure.

## EXPERIMENTAL

To prepare the starting mixtures, we used $Al_2O_3$ of pure grade, $TiO_2$ of special-purity grade, and BAU-A activated carbon. Aluminum titanate was synthesized at 1400°C in the course of 9 h from an equimolar mixture of aluminum and titanium(IV) oxides (Fig. 1, diffraction pattern a). $Ti_2O_3$ was prepared by reducing $TiO_2$ with carbon in a vacuum (residual pressure $10^{-3}$–$10^{-1}$ Pa) at 1600°C with an isothermal exposure for 3 h [15]. The correspondence of the material synthesized to the stoichiometric formula $Ti_2O_3$ was monitored by the weight gain in the oxidation of the material to titanium dioxide by annealing in air at 1000°C for 2 h in accordance with the reaction

$$Ti_2O_{3+x} + \frac{1-x}{2}O_2 \rightarrow 2TiO_2. \qquad (1)$$

The discrepancy revealed between the composition of the material synthesized and the stoichiometric formula is rather small ($x = 0.011$). The presence of an excess oxygen is a consequence of the insufficient amount of carbon in the reduction reaction; an exact calculation of the stock composition is complicated by the fact that the humidity of activated carbon, which is used as a source of carbon, varies from 8 to 10 wt %. The X-ray data (Fig. 1, diffraction pattern b) also confirm that the substance obtained is titanium(III) oxide.

To determine the ranges of existence of $Al_{2-2x}Ti^{3+}_{2x} \cdot Ti^{4+}O_5$ solid solutions, we prepared $Al_2TiO_5 + xTi_2O_3$ mixtures ($x$ is the number of $Ti_2O_3$ moles, varied from zero to unity with a step of 0.1). Billets 20 mm in diameter and 5 mm high for high-temperature treatment were prepared by semidry compaction under a pressure of 150 MPa. The samples were thermally treated under atmospheric pressure in argon at 1400°C for 4 h.

The phase composition of the samples subjected to thermal treatment was studied by X-ray phase analysis on a DRON-3M installation ($Cu_{K_\alpha}$ radiation), using the JCPDS-ICDD database of powdered standards. We used the Powder Cell software [16] to evaluate the content of crystalline phases in the thermal treatment products (with an accuracy of ±5 vol %) and analyze the line intensities by the Rietveld method. The software makes it possible to construct and predict structural models of a solid solution based on aluminum titanate. The position parameters of the aluminum titanate lattice are listed in Table 1. The construction is based on substitution of a part of $Al^{3+}$ ions

**Table 1.** Position parameters of the crystal structure of aluminum titanate (*Cmcm* space group) [17]

| Atom | Ion | Position | *x* | *y* | *z* | Occupancy |
|---|---|---|---|---|---|---|
| Ti | $Ti^{3+}$<br>$Al^{3+}$ | 4*c* | 0.0000 | 0.1863 | 0.2500 | 0.3330<br>0.6670 |
| Al | $Al^{3+}$<br>$Ti^{4+}$ | 8*f* | 0.0000 | 0.8649 | 0.4387 | 0.6670<br>0.3330 |
| O | $O^{2-}$ | 4*c* | 0.0000 | 0.7590 | 0.2500 | 1.0000 |
| O | $O^{2-}$ | 8*f* | 0.0000 | 0.9520 | 0.8820 | 1.0000 |
| O | $O^{2-}$ | 8*f* | 0.0000 | 0.6830 | 0.9250 | 1.0000 |

**Table 2.** Lattice constants (nm) of $Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5$ solid solutions and $Ti_2O_3$ content in the starting mixture and annealing products (composition of the starting mixture $Al_2TiO_5-xTi_2O_3$)

| $x$ | Phase composition of products, vol % | | | $a$ | $b$ | $c$ | $Ti_2O_3$, mol % | |
|---|---|---|---|---|---|---|---|---|
| | $Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5$ | $\alpha$-$Al_2O_3$ | Magneli phases | | | | initial | products |
| 0 | ~100 | ≤5 | – | 0.359 | 0.946 | 0.967 | – | 4.0 |
| 0.1 | 90 | 10 | – | 0.360 | 0.947 | 0.968 | 9.09 | 10.6 |
| 0.2 | 90 | 10 | – | 0.360 | 0.947 | 0.968 | 16.7 | 18.8 |
| 0.3 | 90 | ≤5 | ≤5 | 0.361 | 0.947 | 0.969 | 23.1 | 25.0 |
| 0.4 | 85 | ≤5 | 10 | 0.361 | 0.948 | 0.969 | 28.5 | 32.8 |
| 0.6 | 80 | ≤5 | 15 | 0.361 | 0.948 | 0.969 | 37.4 | 41.0 |
| 0.8 | 75 | ≤5 | 20 | 0.361 | 0.948 | 0.970 | 44.5 | 49.0 |
| 1.0 | 75 | ≤5 | 20 | 0.361 | 0.948 | 0.970 | 50.0 | 51.0 |

in 4*c* and 8*f* positions in the $Al_2TiO_5$ structure [17] with $Ti^{3+}$. The occupancy of the specified positions by $Al^{3+}$ was varied in the range 0.6670 – 0.4670, that by $Ti^{3+}$, in the range 0 – 0.2000. The experimental and theoretical X-ray patterns were compared within the entire pattern profile, and the convergence factor was output as the result of the calculation. The variant with a lower *R*-factor represents the model configuration. The software also makes it possible to compare a description of the structure of a solid solution with experimental data and to carry out a quantitative phase analysis. The lattice constants of the solid solutions based on aluminum titanate (orthorhombic crystal system) were determined using the least-squares method for 12 highest-intensity peaks in the $2\theta$ range from 10° to 80°.

The open porosity *P* and water absorption *W* of the samples were determined in conformity with GOST (State Standard) 18847–84 by hydrostatic weighing. The acid resistance A of the samples synthesized was evaluated, according to GOST 473.1–81, by the change in the mass of the ceramic material after its treatment with concentrated sulfuric acid.

The content of $Ti_2O_3$ in the calcination products was determined by the method of complete oxidation from the weight gain of samples exposed in air at 1000°C for 2 h. The atomic composition of the crystalline phases of the ceramics was found by electron microprobe analysis using a JSM-6400 electron scanning microscope equipped with a Link X-ray energy-dispersion spectrometer with ISIS-300 software. The volume of the substance analyzed was 1 $\mu m^3$. The constituent phases of the samples were analyzed for the content of Al, Ti, and O. To reliably determine the amounts of elements in a phase, we made up to 10 measurements on the sample surface. We used as standards certified Microspec reference samples. The measurement error was ±1%.

Our studies revealed that the phase composition of the samples and the lattice constants of the pseudobrookite phase change, depending on the parameter $x$ of the starting $Ti_2O_3$, upon calcination of the $Al_2TiO_5$–$xTi_2O_3$ mixture. The weight loss upon heat treatment of compacts did not exceed 0.5% for the entire range of compositions, $0 \le x \le 1$. According to the results of an X-ray analysis (Table 2), up to 5 vol % $\alpha$-$Al_2O_3$ is contained in the heat-treatment products at $x = 0$. All the reflections of the aluminum titanate phase in the X-ray diffraction pattern are shifted to smaller $2\theta$ angles owing to the formation of the $Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5$ solid solution via dissociation of aluminum titanate in the atmosphere of argon:

$$Al_2TiO_5 = (1/1 + 2x)Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5 + (3x/1 + 2x)Al_2O_3 + (x/1 + 2x)O. \qquad (2)$$

Analysis for the content of $Ti_2O_3$ confirms the presence of 1.6 mol % $Ti^{3+}$ in the heat-treatment products. The lattice constants of the $Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5$ solid solution, $a = 0.359$, $b = 0.946$, and $c = 0.967$ nm, exceed those of stoichiometric $Al_2TiO_5$ [17]. An examination of the profile of the X-ray diffraction pattern demonstrated that the intensity of peaks changes when the occupancy by $Al^{3+}$ of the positions 4*c* and 8*f* decreases through partial substitution by $Ti^{3+}$. The best result in describing the experimental X-ray pattern was achieved in the case when 5% of $Al^{3+}$ positions in the $Al_2TiO_5$ structure were substituted with $Ti^{3+}$.

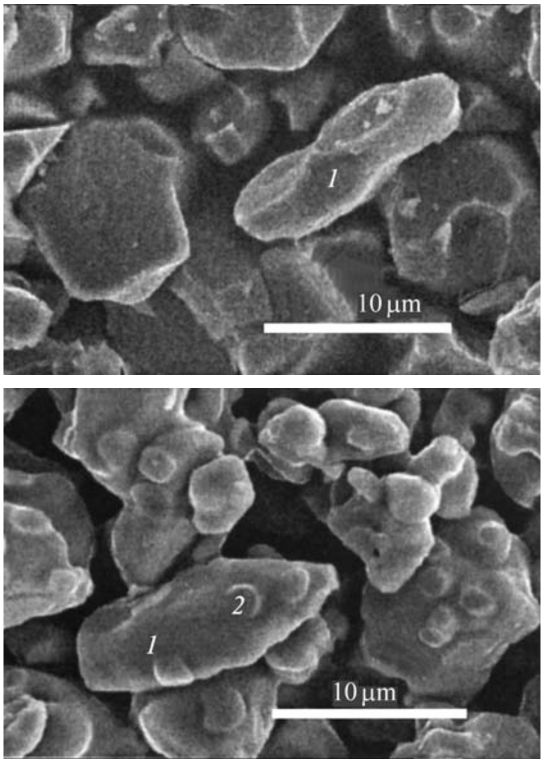

**Fig. 2.** Electron micrographs of the thermal treatment products (a) $Al_2TiO_5$ synthesized in air and (b) that calcined in argon. (*1*) $Al_2TiO_5$ and (*2*) $Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5$.

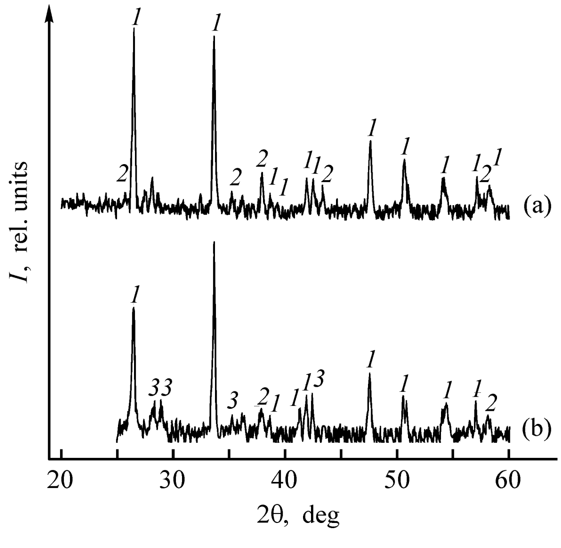

**Fig. 3.** X-ray diffraction patterns of thermal-treatment products: (a) $Al_2TiO_5 + 0.1\,Ti_2O_3$, (b) $Al_2TiO_5 + 1.0\,Ti_2O_3$. (*1*) $Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5$, (*2*) $Al_2O_3$, and (*3*) Magneli phases.

According to electron-microscopic data, aluminum titanate synthesized in air is composed of regularly shaped particles less than 10 μm in size, with the following atomic composition (mol %): Al 25.0, Ti 12.0, and O 63.0, which corresponds to that of stoichiometric $Al_2TiO_5$ (Fig. 2a). Areas with an increased content of titanium (13.0 mol %) are formed on the surface of aluminum titanate particles after annealing of the samples in argon (Fig. 2b). The averaged data of the electron microprobe analysis of the compound correspond to the chemical formula $Al_{1.9}Ti^{3+}_{0.1}Ti^{4+}O_5$.

An $Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5$ solid solution and $\alpha$-$Al_2O_3$ (10 vol %) are formed in the thermal treatment products at $x = 0.1$ (Fig. 3, X-ray diffraction pattern a). The reaction of $Al_2TiO_5$ with $Ti_2O_3$ can be represented by the following equation:

$$Al_2TiO_5 + xTi_2O_3 = Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5 + xAl_2O_3. \quad (3)$$

Triple-charged titanium atoms isovalently substitute aluminum atoms in the $Al_2TiO_5$ crystal lattice to form the individual phase $\alpha$-$Al_2O_3$. In this concentration range ($x = 0.1$), aluminum titanate partially dissociates in accordance with Eq. (1), because the $Ti^{3+}$ content in calcination products (4.2 mol %) exceeds its amount in the starting stock (3.6 mol %). According to the averaged data of the electron microprobe analysis, the compound synthesized contains (mol %): Al 21.0, Ti 16.0, and O 63.0, which corresponds to the chemical formula $Al_{1.7}Ti^{3+}_{0.3}Ti^{4+}O_5$.

An increase in the $Ti_2O_3$ content to $x = 0.2$ is accompanied by formation of $\alpha$-$Al_2O_3$ (up to 10 vol %) in the thermal-treatment products. As $Ti^{3+}$ ions substitute $Al^{3+}$ ions in aluminum titanate the lattice constants of $Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5$ increase further (Table 2). This is due to the larger ionic radius of titanium(III) in octahedral coordination as compared with aluminum [18]: $R(Ti^{3+}) = 0.67$ Å, $R(Al^{3+}) = 0.53$ Å. In modeling of the structure of the solid solution $Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5$ in the sample under consideration, the best result corresponds to the occupancies by $Al^{3+}$ and $Ti^{3+}$ of 0.557 and 0.110, respectively, in $Ti^{3+}$ substitution for $Al^{3+}$ in the aluminum titanate structure [17]. For the composition $x = 1.3$, the content of $\alpha$-$Al_2O_3$ in the final products virtually does not increase. Thus, under the chosen thermal treatment conditions (1400°C), $Ti^{3+}$ occupies no more than 20% of $Al^{3+}$ positions in the $Al_2TiO_5$ structure, and the region of isovalent substitution is limited to the $Al_{1.6}Ti^{3+}_{0.4}Ti^{4+}O_5$ composition.

In the concentration range $0.3 \le x \le 1$, Magneli phases $Ti_nO_{2n-1}$ ($4 < n < 9$) appear in the thermal-treatment products in addition to the phases of the $Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5$ solid solution and $\alpha$-$Al_2O_3$

(Fig. 3, diffraction pattern b). Aluminum titanate reacts with $Ti_2O_3$ to form $Ti_nO_{2n-1}$ in accordance with the equation

$$(n - 2)Al_2TiO_5 + Ti_2O_3 = Ti_nO_{2n-1} + (n - 2)Al_2O_3. \quad (4)$$

The sum of reactions (3) and (4) has the form

$$(n - 1)Al_2TiO_5 + (x + 1)Ti_2O_3$$
$$= Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5 + Ti_nO_{2n-1} + (n - 2 + x)Al_2O_3. \quad (5)$$

The results of an electron microprobe analysis of the products of calcination of the starting $Al_2TiO_5$–$1.0\,Ti_2O_3$ sample confirm the presence of the Magneli phase (Ti 34.5 mol % and O 65.5 mol %) and that of the $Al_{1.75}Ti^{3+}_{0.25}Ti^{4+}O_5$ solid solution. In the concentration range $0.2 < x < 1$, the lattice constants of the resulting $Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5$ solid solutions are close within the experimental error and independent of the $Ti_2O_3$ content in the starting stock (Table 2).

The dependences of the physical characteristics of samples on the content of titanium(III) oxide in $Al_2TiO_5 + xTi_2O_3$ starting mixtures, obtained in this study, show that the water absorption by the material decreases from 17.9 to 4.6%, and the open porosity, from 39.0 to 17.7%, as the $Ti_2O_3$ content in the stock increases, which points to activation of sintering processes (Fig. 4). The strongest effect of the compaction of aluminum titanate ceramics is achieved when 23 mol % $Ti_2O_3$ is introduced, and further increase in the content of $Ti_2O_3$ does not improve the physical characteristics. The resistance of the samples synthesized (Fig. 4) to concentrated $H_2SO_4$ increases as the content of the $Al_{2-2x}Ti^{3+}_{2x}Ti^{4+}O_5$ solid solution enriched with titanium, relative to that of aluminum titanate, in a sample increases. Such a dependence of the acid-resistance on the sample composition can be attributed to a lower mobility of titanium atoms, compared with aluminum atoms, resulting from the difference in their radii $[R(Ti^{3+}) > R(Al^{3+})]$. The improvement of the physical characteristics and the chemical resistance of a ceramic material by introducing $Ti_2O_3$ enables extension of the application area of materials based on $Al_2TiO_5$.

## CONCLUSIONS

It was found that, under the chosen conditions of thermal treatment (1400°C), $Ti^{3+}$ occupies no more than 20% of $Al^{3+}$ positions in the $Al_2TiO_5$ structure and the range of isovalent substitution is limited to the $Al_{1.6}Ti^{3+}_{0.4}Ti^{4+}O_5$ composition.

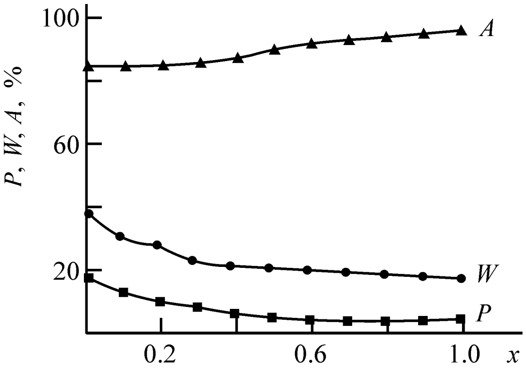

**Fig. 4.** Water absorption *W*, open porosity *P*, and acid-resistance *A* of the material obtained from the $Al_2TiO_5 + xTi_2O_3$ starting mixture vs. the parameter *x*.

The strongest effect of compaction of ceramics based on aluminum titanate is achieved by introducing up to 23 mol % $Ti_2O_3$, and further increase in the content of $Ti_2O_3$ does not result in any noticeable improvement of physical characteristics. The resistance of a ceramic material based on aluminum titanate to concentrated sulfuric acid increases with the content of titanium(III) in the samples studied.

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