Synthesis of Ti$_4$O$_7$ Magneli Phase Using Mechanical Activation

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Abstract: The processes of phase formation by heating of a mechanically activated mixture of Ti + TiO$_2$ in different atmospheres (air, argon, hydrogen) were investigated. The Ti$_4$O$_7$ compound was obtained by annealing of the mixture in hydrogen atmosphere in the interval of temperatures of 900-1200°C, the Ti$_2$O$_3$ oxide formed at 800°C in argon atmosphere and TiO$_2$ formed in air atmosphere. Conductivity and morphology of Ti$_4$O$_7$ samples obtained in hydrogen were studied.

Keywords: Mechanical Activation; Titanium Oxides; Dispersed Particles; Reduction; Sintering.

Резюме: Исследованы процессы фазообразования при нагревании механически активированной смеси Ti + TiO$_2$ в зависимости от атмосферы (воздух, аргон, водород). Получено соединение Ti$_4$O$_7$ отожженной смеси в водороде в интервале температур 900-1200°C, в среде аргона при 800°C образуется соединение Ti$_2$O$_3$, в водородной среде образуется TiO$_2$. Измерена электропроводность и изучена морфология спеченного оксида Ti$_4$O$_7$.

Ключевые слова: Механическая активация, оксиды титана, дисперсные частицы, восстановление, спекание.

Содержание: У овох раду процес формирања фаза током загревања механички активираних смеши Ti + TiO$_2$ у различитим атмосферама (ваздух, аргон, воденик). Једињење Ti$_4$O$_7$ добијено је одгревањем смеши у атмосфири воденика у температурном интервалу од 900-1200°C, оксид Ti$_2$O$_3$ на 800°C у атмосфири аргона и TiO$_2$ одгревањем у ваздуху. Измерена је проводљивост и проучена морфологија синтерованог Ti$_4$O$_7$.

Кључне речи: Механичка активација; оксиди титана; дисперсне честице; редукција; синтеровање.

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1. Introduction

A series of non-stoichiometric oxides exist with the general formula of $\text{Ti}_n\text{O}_{2n-1}$ (where $n = 4$-$10$) in titanium oxides, which have high conductivity compared with the conductivity of graphite. Therefore, they are of great practical interest.

The composition-temperature diagram for the Ti-O system is shown in Fig. 1 [1]. One can see that the boundaries of the existence of these compounds are very narrow; they cover the range from 63.6 to 65.3 at.% of oxygen. It is accepted that transition from one compound to another is continuous in some cases. These compounds are called Magneli phases (in honor of Magneli A. who started investigating compounds of this type in 1959). All of them possess a triclinic system; lattice parameters of these structures are rather close to each other, which lead to difficulties in solving their X-ray spectra. The data on cell parameters of Magneli phases are shown in Tab. I [2].

![Composition-temperature diagram for the Ti-O system](image)

*Fig. 1* The diagram of state for the titanium-oxygen system (according to Wahlbeck and Gilles [1]).

**Tab. I** Cell parameters for the Magneli phases according to data of [2].

<table>
<thead>
<tr>
<th>Phase</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>$\alpha$ (Å)</th>
<th>$\beta$ (B)</th>
<th>$\gamma$ (C)</th>
<th>JCPD file</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ti}_4\text{O}<em>7$ (TiO$</em>{1.750}$)</td>
<td>5.60</td>
<td>7.13</td>
<td>12.46</td>
<td>95.1</td>
<td>95.1</td>
<td>108.8</td>
<td>18-1402</td>
</tr>
<tr>
<td>$\text{Ti}_5\text{O}<em>9$ (TiO$</em>{1.800}$)</td>
<td>5.59</td>
<td>7.12</td>
<td>8.865</td>
<td>97.55</td>
<td>112.34</td>
<td>108.50</td>
<td>11-0193</td>
</tr>
<tr>
<td>$\text{Ti}<em>6\text{O}</em>{11}$ (TiO$_{1.833}$)</td>
<td>5.56</td>
<td>7.14</td>
<td>24.04</td>
<td>98.5</td>
<td>120.8</td>
<td>108.5</td>
<td>18-1401</td>
</tr>
<tr>
<td>$\text{Ti}<em>7\text{O}</em>{13}$ (TiO$_{1.857}$)</td>
<td>5.54</td>
<td>7.13</td>
<td>15.36</td>
<td>98.9</td>
<td>125.5</td>
<td>108.5</td>
<td>18-1403</td>
</tr>
<tr>
<td>$\text{Ti}<em>8\text{O}</em>{15}$ (TiO$_{1.875}$)</td>
<td>5.57</td>
<td>7.10</td>
<td>37.46</td>
<td>97.2</td>
<td>128.8</td>
<td>109.6</td>
<td>18-1404</td>
</tr>
<tr>
<td>$\text{Ti}<em>9\text{O}</em>{17}$ (TiO$_{1.889}$)</td>
<td>5.57</td>
<td>7.10</td>
<td>22.15</td>
<td>97.1</td>
<td>131.0</td>
<td>109.8</td>
<td>18-1405</td>
</tr>
</tbody>
</table>

The data obtained by means of calculation of Magneli phases are also available. They somewhat differ from those listed in Tab. I and were obtained by experimental methods.

At room temperature, metallic behavior is characteristic for three oxides: $\text{Ti}_4\text{O}_7$, $\text{Ti}_5\text{O}_9$ and $\text{Ti}_6\text{O}_{11}$. This is due to the high concentration of delocalized electrons, which is about $10^{22}$ cm$^{-3}$. Their presence is explained by overlapping of d-orbitals of titanium ions, which formed during reorientation of TiO$_6$ octahedrons, as a result of changes in the stoichiometry of
oxides towards a decrease in the oxygen content. A percentage of titanium cations is reduced to the Ti\(^{3+}\) state. As a result, for example, the conductivity of Ti\(_2\)O\(_7\) is comparable with that of graphite. This titanium compound, which is a ceramic material changing its color from blue to black, can be obtained in the form of rods, filaments, foams and powders. Due to its high conductivity and chemical stability, since 1985 it started being used as a ceramic electrode material instead of metal anodes in aggressive electrolytes in galvanic baths [3].

Different methods exist for obtaining Magneli phases. The following methods are used the most: high-temperature decomposition of TiO\(_2\), reduction of TiO\(_2\) by hydrogen, and sintering of a Ti + TiO\(_2\) mixture in vacuum.

The authors of [4] investigated the effect of high-temperature annealing on the extent of decomposition of leucoxene concentrates in weakly oxidizing and reducing atmosphere in a furnace. At the annealing temperature of 1200°C (exposure time 30 min.) rutile is substituted by Ti\(_6\)O\(_{11}\), at 1250°C the anosovite phase Ti\(_3\)O\(_5\) appears and its content becomes predominant at 1300°C.

The Ti\(_2\)O\(_2\) phase was obtained by annealing of TiO\(_2\) in the atmosphere of hydrogen at 1050°C during four hours [5]. Samples with higher oxygen content can be obtained with decreased annealing time in a reductive atmosphere.

Samples with a non-stoichiometric composition of variable oxygen content can be obtained by agglomerating Ti and TiO\(_2\) in vacuum [6]. Synthesis of samples was performed in vacuum at a pressure of 0.0013 Pa (10\(^{-5}\) mm Hg), with intermediate fraying of the agglomeration products every 20 hours. The titanium and oxygen content of the samples was determined using the mass increase after oxidation of the samples in air into TiO\(_2\). Specific resistance of the resulting samples changed from 2 to 4 μΩ m at room temperature.

One can see in the above review that all the methods for obtaining non-stoichiometric oxides are rather complicated and lengthy, which holds back wider use of the indicated compounds with high conductivity.

The present investigation deals with the development of a more efficient method of obtaining the indicated phases on the basis of solid-phase reduction of titanium dioxide by metallic titanium during mechanical activation of the mixture in grinding devices. This method is increasingly widely used for obtaining composite materials based on oxides and metals [7].

2. Experimental Procedure

Mechanical activation of the mixtures was performed in a planetary mill at the acceleration of 40g. The activation time was 15 min. Titanium jars were used. The amount of powder loaded into the mill was 10 g, while the mass of balls made of titanium carbonitride, 10 mm in diameter, was 200 g.

Two types of samples were pressed using the obtained powder: discs 18 mm in diameter and 5 mm thick, and rectangular samples with dimensions of 40 x 15 x 5 mm. The pressing force was 200 kg/cm\(^2\). Glycerol solution (25 %) in water was used as a binder.

The samples were then subjected to reductive treatment. In order to reduce TiO\(_2\) to non-stoichiometric compositions corresponding to Magneli phases, a Ti + TiO\(_2\) mixture (50 mol.% each) was prepared and annealed in argon and in hydrogen. The samples were annealed in an industrial furnace. The sample heating time, exposure to the required temperature, and cooling time were approximately equal to each other.
3. Results and Discussion

The X-ray data obtained are presented in Fig. 2 for samples annealed in argon. One can see that the reduction of titanium dioxide by titanium proceeds during annealing in argon. During annealing at the temperature of 800°C, the Ti$_2$O$_3$ phase starts to form. At increased temperature up to 1000°C, rutile is almost completely reduced to form Ti$_2$O$_3$, giving the corresponding black coloring.

![Fig. 2 Transformations in the titanium-rutile system depending on the annealing temperature in argon: a) initial mixture after mechanical activation; b) annealing at 800°C for 3 hours; c) annealing at 1000°C for 3 hours.](image)

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![Fig. 3 Transformations in the titanium-rutile system depending on the annealing temperature in hydrogen: a) initial mixture after mechanical activation; b) annealing at 800°C for 40 min; c) annealing at 900°C for 1 hour; d) annealing at 1000°C for 1 hour; e) annealing at 1000°C for 2 hours.](image)

Fig. 3 Transformations in the titanium-rutile system depending on the annealing temperature in hydrogen: a) initial mixture after mechanical activation; b) annealing at 800°C for 40 min; c) annealing at 900°C for 1 hour; d) annealing at 1000°C for 1 hour; e) annealing at 1000°C for 2 hours.

In order to further improve the conditions of rutile reduction, the samples were annealed in hydrogen. One can see in Fig. 3 (showing the X-ray data) that the reduction was accelerated substantially and preceded towards formation of Ti$_4$O$_7$ phase, followed by Ti$_3$O$_5$. At first, the shape and intensity of reflections of the initial product changed noticeably and the formation of the Ti$_4$O$_7$ phase started (Fig. 3b). After exposure to 900°C increased to one hour, the amount of the Ti$_4$O$_7$ phase increased noticeably. After annealing for one hour at the temperature of 1000°C (Fig. 3d) an almost monophase product of the Ti$_4$O$_7$ composition formed and nucleation of the Ti$_3$O$_5$ phase started. The amount of Ti$_3$O$_5$ increased noticeably after annealing at 1000°C for two hours. The morphology of Ti$_4$O$_7$ samples synthesized and pressed in the described way is presented in Fig. 4.
Fig. 4 SEM structure of a Ti$_4$O$_7$ sample obtained by reduction in hydrogen at 1100°C of the mechanically activated Ti + TiO$_2$ mixture.

The tablets pressed from this powder had a density of 2.6-2.8 g/cm$^3$ and conductivity of about 10$^{-5}$ S. Thus, this material can be considered suitable for use as a ceramic electrode material.

Annealing of the mechanically activated mixture of Ti + TiO$_2$ in air resulted in oxidation to TiO$_2$.

4. Conclusion

We have developed a method for the synthesis of Ti$_4$O$_7$. However, the achieved results show that the conditions for obtaining a monophase product composed of this phase are rather rigid.

The mechanically activated Ti + TiO$_2$ mixture (1:1) is transformed into the most highly conductive Ti$_4$O$_7$ phase by annealing for one hour at a temperature of 1000°C.

References