Conducting Materials Based on Nanodispersed Titanium Monoxide

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Abstract:

The possibility of obtaining the TiO compound during mechanical activation of rutile and titanium in a planetary mill was studied depending on ball size and the activation time. The initial substances, TiO$_2$ (rutile) and Ti (metal), were shown to change into TiO almost completely during grinding as early as after ten minutes. In this case the cubic modification of TiO formed, with the lattice parameter $a=4.185(7)$ Å and particles of 1–3 $\mu$m, which consisted of units about 10 nm in size. The other subject of our research was the dependence of the conductivity of the products on the conditions under which they were moulded and sintered under argon. The conductivity of the samples was in the range 300 to 600 $\text{S cm}^{-1}$. Their chemical resistance equalled that of Ti$_4$O$_7$ samples.

Keywords: Titanium oxides; Mechanical activation; Ceramic electrodes.

Introduction

Production of conductive ceramics based on Magneli phases of titanium oxides shows considerable promise. Among other things electrodes (anodes) for electrochemical processes can be made of ceramics of this kind instead of metals from the platinum group that are currently used. However, it is quite difficult to obtain these phases. The process proceeds in hydrogen, over a narrow temperature range, and oxygen content in the titanium–oxygen system is in a very narrow range. Of interest is the production of TiO-based conductive ceramics. Production of oxide powders with nanocrystalline particles is one of the problems of the modern ceramic materials technology.

Reduction of titanium dioxide to monoxide by titanium metal is known in metallurgy, so TiO can be obtained by sintering the TiO$_2$–Ti system. However, it used to be questionable if the monoxide could be obtained by grinding TiO$_2$ and Ti.

Experimental

We did experiments using a planetary ball mill with water-cooling barrels [1]. The balls and barrels are made of stainless steel. Our experiments with mechanical alloying [2] had shown that the formation rate of solid solutions and the extent of their supersaturation

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depended heavily on the diameters of the balls used. That is why balls 3 and 8 mm in diameter were used for these experiments. The ball centrifugal acceleration was 600 m s$^{-2}$, the ball weight 200 g, and the weight of the powder under processing 10 g. Mechanical activation was done under argon. Diffraction patterns of the samples were examined by an X-ray apparatus DRON-3, Cu K$_\alpha$ radiation. An electron microscopy study was conducted using a JEOL JSM –T20 scanning microscope.

As mentioned above, the mechanical activation was done in steel barrels and with steel balls. To avoid contamination of the reaction products with the material of the balls and barrels, the latter were not washed of the lining after the experiment; that is why there was no iron in the analysed samples. The experiment time was 1, 10, 30 and 60 minutes.

**Results and discussion**

As is seen from the X-ray diffraction patterns in Fig. 1, after one-minute processing in the barrels there was a mixture of the initial substances, TiO$_2$ (rutile) and Ti metal, with a 1:1 molar ratio; the metal and rutile reflections were widened, and even the phase TiO may have begun to form.

Then we took all the sample substance out of the barrels. The lining remained on the balls and the walls of the barrels. A new sample was put there and activated for ten minutes. As the X-ray diffraction pattern in Fig. 1 shows, the amount of the initial substances decreased sharply, but the amount of the TiO cubic modification, space group Fm3m (no. 225), increased dramatically. The lattice parameter was found to be a=4.188(4) Å, the size of the coherent dispersion blocks 9.9 nm, and their distortion 0.43%.

![Fig. 1 Initial substances TiO$_2$–Ti, with a 1:1 molar ratio. Mechanical activation with balls 8 mm in diameter.](image)

When we took all the sample substance out of the barrels, we saw that the lining on their walls and on the balls had hardened. Notice that in all the cases we emptied the barrels of all the sample substance and filled them with a new sample without removing the lining. After thirty-minute activation traces of the initial substances are observed on the X-ray diffraction patterns, and after sixty-minute activation only the phase TiO is observed. The lattice parameter was a=4.185(7) Å, the size of the coherent dispersion blocks 10.4 nm, and their distortion 0.39%.
The phase composition changed much more slowly during mechanical activation with balls 3 mm in diameter. Fig. 2 shows that even after sixty-minute activation the product still contains not only TiO but also the initial substances.

![Fig. 2 Initial substances TiO₂–Ti, with a 1:1 molar ratio. Mechanical activation with balls 3 mm in diameter.](image)

After titanium monoxide was obtained, we moulded it into samples and sintered the samples in a pipe furnace under argon at 1200°C for two hours. The heating time was two hours, and the samples were cooled in the furnace after it was switched off. The samples were compacted without a binder; the compacting force was 630, 3200 and 5100 kg cm⁻². Tab. I shows the density of the samples before and after sintering as well as their conductivity. The density of TiO, according to different authors, is in the range 4.91 to 4.93 g cm⁻³.

<table>
<thead>
<tr>
<th>Sample density and conductivity</th>
<th>Compacting force, kg cm⁻²</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>630</td>
</tr>
<tr>
<td>Compacted density, g cm⁻³</td>
<td>2.64</td>
</tr>
<tr>
<td>Sintered density, g cm⁻³</td>
<td>2.76</td>
</tr>
<tr>
<td>Conductivity, S cm⁻¹</td>
<td>330</td>
</tr>
</tbody>
</table>

As can be inferred from the data in Tab. I, the density and conductivity of the products depended heavily on the compacting force applied to the initial samples.

The X-ray phase analysis revealed that the surface of the sintered samples was a phase mixture and Ti₃O₅ predominated. According to [3], the conductivity of this phase is much lower than that achieved with our samples. It was interesting to find out the reason for this. The supposition was voiced that the inside and outside of the samples differed in their phase composition. The sample surface was ground off, and an X-ray phase analysis was conducted to test this supposition. As is evident from the X-ray diffraction patterns in Fig. 3, it proved to be true. The sample outside was a mixture of three phases, TiO₂, Ti₃O₅ and TiO, with Ti₃O₅ predominating, whereas inside there was TiO, which ensured high conductivity of the samples. Between them there were layers with variable phase composition. The samples obtained showed high chemical resistance (under acid conditions) and had good current-voltage characteristics, comparable with those of Ti₄O₇ samples [4].
Fig. 3 X-ray phase analysis of samples: a) TiO – sample inside, b) Ti₃O₅+TiO – middle part of the sample, c) TiO₂+ Ti₃O₅+TiO – sample outside

As is seen from the micrographs in Fig. 4, the particles of the initial substances after one-minute activation are sharp, and their size can exceed 100 µm (Fig. 4a).

Fig. 4 Micrographs of samples after mechanical activation: a) x215, activation time – 1 min. b) x215, activation time – 10 min, c) x2150, activation time – 30 min, d) x2100, activation time – 30 min

After ten-minute activation (Fig. 4b) the particle size does not exceed 100 µm any more; the
particles are roundish, and their surface has a loose structure; there are many fine-dispersion particles. After thirty-minute activation (Fig. 4c) the average particle size is up to 10 µm.

The micrograph shows that the particles here are loose globules, which consist of smaller particles. After this sample was prepared in an emulsion, we saw that the smaller particles were a few microns in size (Fig. 4c). As to the sample after sixty-minute activation, here the particle sizes are similar to those for the previous samples. So, during the interaction of the initial substances the small particles of the phase TiO not only form but also agglomerate into large loose globules. As mentioned above, the size of the coherent dispersion blocks of these particles is up to 10 nm.

Conclusions

One can obtain titanium monoxide from TiO$_2$ and Ti by their mechanical activation under argon. Synthesis of TiO is much quicker with balls 8 mm in diameter than with 3 mm ones. The product looks like globules 10–100 µm in size, which consist of small particles 1–3 µm in size. The size of the coherent dispersion blocks of these particles is up to 10 nm.

References