Titania Powder Activation and Rutile Ceramics Structure Formation

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Abstract:
Impact of mechanochemical activation (MCA) in aqueous medium with various organic additives on commercial titania powder and products made of it has been investigated by X-ray diffraction, optical microscopy and Raman spectroscopy. Agar-agar additive has been shown to offer promise for activation of titania powders used in obtaining both dense and porous materials.

Keywords: Mechanochemical activation, Titania, Organic additives, Structure, Porosity.

1. Introduction

At present, much attention is paid to studying powder mechanochemical activation processes since in most cases mechanochemical activation results in intensification of powder material sintering [1, 2]. At that, in many cases mechanochemical activation dose not result in powder particle size reduction while compositions most active in sintering also have a higher specific surface [3]. Mechanochemical activation provides considerable advantages if it allows formation of the particle structure which further facilitates material synthesis or sintering and enables obtaining of its optimum structure [4].

The paper deals with the impact of mechanochemical activation (MCA) in aqueous medium with various organic additives on commercial titania powder and products made of it. Interest taken in titania is due to its unique wettability, biological compatibility, high photocatalytic activity [5]. Formation of titania-based permeable microporous structure allows solving of a number of tasks associated with creation of microreactors which combine intense proceeding of gaseous-phase reactions with simultaneous product transportation, and shows promise for wide application in industry and environmental protection [6].

2. Experimental Part

As the test subject, UHP 5-2 commercial titania was used. The powder was activated for 1 hour in a SAND planetary-type mill at 160 rpm. Activation was carried out in aqueous medium (powder-to-water weight ratio = 1:1) in the presence of agar-agar, gelatin and polyvinyl alcohol (PVA). Agar-agar, the binder of Si-O tetrahedra in plants, particularly in
algae, is a natural polymer based on agarose, a linear polysaccharide constructed of strictly alternating residues of 3-O-substituted β-D-galactopyranose and 4-O-substituted 3,6-ahydro-α-L-galactopyranose. Agar also contains agaropectin, a fraction of acid polysaccharides whose carbohydrate backbone follows the same pattern but its structural regularity is masked by pyruvic acid residues which form cyclic acetals with OH groups at 4,6 positions of certain β-D-galactose residues and H₂SO₄ residues ester-bonded to various OH groups [7]. Thermoconvertible jelly formation characteristic of agar-agar is due to presence of agarose, agaropectin lowers its jelly-forming capacity. Gelatin (collagen), the binder in living beings’ skeletons based on calcium phosphates, consists of sequences of alternating amino acids: glycine, proline and oxyproline. Polyvinyl alcohol is a synthetic polymer widespread as a binder in modern industry. The additives were introduced at 0.5 wt. % as premixed aqueous solutions. The specimens were molded by cold uniaxial pressing and thermogel casting [8].

Pressing was carried out in a closed mold under 200 MPa. If using thermogel casting, slip was prepared with 1% aqueous agar-agar solution as a dispersion medium. At 70 to 80°C the slip was poured out into dies, air-cooled and dried for one day. The molded specimens were annealed and sintered in air atmosphere at 1350 to 1400°C.

The phase composition of activated powders and sintered specimens was investigated by X-ray diffraction in cobalt emission using a ДРОН-3М diffractometer and a β-filter. Phase composition data were also obtained using Raman spectroscopy. Raman spectra were obtained by means of a SENTERRA (Bruker) multifunctional Raman spectrometer including double-laser Raman spectrometer modules and a confocal microscope. The instrument had a spectral range of 80 to 4500 cm⁻¹, spectral resolution of 3 cm⁻¹. The microscope had a spatial resolution of 1 µm. The measurements were performed at room temperature.

Specific surface areas of the powders were determined by the BET method using a ГХ-1 gasometer. The particle size was determined in a МЕТАМ-ЛВ-31 optical microscope. The specimen porosity was determined based on their apparent density using microsections under magnification of 500 to 1000. The open porosity was determined according to SS 25280-82. The compressive strength was determined using a FP 100/1 HECKERT tensile tester at 2 mm/min load rate.

3. Results and Discussion

Specific surface area and grain-size distribution data for titania powders are shown in Tab. I. Initially the titania powder is fine enough. Least of all the powder particle size is influenced if agar-agar is added during activation.

<table>
<thead>
<tr>
<th>Activation additive</th>
<th>BET method</th>
<th>Optical microscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Specific surface area, m²/g</td>
<td>Average particle size, µm</td>
</tr>
<tr>
<td>—</td>
<td>4.8</td>
<td>0.33</td>
</tr>
<tr>
<td>Agar-agar</td>
<td>5.9</td>
<td>0.27</td>
</tr>
<tr>
<td>Gelatin</td>
<td>6.1</td>
<td>0.26</td>
</tr>
<tr>
<td>PVA</td>
<td>6.6</td>
<td>0.24</td>
</tr>
</tbody>
</table>

X-ray diffraction (XRD) showed the powders to consist of well-crystallized anatase
and rutile with a high fine fraction content. Fig. 1 shows the initial titania powder diffraction pattern. Tab. II gives the intensity ratio of closely spaced lines of anatase $I_{100}$ (101) with 0.352 nm interplanar spacing and rutile $I_{100}$ (110) with 0.324 nm interplanar spacing. The increase in the ratio shows the relative anatase content in activated powder to have grown. During activation the titania powder changed its phase composition. Relative anatase content was reduced in case of activation with gelatin and PVA but increased if agar-agar was used. Such increase appears to be an uncommon enough phenomenon since the most stable form of titania is tetragonal rutile. Anatase (also tetragonal) is an unstable form which is transformed to rutile of considerably different density and lattice parameters above 800°C [9].

Tab. II – Impact of activation conditions on relative anatase content of titania powder

<table>
<thead>
<tr>
<th>Activation additive</th>
<th>—</th>
<th>agar</th>
<th>gelatin</th>
<th>PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase-to-rutile peak intensity ratio</td>
<td>0.33</td>
<td>0.36</td>
<td>0.26</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Fig. 2 gives data which illustrate rutile peak intensity ratio in diffraction patterns of activated powders and standard values for synthetic rutile (ASTM file) and natural rutile [10].

![Fig. 1](image1.png)

Fig. 1 – Initial titania powder diffraction pattern.

![Fig. 2](image2.png)

Fig. 2 Comparative characterization of rutile peak intensity ratio in diffraction patterns of titania powders with standard values.
Peak intensities of powders activated in the presence of agar-agar and PVA are virtually identical to corresponding peak intensities of synthetic rutile. Intensities of certain peaks (0.240 nm; 0.219 nm; 0.169 nm) of a powder activated in the presence of gelatin appear to presuppose the presence of both rutile forms in the powder composition.

Fig. 3 shows Raman spectra of rutile (standard data), initial commercial titania powder and titania powder after activation in the presence of agar-agar. Powder polyphasy may also be unambiguously identified on Raman spectra. In the case of activation in the presence of gelatin and PVA anatase-related peaks are less intense with respect to rutile peaks.

![Fig. 3 Raman spectra of titania powders: 1 – rutile; 2 – initial UHP 5-2 commercial titania powder; 3 – titania powder after activation in the presence of agar-agar.](image)

XRD data indicate sintered titania to consist of rutile only. Apparent density of non-activated powder after sintering at 1350°C is 3.53 ± 0.03 g/cm³, at 1450°C 3.63 ± 0.03 g/cm³. Fig. 4 shows apparent density of compacted specimens activated in the presence of various additives, as a function of sintering temperature.

![Fig. 4 Apparent density of sintered titania specimens as a function of sintering temperature: 1 – powder activation in the presence of agar; 2 – powder activation in the presence of gelatin; 3 – powder activation in the presence of PVA.](image)
Fig. 5 gives a compressive strength histogram for specimens activated in the presence of various additives, after sintering at 1350°C to 1400°C. Non-activated initial powder data are given for the sintering temperature of 1450°C since at lower temperatures no powder sintering occurs.

The highest strength was achieved after powder activation in the presence of agar-agar. Gelatin addition has the lowest impact on material strength.

Tab. III gives porosity data for cold-pressed specimens sintered at 1400°C (except for, as in the previous case, specimens made of non-activated initial powder which were sintered at 1450°C). Fig. 6 shows a photograph of a titania specimen microsection prepared from powder activated in the presence of agar-agar. The material contains mostly single pores of an almost regular shape and less than 1 μm in size.
Tab. III  Activation additive impact on the specimen porosity

<table>
<thead>
<tr>
<th>Activation additive</th>
<th>Total porosity (based on apparent density), %</th>
<th>Open porosity (based on hydrostatic weighing), %</th>
<th>Microsection-based porosity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without activation</td>
<td>14.8 ± 0.7</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Agar-agar</td>
<td>7.8 ± 0.3</td>
<td>0.12 ± 0.05</td>
<td>5.26</td>
</tr>
<tr>
<td>Gelatin</td>
<td>8.4 ± 0.7</td>
<td>0.23 ± 0.09</td>
<td>7.28</td>
</tr>
<tr>
<td>PVA</td>
<td>10.1 ± 0.6</td>
<td>0.21 ± 0.13</td>
<td>8.09</td>
</tr>
</tbody>
</table>

Thus, as in case of zirconia [11], one may note it is agar-agar that has a positive impact on the properties of specimens made of activated powder. Gelatin and synthetic polyvinyl alcohol have a smaller impact. The effect noted appears to fall among nanolevel interactions between minerals and organic substances accompanied by energy redistribution, and belongs to processes which ensure appearance of plant organisms on an inorganic substrate [12].

Activated titania-based powders have been demonstrated to be suitable for producing materials by thermogel casting which holds much promise at the moment. In order to form a sol containing ceramic powder particles as a filler and jellifying at temperature fall, aqueous agar-agar solution is often used. Properties of specimens obtained using thermogel casting and sintered at 1400°C are given in Tab. IV.

Tab. IV Properties of sintered titania samples obtained by thermogel casting

<table>
<thead>
<tr>
<th>Organic additive</th>
<th>Apparent density, g/cm³</th>
<th>Agar-agar</th>
<th>Gelatin</th>
<th>Polyvinyl alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1.73</td>
<td>2.82</td>
<td>3.12</td>
</tr>
<tr>
<td>Porosity, %</td>
<td></td>
<td>59.3</td>
<td>33.7</td>
<td>26.8</td>
</tr>
<tr>
<td>Open porosity, %</td>
<td></td>
<td>50</td>
<td>29</td>
<td>19.3</td>
</tr>
</tbody>
</table>

Specimens prepared from pure titania powder and powder activated by agar-agar are most porous. High porosity of non-activated powder is due to bad sinterability of this powder at 1400°C. In all cases the closed porosity is as low as 5 to 9%.

4. Conclusions

Mechanochemical activation of commercial titania powder in aqueous medium in the presence of agar-agar, gelatin or polyvinyl alcohol leads to increase in specific surface area and decrease in powder particle size.

According to X-ray diffraction data and Raman spectroscopy data, the initial powder consists of anatase and rutile. Activation in the presence of gelatin and PVA leads to a decrease in the relative anatase content while the presence of agar-agar results in an increase.

Comparison of rutile peak intensity in titania powders to standard data showed that only activation in the presence of gelatin results in disturbance of ratios typical of synthetic rutile and rutile similar to natural mineral appears in the powder.

Activated powders sinter at temperatures as low as 1350°C. Maximum strength and minimum porosity were noted for compacted specimens prepared from powder activated in
the presence of agar-agar.

When preparing specimens by thermogel casting using 1% aqueous agar-agar solution as a binder, the highest open porosity was achieved on specimens made of powder activated in the presence of agar-agar. Therefore, addition of agar-agar holds promise for activation of powders used in fabricating both porous and dense materials from titania.

Acknowledgments

The authors thank Professor V. N. Antsyferov, member of the Russian Academy of Sciences, member of IISS for his assistance in discussing the experimental results.

The work was supported by a grant from the Russian Foundation for Basic Research RFBR No. 08-08-00253-a.

References