Fabrication of Non-Stoichiometric Titanium Dioxide by Spark Plasma Sintering and Its Thermoelectric Properties

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To obtain non-stoichiometric titanium dioxide, TiO₂ powder was sintered in a graphite die by spark plasma sintering (SPS). The microstructure and the crystal type of the compacts were examined. Thermoelectric properties of the compacts were measured and discussed. The results revealed that TiO₂ could be easily reduced in the graphite die by SPS to obtain non-stoichiometric titanium dioxide, TiO₂−x, especially thermoelectric materials, especially thermoelectric materials, and other functional materials. To increase its electrical conductivity and sensing performance, it is necessary to increase oxygen vacancy in the crystal structure and obtain a non-stoichiometric titanium dioxide, TiO₂−x. In previous work, the powder was poured into a graphite die with a diameter of 0.3 µm and leveled off and set in the SPS system (SPS-1030, Sumitomo Coal Mining Co., Ltd.). Compacts with a dimension of φ40 × 2 mm were fabricated by SPS at 1073, 1173, 1273 and 1373 K. The holding time and pressure were 5 min and 34 MPa respectively. Plate samples with dimensions of 40 × 5 × 2 mm were cut from the disk compacts for thermoelectric properties’ measurements. The surfaces of the plate samples were polished to remove the adhered impurities. The microstructure, the composition and the crystal type were analyzed by SEM, EPMA, and XRD. The density of the compacts was monitored by Archimedean method.

To examine the composition of the TiO₂−x compacts, a thermal balance (TG-DTA 2000S, MAC science Co., Ltd.) was performed by a thermal balance (TG-DTA 2000S, MAC science Co., Ltd.). Specifically, 100 mg compact sample was heated in air up to 1273 K at 80 K/min, and held for 5 h.

1. Introduction

In recent years, thermoelectric materials have attracted much attention due to their potential applications in conversion between heat and electrical power such as electrical power generation from waste heat. Many researchers have focused on oxide thermoelectrics because they have many advantages such as non-toxicity, thermal stability, and high oxidation resistance, among others. In this condition, titanium dioxide has come within researchers’ range of vision for its applications as photocatalysts, especially thermoelectric materials, and other functional materials. To increase its electrical conductivity and catalytic activity and sensing performance, it is necessary to increase oxygen vacancy in the crystal structure and obtain a non-stoichiometric titanium dioxide, TiO₂−x. In previous work, the powder was poured into a graphite die with a diameter of 0.3 µm and leveled off and set in the SPS system (SPS-1030, Sumitomo Coal Mining Co., Ltd.). Compacts with a dimension of φ40 × 2 mm were fabricated by SPS at 1073, 1173, 1273 and 1373 K. The holding time and pressure were 5 min and 34 MPa respectively. Plate samples with dimensions of 40 × 5 × 2 mm were cut from the disk compacts for thermoelectric properties’ measurements. The surfaces of the plate samples were polished to remove the adhered impurities. The microstructure, the composition and the crystal type were analyzed by SEM, EPMA, and XRD. The density of the compacts was monitored by Archimedean method.

Besides, spark plasma sintering (SPS), as a rapid sintering process, is usually used to sinter oxides or ceramics. Also, graphite die is frequently used in SPS, and it is proper to sinter and reduce TiO₂.

In the present work, TiO₂ compacts were sintered and reduced in a graphite die during SPS. The compacts with non-stoichiometric titanium dioxide, TiO₂−x, were characterized by scanning electron microscopy (SEM), electron probe microanalysis (EPMA), and X-ray diffraction (XRD) and thermogravimetry analysis (TGA). The thermoelectric properties were measured from approximately 323 K up to 523 K in air.

2. Experimental

2.1 Fabrication of TiO₂−x

Rutile TiO₂ powder with a purity of 99.0% and an average diameter of 0.3 µm was used as the source material. Firstly, the powder was poured into a graphite die with a diameter of 40 mm, leveled off and set in the SPS system (SPS-1030, Sumitomo Coal Mining Co., Ltd.). Compacts with a dimension of φ40 × 2 mm were fabricated by SPS at 1073, 1173, 1273 and 1373 K. The holding time and pressure were 5 min and 34 MPa respectively. Plate samples with dimensions of 40 × 5 × 2 mm were cut from the disk compacts for thermoelectric properties’ measurements. The surfaces of the plate samples were polished to remove the adhered impurities. The microstructure, the composition and the crystal type were analyzed by SEM, EPMA, and XRD. The density of the compacts was monitored by Archimedean method.

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2.2 Measurements of thermoelectric properties

To obtain a uniform temperature gradient along the length direction of the TiO₂−x plate sample for measuring the Seebeck coefficient, a tubular electrical furnace with two
controllable heaters was used. The TiO$_2$-x plate sample was heated, and maintained at the measurement temperature and given a temperature difference, in other words, a temperature gradient between the two sides of the TiO$_2$-x plate sample. In the present study, the temperature differences were 10, 5, 0, $-5$ and $-10$ K. Here, 0 K implies that there was no temperature difference between the two sides. The negative temperature differences mean a reverse temperature gradient. The Seebeck coefficient was calculated from the $\Delta T\sim \Delta V$ curve, which was obtained by measuring thermal power in voltage at the given temperature differences. The electrical resistivity of the TiO$_2$-x plate sample at the elevated temperatures was measured when the temperature difference was 0 K. The measurements of thermoelectric properties were carried out in air from approximately 323 K up to 523 K, under which the effect of the re-oxidation during the measurements of thermoelectric properties was rather weak and can be neglected. That was conformed in the pro-experiments.

### 3. Results and Discussion

#### 3.1 Characterization of the compacts

A photograph of the compacts with a dimension of $\phi 40 \times 2$ mm fabricated by SPS is shown in Fig. 1. It can be seen that after SPS, the compacts got black from the white color of TiO$_2$ powder, and became blacker with increase of SPS temperature. The color change was probable related to the reduction of TiO$_2$ by the graphite die during SPS. The density and the electrical resistivity of the compacts at room temperature are listed in Table 1. When SPS temperature was above 1173 K, the density was close to the true density, and higher than that (3.44 g·cm$^{-3}$) of TiO$_2$-x formed in the reduction treatment using carbon powder reported in our previous work.$^{23}$ The electrical resistivity at room temperature decreased significantly with increase of SPS temperature, probably resulted from the reduction of TiO$_2$ to TiO$_2$-x. When SPS temperature was 1373 K, the electrical resistivity at room temperature was only 1.52 $\Omega$·mm, which was lower than that (2.20 $\Omega$·mm) of the reduced TiO$_2$-x at the same temperature in the previous work.$^{23}$ EPMA analysis for the composition of the compact fabricated by SPS at 1373 K is shown in Fig. 2. It shows that titanium and oxygen distributed uniformly across the cross section while carbon was not detected in the compact. It means the carbon of the graphite die did not penetrate the compact during SPS. In addition, the color uniformity of the compact also demonstrated that the composition of the compact was homogeneous. The rutile form was reserved after SPS process, as indicated by the XRD patterns of the compacts shown in Fig. 3. However, the peaks of (110) plane shifted to

<table>
<thead>
<tr>
<th>SPS temperature, K</th>
<th>Density, g/cm$^3$</th>
<th>Relative density</th>
<th>Electrical resistivity, $\Omega$·mm</th>
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<tbody>
<tr>
<td>1073</td>
<td>3.44</td>
<td>0.81</td>
<td>1590</td>
</tr>
<tr>
<td>1173</td>
<td>4.19</td>
<td>0.98</td>
<td>138</td>
</tr>
<tr>
<td>1273</td>
<td>4.25</td>
<td>0.99</td>
<td>12.1</td>
</tr>
<tr>
<td>1373</td>
<td>4.24</td>
<td>0.99</td>
<td>1.52</td>
</tr>
</tbody>
</table>

Note: true density is 4.26 g/cm$^3$
larger angles with increase of SPS temperature. The lattice plane distance of the (110) plane became narrow due to the loss of oxygen atoms in the crystal structure of TiO$_2$ as shown in Table 2. TGA of the compact fabricated by SPS at 1273 K was performed during heating to 1273 K for 5 h in air as shown in Fig. 4. The weight increase indicated that the compact has a composition of non-stoichiometric TiO$_2$$^{1-x}$. For the compact fabricated by SPS at 1273 K, the value of $x$ reached 0.02. Although the weight increase was very tiny and could not be detected when SPS temperatures were below 1373 K, it can be sure that the value of $x$ went up with increase of SPS temperature. From these results, the compacts with uniformly distributed non-stoichiometric, TiO$_2$$^{1-x}$ can be obtained in the graphite die by SPS. Also, the compacts had high density and low electrical resistivity.

3.2 Thermoelectric properties of TiO$_2$$^{1-x}$

The electrical resistivity and the absolute values of the Seebeck coefficient of the TiO$_2$$^{1-x}$ compacts from approximately 323 K up to 523 K are shown in Figs. 5 and 6, respectively. For comparison, the data of the TiO$_2$$^{1-x}$ plate fabricated by reducing TiO$_2$ plate through reduction treatment using carbon powder in the previous work$^{22}$ are also shown in Figs. 5 and 6. It can be seen that the electrical resistivity of the TiO$_2$$^{1-x}$ compacts decreased significantly with increase of SPS temperature, and tended to decrease with increase of measurement temperature. In other words, they showed a behavior of semiconductor. From Fig. 6, the Seebeck coefficient showed a similar evolution as the electrical resistivity. Besides, they are negative which means that the TiO$_2$$^{1-x}$ compacts are n-type thermoelectric material. Furthermore, Fig. 6 reveals that the Seebeck coefficient maintained at large absolute values, over 300 $\mu$V K$^{-1}$ in a wide temperature range up to 523 K. The activation energy of the TiO$_2$$^{1-x}$ compacts was calculated from ln $\rho$−1/T plots as listed in Table 3. It can be seen that the activation energies of the TiO$_2$$^{1-x}$ compacts were very small and decreased with increase of SPS temperature. It means that the TiO$_2$$^{1-x}$ compacts are in the state of the thermal activation. These results indicate that the value increase of $x$ led to the increase of carrier density. Therefore, the electrical resistivity and the absolute values of the Seebeck coefficient of the compacts went down. The power factor $P (= S^2/\rho)$ increased with increase of SPS temperature and reached a relatively large value of $5 \times 10^{-5}$ W m$^{-1}$K$^{-2}$ as shown in Fig. 7. The compacts with non-stoichiometric TiO$_2$$^{1-x}$ had a high thermoelectric performance. It is expected that the power factor can be increased by further reduction process.

<table>
<thead>
<tr>
<th>SPS temperature, K</th>
<th>Lattice plane distance of (110), nm</th>
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<tbody>
<tr>
<td>1073</td>
<td>0.3252</td>
</tr>
<tr>
<td>1173</td>
<td>0.3247</td>
</tr>
<tr>
<td>1273</td>
<td>0.3241</td>
</tr>
<tr>
<td>1373</td>
<td>0.3240</td>
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</table>

<table>
<thead>
<tr>
<th>SPS temperature, K</th>
<th>Activation energy, eV</th>
</tr>
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<tbody>
<tr>
<td>1073</td>
<td>0.077</td>
</tr>
<tr>
<td>1173</td>
<td>0.069</td>
</tr>
<tr>
<td>1273</td>
<td>0.022</td>
</tr>
<tr>
<td>1373</td>
<td>0.017</td>
</tr>
<tr>
<td>Reduced TiO$_2$$^{1-x}$ (at 1373 K)</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Fig. 4 Weight increase of the compact fabricated by SPS at 1373 K for 5 min during heated to 1273 K and kept for 5 h in air.
4. Conclusions

The compacts with non-stoichiometric TiO$_{2-x}$ and uniform composition distribution were obtained in graphite die by SPS. The electrical resistivity of the TiO$_{2-x}$ compacts decreased significantly with increase of SPS temperature. The Seebeck coefficient had a large absolute value over 300 $\mu$V K$^{-1}$ in the temperature range up to 523 K. The power factor increased and reached $5 \times 10^{-5}$ W m$^{-1}$ K$^{-2}$ at 523 K.

REFERENCES