Improvement in Thermoelectric Properties of Non-Stoichiometric Titanium Dioxide by Reduction Treatment

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Compacts of non-stoichiometric TiO₂-x were fabricated by SPS and the following reduction treatment in carbon powder. XRD, SEM and EPMA were used to characterize the compacts. The results showed that they were composed of non-stoichiometric TiO₂-x, inside and TiO as the surface layer. The thickness of the surface layer was increased with the increase of the holding time and exceeded 100 µm when it came to 20 h. Carbon did not penetrate into the compacts during the reduction treatment. To examine the carrier density and the non-stoichiometric number, 2-x, thermogravimetry was carried out. The study showed that the value of 2-x was decreased and the carrier density was increased as the holding time increased. The thermoelectric properties including electrical resistivity, Seebeck coefficient and power factor were measured. The electric resistivity was considerably reduced by the reduction treatment. The values of the Seebeck coefficient was also decreased by the reduction treatment but maintained at a large absolute value of 250 µV·K⁻¹. Therefore, the thermoelectric performance was improved by the reduction treatment. The influence of the TiO layer on the thermoelectric performance was also examined. It was believed that the influence should result from its comprehensive effect on Seebeck coefficient and electrical resistivity. [doi:10.2320/matertrans.E-M2013820]

(Received October 19, 2012; Accepted July 8, 2013; Published September 25, 2013)

Keywords: thermoelectrics, non-stoichiometric, titanium dioxide, reduction treatment

1. Introduction

In recent years, titanium dioxide (TiO₂) has been extensively investigated for its applications as photocatalyst,¹ gas sensor² and thermoelectric material,³,⁴ among others. To increase the electrical conductivity of TiO₂,⁵ other oxygens vacancy was introduced into the crystal to obtain non-stoichiometric TiO₂-x. In previous works,⁶,⁷ reduction treatment in an atmosphere of hydrogen or carbon monoxide at elevated temperature was often used to prepare TiO₂-x. Anatase TiO₂ was heated to 1223 K in pure hydrogen stream holding for 1h. Finally, it was reduced to form non-stoichiometric titanium dioxide TiO₂-x. In addition, TiO₂-x films was prepared by reducing TiO₂ films in an atmosphere of hydrogen at 1273 K and the value of x was 0–0.5.⁹ High temperature and hydrogen or carbon monoxide atmosphere are not safe for operation staffs. Therefore, a safer and simpler way to prepare non-stoichiometric TiO₂-x is expected.

In 2006, we proposed and performed a simple reduction treatment by carbon powder to reduce TiO₂ to obtain non-stoichiometric TiO₂-x.¹⁰ In addition, we also prepared non-stoichiometric TiO₂-x compact by spark plasma sintering (SPS) of TiO₂ in a graphite die.¹¹ The thermoelectric properties of TiO₂ were noticeably improved.

In this work, we will attempt to further improve the thermoelectric performance of TiO₂ by SPS with a graphite die and the following reduction treatment in carbon powder. The method is the combination of the two processes used in our early works.¹⁰,¹¹

2. Experimental

2.1 Fabrication of TiO₂-x compacts by SPS

Rutile TiO₂ powder with a purity of 99.0% and an average diameter of 0.3 µm was used as the source material to prepare non-stoichiometric titanium dioxide TiO₂-x. Firstly, 8 g TiO₂ powder was filled into a graphite die with a diameter of 40 mm and leveled off. Secondly, the graphite die filled with the powder was installed into the SPS system (SPS-1030, Sumimoto Coal Mining Co., Ltd.). Then, SPS was performed at 1373 K holding for 5 min with a pressure of 34 MPa. Plate samples with the dimensions of 40 mm × 5 mm × 2 mm were cut from the disk compacts fabricated by the above SPS. Finally, these plate samples embedded into carbon powder in an enclosed crucible experienced reduction treatment. The holding temperature and time were 1373 K and 0–20 h respectively. The heating rate was 10 K/min. A holding time of 0 h means that the samples were heated to 1373 K and immediately cooled to room temperature. The reduction process has been reported in our published work.¹²

To study the effect of the surface layer on their thermoelectric properties, some plate samples after the reduction treatment were polished by about 0.2 µm to remove the surface layer. Thermoelectric properties of these polished and unpolished plate samples were measured in air up to 573 K. The microstructure, the composition and the crystal type of these compacts were characterized by XRD, SEM and EPMA. Their density was monitored by Archimedean method. To examine the carrier density and the non-stoichiometric number of the polished compacts after the reduction treatment, thermogravimetry (TG) was measured by a thermal balance (TG-DTA) (2000S, MAC science Co., Ltd.). Specifically, 50 mg compact sample was heated in air up to 1273 k at 10 K/min and then held for 5 h at the
temperature in air. During the process, $\text{TiO}_2-x$ was totally oxidized and formed $\text{TiO}_2$ again.

### 2.2 Measurements of thermoelectric properties

The measurement method of thermoelectric properties has been described and can be found in our early work\(^{11}\) and it will not be involved here. The Seebeck coefficient and electrical resistivity were measured by the static method and 4-probe method respectively in air from room temperature up to 573 K. In that temperature range, the re-oxidation effect on the thermoelectric properties was rather weak and can be neglected.

### 3. Results and Discussion

#### 3.1 Characterization of the compacts

The photographs of the samples are shown in Fig. 1. It can be seen that the surface of the sample after the reduction treatment was red brown while the sample showed gray color after being polished. It indicates that the substances of the surface and the inner part of the sample should be different. Before the reduction treatment in carbon powder, the surface color of the sample was gray. It indicates that the surface layer should be formed in the reduction treatment.

The XRD patterns of the polished and unpolished samples are shown in Fig. 2. For the unpolished one (Fig. 2(a)), the diffraction peaks of rutile $\text{TiO}_2$ became lower and lower as holding time increased. At the same time, the peaks of $\text{TiO}$ got higher and higher. It means that the reduction treatment in carbon powder has great reducibility, even can reduce rutile $\text{TiO}_2$ on the surface of the compact to $\text{TiO}$. On the other hand, the inner substances of the compacts exposed after being polished (Fig. 2(b)). It can be seen that the peaks of Magneli phase $\text{Ti}_8\text{O}_{15}$ appeared and those of rutile $\text{TiO}_2$ became lower with the increase of holding time. It is obvious that the compacts reduced at 1373 K for 10 and 20 h are consist of Magneli phase $\text{Ti}_8\text{O}_{15}$ and rutile $\text{TiO}_2$. Magneli phases of titanium sub-oxides have been attracted much attention in numerous research fields due to their special properties of metal-nonmetal transition, electrical, thermal, optical property, among others.\(^{13-16}\) Although the compacts is not single Magneli phase, thereafter we will be care to observe the influence of the Magneli phase on thermoelectric properties. In addition, some trivial peaks also appeared in Fig. 2. Therefore, it can be confirmed that $\text{TiO}_2$ was reduced and the phases of non-stoichiometric $\text{TiO}_2-x$ were formed during the reduction treatment. However, the peaks of $\text{TiO}$ cannot be seen. From Figs. 1 and 2, it also can be concluded that the surface layer of the compacts should be $\text{TiO}$ which was formed by reducing $\text{TiO}_2$.

Figure 3 shows the SEM cross section images of these plate samples after reduction treatment for different holding time. A surface layer of dark color can be seen and the thickness of the surface layer was increased with the increase of holding time of the reduction treatment. The surface layer has been confirmed to be $\text{TiO}$ as discussed above. In addition, more pores were formed as holding time increased. The density of the compacts and the thickness of $\text{TiO}$ layer were given in Table 1. With the increase of holding time, the density of the compacts decreased due to the formation of...
pores. Furthermore, the thickness of TiO layer was also increased in the reduction treatment and reached 116 µm when holding time came to 20 h.

The results of EPMA line analysis of Ti, O and C on the cross sections of the plate samples are shown in Fig. 4. Ti and O distributed in the samples and carbon element nearly cannot be found in the samples. It means that carbon should not penetrate into the samples during the reduction treatment.

Figure 5 shows the weight increase of these samples during heating to 1273 K and holding for 5 h.

Table 1 Density of these compacts and thickness of TiO layer.

<table>
<thead>
<tr>
<th>Holding time (h)</th>
<th>Density (g·cm⁻³)</th>
<th>Thickness of TiO layer (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPS</td>
<td>4.24</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>4.18</td>
<td>23</td>
</tr>
<tr>
<td>1</td>
<td>4.19</td>
<td>51</td>
</tr>
<tr>
<td>10</td>
<td>4.07</td>
<td>91</td>
</tr>
<tr>
<td>20</td>
<td>4.02</td>
<td>116</td>
</tr>
</tbody>
</table>

Table 2 Carrier density and value of 2 − x for the samples after reduction treatment.

<table>
<thead>
<tr>
<th>Holding time (h)</th>
<th>Carrier density ( n_e \times 10^{18} ) (mm⁻³)</th>
<th>( 2 − x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.07</td>
<td>1.98</td>
</tr>
<tr>
<td>1</td>
<td>3.41</td>
<td>1.95</td>
</tr>
<tr>
<td>10</td>
<td>4.29</td>
<td>1.93</td>
</tr>
<tr>
<td>20</td>
<td>5.39</td>
<td>1.91</td>
</tr>
</tbody>
</table>

Table 3 Electrical resistivity of the polished and unpolished samples measured at room temperature.

<table>
<thead>
<tr>
<th>Holding time (h)</th>
<th>Electrical resistivity (Ω·mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unpolished</td>
</tr>
<tr>
<td>0</td>
<td>0.46</td>
</tr>
<tr>
<td>1</td>
<td>0.27</td>
</tr>
<tr>
<td>10</td>
<td>0.21</td>
</tr>
<tr>
<td>20</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Fig. 4 EPMA line analysis of these plate samples after reduction treatment for different holding time: (a) 1 h and (b) 20 h.

weight should come from the captured oxygen from air. Assuming that \( \text{TiO}_2-x \) was totally oxidized to form \( \text{TiO}_2 \), the carrier density and the value of \( 2 − x \) can be calculated by the weight increase. The calculation results are given in Table 2. It can be seen that the carrier density was increased but the value of \( 2 − x \) was decreased as holding time increased.

3.2 Thermoelectric properties

The electrical resistivity of the unpolished and polished samples was measured at room temperature as shown in Table 3. For polished and unpolished samples, the electrical resistivity was considerably decreased as holding time increased. The electrical resistivity of the unpolished samples was smaller than that of the polished samples.

The electrical resistivity of the samples before and after the reduction treatment at elevated temperatures up to 573 K was measured and the results are shown in Fig. 6. For the unpolished samples, the electrical resistivity hardly changed during the whole temperature range (Fig. 6(a)). For those fabricated by SPS (before the reduction treatment), the
electrical resistivity was much higher than those after the reduction treatment and decreased during the whole temperature range (Fig. 6(b)). On the other hand, the electrical resistivity of the polished samples was slightly decreased as a semiconductor. The electrical resistivity of TiO is approximately $3 \times 10^{-19} \text{m}$ at 300 K, and smaller than those of TiO$_2$ (x = 0–1). Therefore, the electrical resistivity of the unpolished samples was smaller than that of the polished samples, especially, it became smaller as the thickness of the TiO layer on the surface increased. The activation energy of the polished samples was calculated from $\ln \rho \sim 1/T$ curves and is listed in Table 4. It can be seen that the activation energy of the compacts was very small and increased with the increase of holding time.

The Seebeck coefficient of the polished and unpolished samples at elevated temperature up to 573 K is illustrated in Fig. 7. For convenience, the Seebeck coefficient having minus value is shown by the absolute value in the work. It can be seen that the Seebeck coefficient of the unpolished samples was increased but lower than 170 $\mu \text{V} \cdot \text{K}^{-1}$ as temperature increased. On the other hand, the Seebeck coefficient of the polished samples was between 150–250 $\mu \text{V} \cdot \text{K}^{-1}$ and the change was not evident during the whole temperature range. The electrical resistivity of the unpolished samples was decreased due to the TiO layer as above. The carrier density of TiO reported by D. S. McLachlan is approximately $3 \times 10^{19} \text{m}^{-3}$, which is larger than TiO$_2$, which is listed in Table 2. It led that the Seebeck coefficient of the unpolished samples was small than that of the polished samples.

The power factor, $P = S^2/\rho$ of the unpolished and polished samples was given in Fig. 8. The power factor, P of the samples after the reduction treatment was higher than that of the sample by SPS only (before the reduction treatment) (Fig. 8(b)). It means that the thermoelectric performance of the samples was improved by the reduction treatment. The sample with the holding time of 10 h had the greatest power factor and reached about $2 \times 10^{-4} \text{m}^{-1} \text{K}^{-2}$ at 573 K, which is a close value reported in Harada’s work. The value was much higher than those by SPS or reduction treatment in our early works. It suggests the combination of SPS and the following reduction treatment is effective and feasible to improve the thermoelectric performance of TiO$_2$. For the unpolished sample (Fig. 8(a)), the greatest power factor was realized when the holding time was 0 h. From the comparison, it can be confirmed that the surface layer of TiO had a certain influence on the thermoelectric performance of the samples. The influence should result from its comprehensive effect on Seebeck coefficient and electrical resistivity of the samples as discussed above. Indeed, the TiO layer on the surface of the compacts brought the decrease of the electrical resistivity, however led the fall of the Seebeck coefficient. It resulted that the TiO layer did not bring enhancement of the power factor as shown in Fig. 8. Besides, although Magneli phase Ti$_8$O$_{15}$ appeared in the compacts...
reduced at 1373 K for 10 and 20 h as above, the influence of
the Magneli phase on thermoelectric properties was not clearly
observed. It is probably due to forming only a few of the
Magneli phase Ti$_8$O$_{15}$ in the compacts. The present process is
a very simple preparation method of thermoelectric materials
and a considerable improvement on thermoelectric perform-
ance is expected through further reduction treatment.

4. Conclusions

Compacts composed of non-stoichiometric TiO$_{2-x}$ inside
and a surface layer of TiO were fabricated by SPS and the
following reduction treatment. The thickness of the surface
layer was increased as the holding time of the reduction
treatment increased. The value of 2 - x of the polished
compact was decreased and the carrier density was increased
with the increase of the holding time. The electric resistivity
was considerably reduced by the reduction treatment. The values of the Seebeck coefficient was also decreased by the
reduction treatment but maintained at a large absolute value
of 250 µV·K$^{-1}$ at 573 K. The thermoelectric performance was
improved by the reduction treatment. Power factor reached
2 × 10$^{-4}$ W·m$^{-1}$·K$^{-2}$ at 573 K. A complicated influence
of the surface layer of TiO on the thermoelectric performance
was confirmed. It was believed that the influence should
result from its comprehensive effect on Seebeck coefficient
and electrical resistivity. The improvement on the thermo-
electric performance of TiO$_2$ suggests that the combination
of SPS and the following reduction treatment was effective
and feasible.

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