Efficacy of Acid Cleaning on the Deoxidation of Titanium Powder Using Calcium

Chon-II Hong and Jae-Won Lim*
Division of Advanced Materials Engineering and Research Center for Advanced Materials Development, College of Engineering, Chonbuk National University, Jeonju 54896, Republic of Korea

Abstract: The optimum acid cleaning conditions for removing CaO formed by the reaction of Ca with Ti powder were investigated in this study. In this experiment, we used Ti powders composed of irregular polygonal Ti particles with average sizes of 125 mm and 250 µm. Ca granules were charged at 50% of the Ti mass into a deoxidation pot with Ti powder, and then the Ti powder with the Ca granules was deoxidized at 800 °C in a vacuum atmosphere of 5.0 × 10⁻⁴ torr. It was confirmed that subsequent acid cleaning with 10% HCl for 5 minutes reduced the initial oxygen concentration of the 125 µm-sized Ti powder from 2,000 ppm to 1,105 ppm. In the case of the non-contact deoxidation using Ca vapor at 900 °C, it was established that the non-contact deoxidation effect was higher than the contact type under the optimum acid cleaning condition of 10% HCl for 5 minutes. XRD and SEM analyses detected some Ca particles, and residual CaO on the Ti powder surface was confirmed without acid cleaning, but the acid cleaning process completely removed the residual CaO. It was also found that the deoxidation and acid cleaning decreased the c/a axial ratio of the Ti powder from 1.5885 to 1.5851.

(Received October 23, 2017; Accepted December 29, 2017)

Keywords: titanium, powder, deoxidation, acid cleaning, calcium

1. INTRODUCTION

Titanium is a light-weight metal and has excellent properties including high strength, corrosion resistance, and biocompatibility. It attracted wide attention in major industrial fields, such as medical, sports, leisure, energy, bio, and aerospace [1]. However, Ti is a costly material, and because of its high oxygen affinity and high reactivity, it is harder to process and mold than other metals. At the same time, advances in medical technology in recent years have increased the demand for products with more complex shapes, e.g., scaffolds. Because of this, there has been growing interest in methods that can fabricate products closer to their final shapes, which would minimize costly traditional finishing steps, such as grinding and polishing. Such ‘Near Net Shape’ fabrication of involves additional manufacturing, which can reduce material and processing costs [1,2]. The most significant problem in powder metallurgy is the high oxygen affinity of Ti. Oxygen can be present in a Ti matrix as an interstitial solid solution at up to about 33 at%. It also has a great influence on physical properties. Research to reduce the oxygen content of Ti has thus been a global challenge [3-7].

Oh et al. [4] reported that deoxidation in the solid state (DOSS) using Ca produced low-oxygen Ti powder, with less than 1,000 ppm of oxygen, a 60% oxygen reduction compared to the raw material. According to Okabe et al. [5], the Ti powder in DOSS was deoxidized by the reaction of Ca (g) + O (in Ti) = CaO (s). It has been known that the theoretical deoxidation limit could be increased by increasing the amount of added Ca and with heat treatment. One important step in the deoxidation process using calcium is to effectively remove enough of the CaO formed on the surface of the Ti powder after completion of the reaction. However, thus far there have been no quantitative studies on CaO removal after deoxidation. Therefore, in this study, we investigated an optimum condition for acid cleaning...
efficacy to remove CaO formed by the reaction of Ti powder and Ca in the deoxidation process.

2. EXPERIMENTAL PROCEDURES

The experimental procedure in this study is shown in Fig. 1. The Ti powder used in the experiment was irregular powder with average particle sizes of 125 μm and 250 μm, and the oxygen content of the raw material was analyzed to be 2,000 ppm. The deoxidizer of the Ti powder was 5-mm-sized Ca granules (purity of 99.5%). Ti powder and Ca were charged in a stainless-steel pot at a weight ratio of 2:1. Figure 2(a) is a schematic diagram of the deoxidation apparatus used in this experiment. In the experiment, deoxidation was performed at 800 °C. The deoxidation heat treatment was started under a vacuum pressure of 5 × 10⁻⁴ torr. The temperature was raised by 5 °C/min and maintained at 800 °C for 30 minutes. After completion of the deoxidation heat treatment, acid cleaning was performed for 1, 3, 5, 10, and 30 minutes using 5, 10, and 20% HCl, to remove the CaO from the Ti powder. As shown in Fig. 2(b), a stirrer was used for the acid and water washing steps. The net result of this basic experiment was to confirm that washing with water did not remove much of the CaO. The residual HCl and foreign matter were removed by washing with water for 5 minutes before and after the acid cleaning. After washing, the Ti powder was dried at 60 °C for 2 hours using a vacuum oven. Oxygen was measured with an oxygen/nitrogen analyzer (ON-900, ELTRA), using the average value of three analyses, and SEM and XRD analyses were performed.

3. RESULTS AND DISCUSSION

In general, separating Ti powder is known to be difficult because of the high melting temperature (≥838 °C) of Ca [4], while the self-diffusion of interstitial elements in Ti start at 670 °C. Not only the surface oxide layer, but also the thermodynamically stable internal oxygen diffuses to the surface, and the deoxidation effect has been reported to be greater at higher temperatures [4,5]. Accordingly, we selected a treatment temperature of 800 °C, which was effective for separating the powder and Ca after deoxidation with heat treatment.

Figure 3 shows photographs of the raw Ti powder and calcium before and after deoxidation. Although some particles were observed in the Ti powder by the naked eye after deoxidation, these particles were identified by XRD analysis as Ca separated during the heat treatment. According to Yoon et al. [6] unreacted Ca and CaO are converted to Ca(OH)₂ by washing with water and can be easily removed using acid.

\[ \text{Ca(s)} + 2\text{H}_2\text{O(l)} = \text{Ca(OH)}_2 + \text{H}_2(g) \]  \hspace{1cm} (1)

\[ \text{CaO(s)} + \text{H}_2\text{O(l)} = \text{Ca(OH)}_2 \]  \hspace{1cm} (2)
In this study, since 125 μm-sized Ti powders were used, it was possible to separate primary Ca particles using a 150 μm sieve before the washing process. In addition, there was no significant change in the oxygen concentration of the raw material after washing the powder with water. As a result, it was confirmed that the process of washing with water had no significant effect on the experimental results. Therefore, it was established that the most critical part of the washing process was the removal of CaO from the surface of the Ti powder with an acid. It has been reported that CaO on the surface of titanium powder can be easily removed by using HCl to form CaCl$_2$, as shown in the following reaction [6].

$$\text{CaO} + 2\text{HCl} = \text{CaCl}_2(l) + \text{H}_2\text{O}(l)$$

Changes in the oxygen concentration of the Ti powder depending on acid cleaning conditions are shown in Fig. 4. Ti powder containing CaO after deoxidation was analyzed to be 2210 ppm higher than raw material. Also, when the water cleaning was performed, the oxygen content of the titanium powder was 1925 ppm, which was not significantly different from that of the raw material, and confirmed that the acid cleaning plays the most important role in oxygen reduction. When the reaction was carried out for a long time (regardless of the concentration of HCl), the Ti powder tended to be re-oxidized by HCl. When using 5% HCl, the lowest oxygen content was obtained after a 10-minute reaction. When using 20% HCl, the lowest oxygen content of the powder was achieved after a 5-minute reaction. The result showed that using a high concentration of HCl accelerates the completion of the reaction. The optimum acid cleaning conditions were attained with 10% HCl and a 5-minute reaction. The oxygen concentration of the raw materials was reduced from 2,000 ppm to 1,105 ppm. In addition to the small size of the powder, the increasing irregularity of the particles increased their specific surface areas, thus sensitizing the product to the acid cleaning reaction [4]. It was therefore suggested that standardized conditions for powder sizes and shapes should be considered for industrial applications.

We also investigated the effect of powder size on the deoxidation of Ti powder. Table 1 shows the oxygen concentration according to acid cleaning conditions of 250 μm-sized Ti powder with irregular

<table>
<thead>
<tr>
<th>Powder size (Average value)</th>
<th>Time (min)</th>
<th>Raw (ppm)</th>
<th>Deoxidized (ppm)</th>
<th>Reduction rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 μm</td>
<td>10</td>
<td>1700</td>
<td>930</td>
<td>45.2</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1700</td>
<td>970</td>
<td>42.9</td>
</tr>
</tbody>
</table>
shapes. The oxygen concentration of the 250 μm-sized Ti powder also decreased as a function of the reaction time and then increased again. Since the specific surface area was smaller than that of 125 μm-sized Ti powder, the optimum reaction time was 10 minutes. Table 2 shows changes in oxygen concentration depending on the type of deoxidation heat treatment. Two types of such treatment were performed i.e., contact and non-contact. According to Oh et al. [4,9], a non-contact deoxidation process using only Ca vapor was devised because it was hard to recover the Ti powder after the deoxidation at ≥838 °C, given the melting temperature of Ca. In this study, the deoxidation heat treatment using Ca vapor at 900 °C was performed to confirm the oxygen concentration under the optimum acid-cleaning conditions. As a result, it was established that the non-contact deoxidation effect was higher than that of the contact type under the optimum acid-cleaning condition (10% HCl cleaning for 5 minutes). In the non-contact deoxidation process using Ca vapor, oxygen was diffused more easily by the transformation from α-Ti to β-Ti at 882 °C [4,5,9]. For this reason, the non-contact type was more effective for reducing oxygen.

Figure 5 shows the XRD analyses of the raw Ti powder materials before and after the acid cleaning process. The XRD peaks of all the Ti powders were confirmed to be the same α phase. However, because of the reduction in oxygen, the peaks were shifted 0.08° toward a high angle after deoxidation [3,7]. Also, the Ca peak was detected in the XRD peak of the Ti powder before the acid cleaning, but it disappeared after sufficient cleaning with HCl. Figure 6 shows the results of EDS mapping of the titanium powder before acid cleaning. After the deoxidation heat treatment, some Ca particles were observed in the Ti powder. The mapping results confirmed that oxygen reacted with Ca after deoxidation and existed in the entire region of the CaO formed on the surface of the Ti powder.

### Table 2. Oxygen concentrations in the Ti powder obtained under different deoxidation conditions (after optimum acid cleaning with 10% HCl for 5 minutes).

<table>
<thead>
<tr>
<th>Deoxidation type</th>
<th>Temperature (°C)</th>
<th>Vacuum (torr)</th>
<th>Raw (ppm)</th>
<th>Deoxidized (ppm)</th>
<th>Reduction rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact</td>
<td>800</td>
<td>5.0 × 10⁻⁴</td>
<td>2000</td>
<td>1105</td>
<td>44.8</td>
</tr>
<tr>
<td>Non-contact</td>
<td>900</td>
<td>5.0 × 10⁻⁵</td>
<td>1915</td>
<td>840</td>
<td>56.1</td>
</tr>
</tbody>
</table>

Fig. 5. XRD results of the Ti powder before and after acid cleaning.

Fig. 6. EDS mapping results of the Ti powder before acid cleaning.
Table 3. Comparisons of lattice parameters a, c, and axial ratios (c/a) of the raw and the deoxidized Ti powder after optimum acid cleaning with 10% HCl for 5 minutes.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Oxygen (ppm)</th>
<th>Lattice parameters</th>
<th>Forms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heo et al. [8]</td>
<td>2712</td>
<td>0.2953</td>
<td>0.4702</td>
</tr>
<tr>
<td></td>
<td>1593</td>
<td>0.2946</td>
<td>0.4667</td>
</tr>
<tr>
<td>Oh et al. [9]</td>
<td>2500</td>
<td>0.2946</td>
<td>0.4678</td>
</tr>
<tr>
<td></td>
<td>920</td>
<td>0.2946</td>
<td>0.4669</td>
</tr>
<tr>
<td>This study</td>
<td>2000</td>
<td>0.2943</td>
<td>0.4675</td>
</tr>
<tr>
<td></td>
<td>1105</td>
<td>0.2945</td>
<td>0.4668</td>
</tr>
</tbody>
</table>

Table 3 shows the lattice parameters and the c/a axial ratio of the Ti powder after the deoxidation. Since the interstitial oxygen atoms are reduced by the deoxidation process, the ‘specific lattice volume’ was decreased, and the c/a axis ratio tended to decrease [10-12]. The c/a axial ratio was also used as a criterion for calculating the number of interstitial elements of Ti. In this study, it was confirmed that the c/a axial ratio decreased from 1.5885 to 1.5851 after the deoxidation and acid cleaning processes.

4. CONCLUSIONS

In this study, we investigated variables that would lead to optimal acid cleaning conditions for the efficient deoxidation of Ti powders. Deoxidation of Ti powders was carried out by deoxidation heat treatment under a vacuum atmosphere through DOSS using Ca. The following conclusions were obtained:

(1) The optimum acid cleaning efficacy of 125 μm sized Ti powder was reduction for 5 minutes using 10% HCl, which resulted in a reduction from an initial oxygen concentration of 2,000 ppm to 1,105 ppm. When the reaction time was prolonged with a high concentration of HCl, re-oxidation of the Ti powder occurred during the acid cleaning process.

(2) XRD and SEM analyses showed some Ca particles and residual CaO on the Ti powder surface before acid cleaning; the acid cleaning process completely removed them. It was also confirmed that the deoxidation and acid cleaning processes decreased the c/a axial ratio from 1.5885 to 1.5851.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2017R1A2B4007005).

REFERENCES