Oxygen behavior during non-contact deoxidation of titanium powder using calcium vapor

Jung-Min Oh [a], Hanjung Kwon [a], Wonbaek Kim [a], Jae-Won Lim [b],*

[a] Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources, Daejeon 305-350, Republic of Korea
[b] Division of Advanced Materials Engineering and Research Center for Advanced Materials Development, College of Engineering, Chonbuk National University, Jeonju 561-756, Republic of Korea

ABSTRACT

Deoxidation behavior before and after deoxidation during preparation of low oxygen titanium powder was discussed. Transmission electron microscopy and secondary ion mass spectraoscopy studies revealed that the oxide layer was reduced to a thickness of 3 nm from 11 nm and the oxygen content within the powder was decreased from 2500 ppm to 920 ppm. The reduction of oxygen content resulted in the decrease of the lattice parameters and axial ratios. The surface oxide of deoxidized powder was quite stable in air showing no increase in the oxygen content after the exposure for one month.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Oxygen is a major interstitial element in titanium and a cause for defects. Thus, there have been active researches on reducing the oxygen content of titanium [1–3]. The deoxidation method most widely used nowadays involves the use of calcium and calcium chloride having high oxygen affinity [4–7]. The greatest driving force of titanium deoxidation is the diffusion of oxygen atoms within titanium [8]. When the deoxidation of titanium is carried out above 1155 K, titanium transforms from a hexagonal close-packed (HCP) to body-centered cubic (BCC) crystal structure. In the latter structure, the diffusion of oxygen becomes relatively more active. Before reaching the transformation temperature of titanium, the diffusion speed of oxygen is low and the change is minimal; however, after transformation to BCC structure at the high temperature above transformation, atomic movement occurs more than 100 times faster than before [8,9]. The above-mentioned studies, however, pertain to bulk titanium, and there are few studies reported on titanium powder. Because there is a technical difficulty of the sound recovery of powder due to the melting of calcium at the relatively high deoxidation temperatures in the case of powders. In order to

overcome this issue, we previously manufactured a non-contact deoxidation pot for use with calcium vapor. The titanium powder was deoxidized at a temperature above the transformation temperature, and the resulting recovered powder had a low oxygen content of less than 1000 ppm [10–12]. The non-contact deoxidation method using calcium vapor for reduction of TiO_2 was originally designed by Okabe et al. [13]. On the other hand, we modified the non-contact deoxidation method for titanium powder using a sieve to obtain extremely low oxygen concentration.

The mechanism of calcium-induced oxygen removal from titanium is explained using Gibbs free energy and the respective partial pressures of the substances [14,15]. The explanation is that oxygen present within the titanium powder diffuses more easily with an increase in the deoxidation temperature, forming an oxide layer on the surface of the titanium powder. At this point, the high oxygen affinity of calcium, the deoxidizing agent used, leads to the decomposition of the titanium oxide layer and the subsequent formation of calcium oxide. However, although there are numerous deoxidation studies, most of these studies only measured the changes in the oxygen content before and after deoxidation. There have been no reports on the changes in the surface oxide layer, oxygen content inside titanium, or lattice strains before and after deoxidation.

Therefore, in the present study, we have investigated the deoxidation behavior by analyzing the surface oxide layer, lattice strains, and internal oxygen content before and after deoxidation during preparation of low oxygen titanium powder of less than 1000 ppm. Further, we

* Corresponding author. Tel.: +82 63 270 2307; fax: +82 63 270 2305.
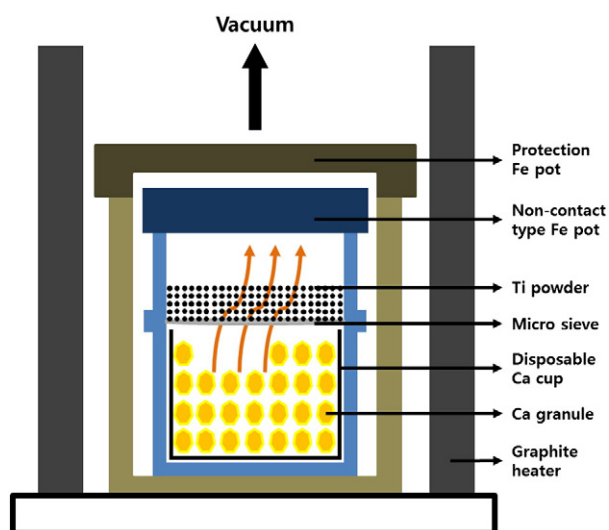 *E-mail address:* jwlim@jbnu.ac.kr (J.-W. Lim).

Fig. 1. Schematic diagram of deoxidation of Ti powder at above the beta Ti temperature.

have investigated whether the produced titanium powder oxidized again on exposure to air for an extended period of time after deoxidation.

2. Experimental details

The titanium powder and calcium are products of High Purity Chemicals (Japan) with a purity of 99.9%, and JUNSEI (Japan) with a purity of 99.5%. The schematic diagram of the deoxidation experiment conducted in this study is shown in Fig. 1. The deoxidation experiment involved a specially manufactured deoxidation pot that did not allow contact between the calcium and titanium powders. A microsieve (100 μm) was placed in the top portion of the deoxidation pot, and 50 g of titanium powder was placed on top of the sieve. In the bottom portion, an equal amount of calcium was weighed and placed. The top and bottom parts of the pot were bolted together, and the deoxidation pot was sealed. The deoxidation pot was placed in a vacuum heat-treatment furnace, and the vacuum inside the furnace was reduced to 6.7×10^{-3} Pa. The furnace temperature was then raised to 1273 K and maintained for 2 h. After the completion of deoxidation, the titanium powder and calcium were removed from the deoxidation pot. Then, the titanium powder was cleaned for removing CaO using a series of separation, water wash, acid wash, and drying process [10–12].

The thus-obtained titanium powder was then analyzed with an oxygen analyzer (LECO, TCH-600), using a tin capsule for the powder, to measure the oxygen content of the deoxidized powder. The oxygen content of a blank tin capsule was determined to be 70 ppm. Therefore, 70 ppm was subtracted from each of the oxygen content values obtained from the analysis of the titanium powder. The average error range for

the oxygen analyzer was ±50 ppm. Scanning electron microscopy (SEM, Jeol, JSM-6380LA) was also conducted to observe the macroscopic surface conditions of the raw and the deoxidized powders. An X-ray diffraction analysis (Rigaku, RTP 300 RC) was carried out to confirm the phase changes and the presence of the remaining calcium. A focused ion beam (FIB) was used for creating a sample slice for the transmission electron microscopy (TEM, Jeol, JEM-2100F) analysis of the changes in the surface oxide layer after deoxidation of the titanium powder. Furthermore, secondary ion mass spectrometry (SIMS, CAMECA, IMS 7f) was used for analyzing and comparing the differences in the surface and the internal oxygen contents of the source material and the deoxidized powders. The primary ion source used for determining the contents of Ti^- and O^- ions was Cs^+.

3. Results and discussions

The raw titanium powder had a particle size distribution of approximately 100–150 μm and an average particle size of 115 μm. The shape was determined to be irregular, the typical geometry of titanium powders produced by a hydrogenation-dehydrogenation process. The deoxidized titanium powder was almost identical to the raw powder in terms of particle size and shape. The size and shape of the original and deoxidized titanium powders is detailed in Fig. 2. The changes in the oxygen content during the deoxidation process were found not to have caused any changes in the structure of the deoxidized powder. Next, the changes in the oxygen content in the two powders were measured. The raw titanium powder was found to have an oxygen content of 2500 ppm. In the deoxidized powder, the oxygen content was 920 ppm. This reflected a 63.2% decrease from the raw oxygen content and confirmed that it was possible to produce low oxygen titanium powder (<1000 ppm of oxygen) through a non-contact deoxidization method using calcium vapor, which was reported before [10]. Unlike bulk titanium, it is very difficult to produce titanium powder with low oxygen content because of the surface oxide layer formation due to an increase in the specific surface area of powders. There has been no report of a highly pure, commercial titanium powder with an oxygen content of less than 1000 ppm.

The deoxidation of titanium is known to occur in the following manner: oxygen within the titanium reacts with calcium above a certain temperature and is eliminated as calcium oxide. In order to specifically investigate this process, XRD, TEM, and SIMS analyses were carried out on the raw powder and the produced low oxygen titanium powder. Fig. 3 shows the XRD results of the raw and the deoxidized titanium powders. Both the raw and the deoxidized powders showed diffraction peaks corresponding to α-titanium. This could be attributed to the fact that at the deoxidation temperature of 1273 K, titanium exists as β-titanium and exhibits BCC structure; however, as the titanium is cooled after deoxidation, it transforms to the stable α-titanium at room temperature. Several studies have reported that calcium oxide and calcium–titanium compound residues were found after the completion
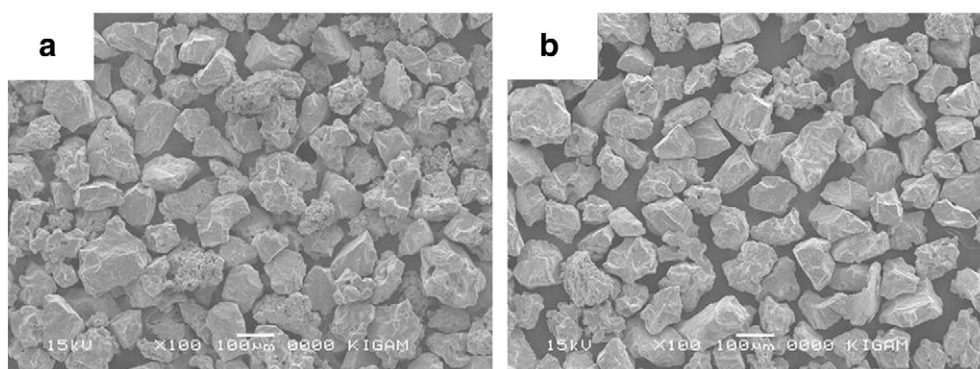

Fig. 2. SEM images of (a) the raw and (b) the deoxidized Ti powder.