Deoxidation of Ti Powder and Preparation of Ti Ingot with Low Oxygen Concentration


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In this experiment, we carried out a two-step deoxidation process to obtain Ti ingots with low oxygen concentration from commercial Ti powder. The first step was to primarily reduce oxygen in Ti powder using Ca and the second was to melt the deoxidized Ti powder in Ar atmosphere with added hydrogen using a vacuum arc melting system. We used two types of raw Ti powder, one with a high oxygen concentration of 5,600 ppm and average powder size of 35 µm, and the other with 2,200 ppm and 115 µm. The high oxygen of 5,600 ppm in the Ti powder was reduced to approximately 1,460 ppm by the two-step process of melting after deoxidizing the Ti powder with Ca at 973 K. On the other hand, in the case of the Ti powder with low oxygen of 2,200 ppm, the Ti ingot with low oxygen of 600 ppm could be prepared by the two-step process of melting after deoxidizing at 1,103 K. The Vickers hardness and c/a value of Ti ingots decreased as the oxygen concentration decreased. [doi:10.2320/matertrans.M2012004]

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1. Introduction

The maximum solubility of oxygen is approximately 30 at% in Ti and the dissolved oxygen largely affects the physical, mechanical and electrical properties of Ti.1,2) For example, Ti has recently been used as a sputtering target in the electronic industries. The oxygen concentration in Ti should be regulated because its oxygen concentration degrades the electrical properties of the sputtered film. Heo et al.3) reported that when the oxygen concentration in Ti increased from 500 to 7,910 ppm, the resistivity increased about 42%. Researches for the deoxidation of Ti in Japan showed the method to reduce oxygen using halide flux such as Ca/ CaCl2 which has the large solubility.4,5) Suzuki et al.6) and Song et al.7) reported that the oxygen concentration in Ti was reduced to 20% in comparison with the value of starting materials as a result of the above experiment.

On the contrary, few studies on the deoxidation from Ti powder had been reported, because it is difficult to recover Ti powder due to the liquid sintering with a melt of Ca in Ca/ CaCl2. The DOSS (DeOxidation in Solid State) process which was developed by RMI Titanium in the USA8) used high vapor pressure of metal Ca without flux such as Ca/ CaCl2 for the deoxidation of Ti. The exposure of Ti powder to the liquid Ca can be minimized when the gaseous Ca is applied. However, the DOSS process has a deoxidation limit because it conducts deoxidation below the melting point of Ca. To overcome the deoxidation limit, we carried out a two-step process to maximize the deoxidation effect at a temperature below the melting point of Ca and to obtain Ti ingots with low oxygen concentration by vacuum melting. At first we primarily reduced oxygen in Ti powder using Ca vapor and then prepared Ti ingots using the deoxidized Ti powder in an Ar atmosphere with added hydrogen.

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2. Experimental

The experiment procedure for this study is shown in Fig. 1. We used two types of raw Ti powder, one with a high oxygen concentration of 5,600 ppm with an average powder size of 35 µm, and the other with 2,200 ppm and 115 µm. Both Ti powders with high and low oxygen concentration are products of HIGH PURITY CHEMICALS (Japan) with a purity of 99.9%, and the Ca is JUNSEI (Japan)’s products with a purity of 99.5%. The Ca used in the experiment was granular with an average size of less than 5 mm. As a preliminary experiment, we investigated the effect of Ca addition for the deoxidation. The weight ratio of Ca addition was changed from 30 to 100% against the Ti powder. As a result, we obtained the highest deoxidation effect at the 50% of Ca addition. Therefore, the weight ratio of the Ca addition for the deoxidation was fixed at 50% against the Ti powder. A heat treatment process for the deoxidation was carried out by charging Ti powder (100 g) and Ca (50 g) in a stainless vessel together, and then the vessel was heated at the rate
of 283 K/min at 6.6 × 10⁻⁴ Pa and held for 1 h. The CaO remained on the Ti powder deoxidized by Ca and it was removed through the following process: washing, filtering, and drying. The collected Ti powder was then compressed into the tablet (30 g, φ25 mm) for vacuum arc melting. The Ti compaction was loaded into a water-cooled copper mold in a melting furnace. The base vacuum pressure before introducing Ar–5%H₂ gas was 1.3 × 10⁻³ Pa. The Ti compaction was melted at 300 A and 10 V in an Ar–5%H₂ atmosphere for 2 min. The size of the Ti ingot was φ35 mm and 15 mm in height. Oxygen concentration in the deoxidized Ti powder and the ingots were measured using an oxygen gas analyzer (LECO TC–436). To verify residual Ca in the deoxidized Ti powder and the ingot, Inductively Coupled Plasma (ICP, Jobin Yvon, JY38 plus) analysis was carried out. X-ray diffraction analysis (Rigaku, RTP 300 RC) and the Vickers hardness test (Akashi, MVK–E) with 300 g load were used to examine the lattice strain in the Ti ingots and the change in hardness due to oxygen concentration.

3. Results and Discussion

We defined Ti powder with high and low oxygen concentrations as Ti A and Ti B, respectively. The deoxidation process using Ca is composed of the reaction formula: Ca + O (in the Ti powder) = CaO (s). Fig. 2 shows the variation of oxygen concentration in the Ti powder as a function of deoxidation temperature at the range of 773–1,103 K. Oxygen reduction in the Ti powder A and B was not distinctly observed at 773 K, while oxygen concentration was considerably reduced at 873 K. This can be explained by the tenfold difference in the equilibrium vapor pressure of Ca between 773 and 873 K, which results in the outstanding deoxidation effect at 873 K. For Ti A, the oxygen concentration at the range of 773–973 K was reduced from the initial concentration of 5,600 to 1,940 ppm and then conversely increased to 3,000 ppm at 1,103 K. Recovery of the sound Ti powder was possible up to 973 K. However, it was difficult to recover sound Ti powder since the sintering between Ti powder and CaO partially or wholly occurred at 1,073 and 1,103 K. In the case of Ti B, the oxygen concentration was continuously reduced from the initial concentration of 2,200 to 1,080 ppm when the temperature increased from 773 to 1,103 K. It was found that the oxygen concentration was reduced to the lowest value at 1,103 K, which was close to the melting point of Ca (1,111 K). The reason for the different tendency was the difference in powder size of Ti A and B. The average powder sizes of Ti A and B was 35 ± 3 and 115 ± 5 µm, respectively. For Ti A, due to the larger surface area based on the three times smaller than average powder size, the sintering phenomena with CaO began to occur above 1,073 K. From the experimental results, it was found that it is difficult to recover sound Ti A due to the sintering with CaO even though the deoxidation temperature is below the melting point of Ca.

As a second step, a button type of Ti ingot was prepared by vacuum arc melting in the Ar–5%H₂ atmosphere using Ti powder deoxidized with Ca. For Ti A, the Ti powder deoxidized at 973 K was tested to prepare a Ti ingot, while all the Ti B powder deoxidized at 773–1,103 K was used to obtain Ti ingots with a low oxygen concentration. In the case of Ti A powder, a Ti ingot with an oxygen concentration of 1,460 ppm could be prepared after melting. The variation of oxygen concentration in the Ti ingots and raw Ti B powder as a function of deoxidation temperature are shown in Fig. 3. It was confirmed that when the raw Ti powder was melted, an approximate 400–500 ppm of oxygen reduction occurred for the entire range of deoxidation temperatures. As a result, we could obtain a Ti ingot with 600 ppm by vacuum arc melting starting from the Ti powder with 1,100 ppm deoxidized at 1,103 K. The additional deoxidation effect of Ti powder during melting in the Ar–5%H₂ atmosphere can be explained as follows: easy vaporization of Ti sub-oxides on the surface of Ti powder with high vapor pressure in the vacuum system.

To verify residual Ca in the deoxidized Ti powder and the ingot, we measured residual Ca concentration using ICP analysis for Ti powder and ingot after deoxidation process. The Ca concentration in the raw Ti B powder was 156 ppm. When the deoxidation temperature of the Ti B powder with Ca was at 773, 873, 973, 1,073 and 1,103 K, the Ca concentrations in the Ti B powder after deoxidation were changed to 157, 155, 154, 170, and 260 ppm respectively. There was no distinct change in the Ca concentration in the Ti B powder before and after deoxidation at the range of 773–1,073 K. On the other hand, the Ca concentration in the
Ti B powder deoxidized at 1,103 K remarkably increased to 260 ppm. We found that the Ti ingot obtained using Ti B powder deoxidized at 1,103 K contained approximately 50 ppm of Ca. This suggests that the Ca concentration remaining in the Ti powder after deoxidation considerably reduced to the level below 50 ppm after melting for 2 min due to the high vapor pressure of Ca during melting.10)

The change in hardness according to oxygen concentration in the Ti ingot prepared by vacuum arc melting was also studied. The oxygen concentration in Ti significantly increases its hardness.11) To examine the relationship between the lattice strain and the hardness in Ti due to oxygen concentration, we plotted the hardness change and the \( \frac{c}{a} \) value of the Ti ingots as a function of oxygen concentration, which are shown in Fig. 4. The hardness of the Ti ingots increased with the oxygen concentration. The oxygen concentration and the hardness of the Ti ingot prepared using the raw Ti B powder were 1,850 ppm and 219 Hv. The hardness of the Ti ingot with 600 ppm was 150 Hv. Generally, the hardness of Ti decreases when interstitial impurities such as oxygen and nitrogen are reduced. Because of this, the \( \frac{c}{a} \) value of Ti decreases as the interstitial impurities are reduced, the number of slip plane in the hcp structure increases and the hardness accordingly decreases.3) According to the lattice strain in Fig. 4, it was found that the \( \frac{c}{a} \) value of the hcp structure such as Ti decreases according to the decrease in oxygen concentration. It was confirmed that the \( \frac{c}{a} \) value of the Ti ingot with 1,850 ppm of oxygen concentration was 1.5863, and when the oxygen concentration decreased to 600 ppm, the \( \frac{c}{a} \) value decreased to 1.5818.

4. Conclusions

To overcome the deoxidation limit of the DOSS process without CaCl\(_2\) halide flux, we carried out the two-step deoxidation process to obtain Ti ingots with low oxygen concentration from commercial Ti powder. High oxygen of 5,600 ppm in the Ti powder was reduced to approximately 1,460 ppm by the two-step process of the melting after deoxidizing Ti powder with Ca at 973 K. In the case of the Ti powder with low oxygen of 2,200 ppm, we could obtain the Ti ingot with 600 ppm by melting in the Ar–5%H\(_2\) atmosphere via the Ti powder with 1,100 ppm deoxidized at 1,103 K. It was confirmed that the Ca concentration remained in the Ti powder after deoxidation decreased below 50 ppm after melting for 2 min. Concerning the relationship between the lattice strain and hardness, it was also found that the \( \frac{c}{a} \) value of the Ti ingot with 1,850 ppm of oxygen concentration was 1.5863. Additionally when the oxygen concentration decreased to 600 ppm, the \( \frac{c}{a} \) value decreased to 1.5818.

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REFERENCES