Deoxidation Thermodynamics of β-Titanium by Ca-CaCl$_2$ and Ca-CaF$_2$ Fluxes

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Deoxidation of β-titanium was investigated by Ca-CaCl$_2$ and Ca-CaF$_2$ fluxes at 900 to 1400°C. The content of oxygen in Ti was strongly dependent not only on the Ca potential but on the stability of CaO in the fluxes. The present experimental results indicate that deoxidation of Ti by Ca-calcium halide fluxes could be controlled by the activity ratio of CaO to Ca. The ratio of $a_{\text{CaO}}/a_{\text{Ca}} = 0.06$–0.1 was strongly recommended for obtaining oxygen content of 40–160 ppm [doi:10.2320/matertrans.MRP2008284]

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Titanium has been used in novel applications because of its inherent specific strength and corrosion resistance, which are dependent on the concentration of oxygen in Ti. However, oxygen in Ti has been known to be a controlling element for the mechanical properties of Ti due to its strong affinity with Ti.$^{1,11}$ However, one of the difficulties with the oxygen concentration in Ti is the lack of metallurgical options for deoxidation due to the large solubility and strong affinity of oxygen in Ti. Two concepts for oxygen controlling for purification of Ti have been applied up to now: electrochemical method$^{3–8}$ and molten flux method.$^{12–18}$ Since the electrochemical method$^{3–8}$ has been reported the possibility for deoxidation of Ti by electrochemistry with molten halide salt$.^{9–11}$

On the other hand, recent studies have usually focused on deoxidation of solid Ti by applying chemical refining technology with molten flux in view of mass producing process, energy efficiency, etc.$^{12–18}$ However, these studies for chemical refining technology also found that the content of oxygen in Ti equilibrated with pure metallic calcium is higher than the expected value in view of thermodynamics because of local precipitation of CaO on the surface of Ti. Based on these experimental results, Okabe et al.$^{12–16}$ and Suzuki et al.$^{17,18}$ proposed that deoxidizing efficiency could be increased by using molten fluxes (Ca-CaO, Ca-CaCl$_2$, and Ca-BaCl$_2$). These previous results concluded that the removal of precipitated CaO on Ti surface plays an important role in improving the efficiency of deoxidation of Ti by using Ca bearing salt. Even though these recent studies proposed the possibility for deoxidation of Ti with Ca-calcium halide flux, together with the deoxidation mechanism, the optimum condition for the maximization of oxygen removal from Ti is still not clearly understood.

Therefore, the present study focused on the effects of the calcium halides (CaCl$_2$ and CaF$_2$) that might prove suitable as a solvent for dissolution of CaO and temperature on deoxidation of Ti. Furthermore, the effect of activity of Ca and CaO in calcium halide fluxes on the degree of deoxidation was analyzed to propose the optimum condition for minimizing the oxygen content in β-titanium using the thermochemical equilibration technique.

A SiC electric resistance furnace was used for equilibrating Ti located on a molybdenum basket with the Ca-CaO-CaX$_2$ (X = Cl and F) flux charged in a capped iron crucible (>99.9%, 27 mm outer diameter × 20 mm inner diameter × 37 mm height). The crucible assembly was maintained in an Al$_2$O$_3$ holder (52 mm outer diameter × 48 mm inner diameter × 70 mm height) filled with alumina powder (>99.9%) and then placed in the furnace for 12 h. Equilibration time had been considered 12 h after preliminary test using 17 mol% Ca-CaCl$_2$ flux at 900°C. The temperature was controlled within ±2°C using an R-type (Pt-13% Rh/Pt) thermocouple and a proportional-integral-differential controller. In order to guarantee the uniform initial content of oxygen and nitrogen in solid Ti, the LECO® standard samples (Part No. 502–201, 0.2670 (±0) mass% O and 0.0170 (±0) mass% N) were used. Calcium granules (>99.9%), and dehydrated CaCl$_2$ and CaF$_2$ powders (>99.9%), which were kept in vacuum desiccators to protect them from air and moisture, were employed in the present study. The CaO powder was calcined from CaCO$_3$ of reagent grade at 1000°C for 4 h. The experimental apparatus is shown in detail in a previous article.$^{19}$ After the experiment, the iron crucible was quenched by an Argon gas stream. To remove the residual chloride flux adhered to the Ti sample, the samples were treated in diluted HCl (1:20) solutions at 70°C for 10–60 min. In the case of the fluoride flux, the diluted HCl (1:20) solutions were used at 70°C for 5–10 min. The contents of oxygen and nitrogen in Ti were analyzed by an inert gas fusion-infrared absorption method using LECO® TC-300. It was confirmed that the nitrogen content was less than about 50 ppm.

The equilibrium concentration of oxygen in β-titanium equilibrated with calcium can be estimated as follows;

$$\Delta G^\circ = -2.303RT \log \frac{a_{\text{CaO}}}{a_{\text{Ca}}} \cdot \frac{1}{f_{\text{O}_{2},\text{Ti}}} \cdot \text{mass}\% \text{O}_{\text{m,Ti}}$$

$$= -583,000 + 88.57T \text{[J/mol]} \ (900–1100°C)^{22}$$

$$= -562,000 + 91.67T \text{[J/mol]} \ (1050–1300°C)^{20}$$

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where $\alpha_{\text{CaO}}$ and $\alpha_{\text{Ca}}$ are the activity of CaO and Ca, respectively. $f_{\text{Ca}_1\text{Ti}_n}$ is the Henrian activity coefficient of oxygen in $\beta$-titanium, which can be assumed to be unity by regarding the standard state as that of 1 mass% oxygen. Thus, eq. (2) is rearranged as follows;

$$\log[\text{mass}\% \text{O}_{\text{in Ti}}] = \log \left( \frac{\alpha_{\text{CaO}}}{\alpha_{\text{Ca}}} \right) + \frac{\Delta G^f}{2.303RT}$$  

(3)

Equation (3) indicates that the content of oxygen in Ti has a linear relationship with temperature and the ratio of $\alpha_{\text{CaO}}$ to $\alpha_{\text{Ca}}$ in the flux in logarithmic scale. In the present study, the activity of CaO in flux was estimated from the activity of Ca in Ca-CaX$_2$, which was calculated with equation of activity coefficient after Fishbach,\textsuperscript{21} and the concentration of oxygen in Ti at a given temperature.

Deliberating that the phase diagram of Ca-CaX$_2$ and CaO-CaX$_2$ binary systems proposed the maximum chemical potentials of Ca and the minimum of CaO in each flux, the optimization of chemical potentials between CaO and Ca in the flux would be an important factor to determine the efficiency of deoxidation of Ti. If the chemical potential of CaO in the flux was higher than the solubility, the precipitated solid CaO film on the surface of Ti would act in Ca-CaX$_2$ flux system can be obtained at 1100°C. The pronounced condition for the critical content of oxygen in Ti in case of Ca-CaCl$_2$ and Ca-CaF$_2$ flux can be obtained at $\alpha_{\text{CaO}}/\alpha_{\text{Ca}} = 0.06$ and 1.0, respectively. In Fig. 2(a), a dashed line indicates a Ca saturated composition in the Ca-CaCl$_2$ flux system, which was measured by Staffansson and Sichen,\textsuperscript{23} and this is in good accordance with the lowest concentration of oxygen in Ti at fixed temperature. On the other hand, a chain line for the Ca-CaF$_2$ system in Fig. 2(b) is not a Ca saturated composition in the Ca-CaF$_2$ flux. The activity of Ca on a chain line changes from about 0.8 to 0.5 with increasing temperature. If the activity of Ca in the Ca-CaF$_2$ flux should be increased to unity, the chain line for the Ca-CaF$_2$ system would be lowered to a chain double-dashed line.

These complex behaviors of equilibrium oxygen in Ti can be understood by taking the phase diagram into account as follows. The phase diagram of the Ca-CaCl$_2$ binary system that had been determined by Eastmann et al.\textsuperscript{24,25} indicates that the solubility of Ca exhibits a minimum at about 1000°C when temperature increases to greater than 825°C. This
means that the activity coefficient of Ca in the flux is maximized at 1000~1100°C. However, this phase diagram has a discrepancy in the solubility from the result of Staffansson and Sichen. In the present study, the solubility of Ca in the Ca-CaCl₂ binary system is in good agreement with the phase diagram of Staffansson and Sichen. On the other hand, the solubility of CaO in the CaO-CaCl₂ binary system steadily increases with increasing temperature. This means that the activity of CaO shows a positive deviation and decreases with increasing temperature at a fixed composition. Therefore, the activity of Ca in the flux is a dominant factor affecting the deoxidation limit of Ca-CaCl₂ flux at 1000~1100°C.

In the case of a Ca-CaF₂ flux system, the pronounced condition of deoxidation is obtained at 1200~1300°C, which corresponds to a maximum solubility of Ca from the phase diagram of a Ca-CaF₂ binary system. At this temperature region, the CaO+CaF₂ solid solution could be formed from the CaO-CaF₂ binary phase diagram. Since the thermodynamic behavior of Ca and CaO in the Ca-CaO-CaF₂ ternary system has not been experimentally proved yet, further studies will be required.

Figure 3 shows the effect of CaO concentration on deoxidation efficiency of Ti at 1000°C. The equilibrium concentration of oxygen in Ti gradually increases by increasing the content of CaO in the 5 mol% Ca-CaCl₂ flux up to about 10 mol% CaO, followed by a constant value of 5 mass% O. This tendency is in qualitatively good agreement with the results measured by Suzuki et al. The activity of Ca in the Ca-CaCl₂ and that of CaO in the CaO-CaCl₂ system are also shown. The maximum difference in the activity between CaO and Ca can be obtained at about 7 mol% Ca or CaO, viz. 93 mol% CaCl₂, where \( \alpha_{\text{CaO}} = 0.34 \). If Ca content is higher than the saturated composition, the difference in the activity between CaO and Ca decreases and thus the deoxidation efficiency diminishes sharply. Therefore, it is suggested that the activity ratio of CaO to Ca can be considered as a deoxidation index of Ca-calcium halide flux.

The iso-oxygen content lines in Ti, which is equilibrated with the CaCl₂ rich Ca-CaO-CaCl₂ flux at 1000°C, were shown in Fig. 4. The iso-oxygen lines lean to the Ca-CaCl₂ binary side and increase from 60 to 110 ppm O in Ti with increasing CaO content. This tendency can be understood by the activity change of Ca and CaO in the flux.

We can summarize that deoxidation of β-titanium with Ca is strongly affected by the stability of byproduct (CaO) and can be controlled by calcium halide fluxes, such as CaCl₂ and CaF₂. And there exists a critical point of deoxidation of Ti which combined the lowest content of oxygen in Ti and corresponded with the minimum \( \alpha_{\text{CaO}}/\alpha_{\text{Ca}} \) at specific temperature. In calcium halide fluxes such as CaCl₂ or CaF₂, the lowest content of oxygen in Ti could be attained by the optimization of the activity ratio of CaO to Ca as 0.06 at 1100°C and 0.1 at 1300°C, respectively. The activity ratio of byproduct to reactant can be suggested for the deoxidation index of β-titanium with calcium halide flux.

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