Equilibrium Relationship Between Titanium and Oxygen in Molten Fe-Ti Alloy With High Concentration of Titanium

Yong Woo Kim¹, Min-Kyu Paek², Sun-Joong Kim¹*

¹Chosun University
309 Pilmun-daero, Dong-gu, Gwanju, Republic of Korea, 61452
Phone: +82-62-230-7200
Email: ksjoong@chosun.ac.kr

²Umicore
Watertorenstraat 33, Olen, Belgium, 2250

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INTRODUCTION

Metallic titanium is generally obtained by chlorination treatment of high-grade rutile ore (TiO₂). This process is known as the Kroll method, which produces the sponge Ti containing O in the range of 300 to 1000 ppm.¹ However, the O content in the Ti alloy can be increased through subsequent remelting, casting, and machining processes. Also, the off-grade sponge Ti with high Fe solubility can be formed during the Kroll process by the reaction with the low-carbon steel sheet of the vessel. Such impure sponge Ti is used as an alloying source of Ti or deoxidizer in the steelmaking processes.² Moreover, there are various processes for the production of Ti alloys such as the FFC Cambridge process,³ the Ono Suzuki process,⁴ the molten oxide electrolysis process,⁵ the performing reduction process,⁶ and the USTB titanium process.⁷ Although Ti has excellent mechanical properties, the manufacturing costs are expensive compared to the other alloy production due to its high melting point, high reactivity, and difficult machinability. Alternatively, great efforts are being made to develop low-cost recycling technology using titanium alloy scrap.⁸,⁹ More strict O control can be required to produce ferrotitanium alloys by the pyrometallurgical recycling process at high temperatures because that will directly affect the quality of the final product. However, the studies on the oxide formation and equilibrium O content in the ferrotitanium containing high Ti up to 70 mass% are very limited.

Therefore, in the present study, deoxidation equilibria in molten Fe-Ti alloys were studied over the entire Ti concentration range to provide accurate thermodynamic information for the refining of ferro-titanium alloys. The Ti-O relation in Fe-Ti alloy melts in equilibrium with TiO was measured from 10 to 70 mass% of Ti at 1873 K. However, the experimental results and calculation of the Ti-O relation in liquid iron using Wagner’s formalism were inconsistent with each other, especially at high Ti concentration. This can be caused by the extremely strong attraction force between Ti and O in liquid iron with the limitation of the dilute solution model. In order to describe the strong interaction, Modified Quasichemical Model (MQM) in pair approximation was applied to consider it as the Short-Range Ordering (SRO) in the alloy melt.¹⁰ The present model successfully reproduced the deoxidation equilibria for the entire Fe-Ti melt. The fundamental thermodynamic properties such as the activity of Ti, equilibrium oxygen content, oxygen partial pressure, stable oxide phase information, etc. were predicted for the refining of the ferro-titanium recycling process.

METHODOLOGIES

1. Experimental

The Ti deoxidation equilibria were determined at 1873 K by measuring the pure solid TiO. In order to obtain the equilibrium value under the TiO stable region, the TiO-lined MgO crucible was used as shown in Figure 1. Three hundred grams of pre-melted Fe-Ti alloys were melted using a high-frequency induction furnace. The purified Ar gas was blown after passing through the pre-heating furnace charged with the sponge Ti (99.9 %purity). The gas flow rate was adjusted to 0.5 L/min. The oxygen partial pressure of the outlet gas was measured using a zirconia oxygen sensor and monitored during the entire reaction time for 2 hours. The melt temperature was accurately controlled within 2 K by immersing a B-type thermocouple with a magnesia protective tube. The alloy samples were taken after furnace cooling with helium gas blowing and suction sampling by quartz tube to compare the effect of cooling rate on the total O content in the solidified samples. The quenched samples were cut for
chemical analysis and polished to remove the oxide layer formed on the surface. The total O contents of metal samples were measured by the inert gas fusion-infrared absorptiometry technique using the N/O analyzer. The concentration of Ti in the metal sample was analyzed by the Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The equilibrium oxide phase and its structure was characterized by the electron backscatter diffraction (EBSD).

2. Thermodynamic Modeling
Deoxidation equilibria have been described using Wagner’s formalism based on the random distribution of atoms in the liquid solution. However, when the atoms in the liquid solution exhibit a strong interaction with each other, the array of atoms can be affected. Since Ti and O in liquid iron also show a negative interaction, an inappropriate evaluation of the ideal configurational entropy of mixing will occur. In order to overcome this problem, Modified Quasichemical Model (MQM) in the pair approximation was used in this study. The Short-Range Ordering (SRO) caused by the strong attraction force between atoms was reasonably accounted for by the negative Gibbs energy of the following pair exchange reaction.

\[(A-A)+(B-B)=2(A-B); \quad \Delta g_{AB} \quad (1)\]

The non-ideal mixing entropy of solution was explicitly considered in MQM according to the interactions of the solution species in the Fe-Ti-O and its sub-systems such as Fe-Ti, Fe-O, and Ti-O systems. Detailed descriptions and the associated notations of MQM are available elsewhere.\[2]

RESULTS AND DISCUSSION

1. Ti-O Relation in Fe-Ti Alloy Melt
The Ti deoxidation equilibrium in Fe-Ti alloy melt is represented by the dissolved Ti and O contents in equilibrium with solid titanium oxide. The contour line of the Ti-O relation gives the Ti deoxidation curve. Since the stable titanium oxide phase can be changed depending on the equilibrium oxygen potential between the oxide phase and Fe-Ti alloy melt, various equilibrium reactions have to be considered to understand the Ti deoxidation equilibria in Fe-Ti melt over the wide concentration range. In particular, it is well known that the Fe-Ti melt can be saturated with TiO in the composition range of ferrotitanium alloys. Cha et al.\[12] measured the Ti-O relation in Fe-Ti melt by changing Ti concentration from 4 ppm Ti to 16.6 mass%Ti at 1873 K. They
confirmed that the NaCl type cubic structure of TiO can be the stable equilibrium oxide phase at high Ti concentration above 10.6 mass%Ti. Hadley and Derge\textsuperscript{13} measured the Ti-O relation up to a much higher Ti level of about 46 mass%Ti at 1873 K. However, no equilibrium oxide phase information was reported at a high Ti concentration range. Therefore, in order to check the accuracy of the previous experiments at a high Ti concentration range, the Ti-O relation in Fe-Ti alloy melt was measured over the wider Ti concentration range from 10 to 70 mass%Ti at 1873 K. As shown in Figure 2, the previous experimental results by Cha et al.\textsuperscript{12} and Hadley and Derge\textsuperscript{13} have good correlation with each other at high Ti concentration range, whereas the O contents of the present experimental data were much lower and the difference was getting bigger with increasing Ti content. It can be caused by the total O difference with the quenching rate. In our preliminary experiment at 50 mass%Ti, it was confirmed that the O content of the sample taken from the solidified alloy in the furnace was much higher than the sample by the water quenching. Even though the O content of the furnace-cooled sample shown as an open circle in the figure matched well with Hadley and Derge\textsuperscript{13}’s experimental result, a lot of oxide inclusions were observed by SEM-EDS analysis.

2. Thermodynamic Modeling of Liquid Fe-Ti-O Alloy System
The present experimental results measured by the rapid sampling and water quenching were directly used as the input value of thermodynamic modeling for the Fe-Ti-O ternary system. As mentioned earlier, MQM was used to consider the SRO among the Fe, Ti, and O atoms exhibited in the liquid solution. Figure 3 shows the Ti deoxidation equilibria in Fe-Ti alloy melt in log scale together with the experimental results\textsuperscript{12-15} and calculated deoxidation curves.\textsuperscript{16} For the description of the Ti deoxidation in Ti bearing steels and stainless steels, Wagner’s formalism has been widely used because it can cover the Ti concentration range of these steel grade. However, as shown in the figure, the deoxidation curve by Wagner’s formalism with the Japan Society for the Promotion of Science (JSPS) recommended value of interaction parameters has a maximum value at around 7 mass% and sharply decreases. It can be attributed to the thermodynamic inconsistency of this dilute solution model at a high alloy concentration range. On the other hand, the present model reproduced the experimental results from pure Fe to Ti-rich side successfully using MQM.
CONCLUSIONS

The Ti-O relation in Fe-Ti alloy melt was determined by measuring Ti and O contents in the high Ti concentration range from 10 to 70 mass% at 1873 K. Present experimental data was thermodynamically analyzed using the Modified Quasichemical Model to account for the strong attraction force between atoms in the liquid solution as Short-Range Ordering. The present model successfully reproduced the Ti deoxidation equilibria in Fe-Ti alloy melt over the entire composition range of Ti. The developed database was used for the optimization of the ferrotitanium recycling process by providing fundamental thermodynamic information.

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REFERENCES