

Note

Reassessment of Oxide Stability Diagram in the Fe–Al–Ti–O System

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Phase equilibria of Fe–Al–Ti–O system is shortly reviewed, in particular for stability of oxide phases in equilibrium with liquid Fe alloy in dilute concentration. This system is relevant to Ultra Low Carbon steel with Ti alloying (Ti-ULC), often causing clogging of Submerged Entry Nozzle (SEN) during continuous casting. In order to predict stable oxides in the Ti-ULC steel, thermodynamic calculation using CALPHAD approach was employed. Previously available thermodynamic calculations were examined, and compared with available experimental data. A slight modification of thermodynamic modeling of previous investigation resulted in noticeable improvement for the prediction of stable phases by thermodynamic calculation. Significance of the present revision of the thermodynamic modeling is discussed in the view of nozzle clogging of Ti-ULC casting.

KEY WORDS: Fe–Al–Ti–O system; phase diagram; calphad; nozzle clogging; ultra low carbon steel.

1. Introduction

It has been a long-standing problem that clogging of Submerged Entry Nozzle (SEN) occurs during continuous casting of Ti added Ultra Low Carbon (Ti-ULC) steel. Increasing Ti content significantly increases extent of the nozzle clogging. Although cause and countermeasure of the nozzle clogging for Ti-free steel has been known, those for Ti-ULC are still unclear. Basu *et al.* reported interesting phenomena and possible mechanism during continuous casting of Ti-ULC.¹⁾ However, correct mechanism has not been elucidated yet. A number of researchers have paid attention to non-metallic inclusions in the Ti-ULC steel.^{2–6)} It is easily thought that inclusions as a deoxidation product may consist of Al–Ti–O. Various kinds of oxides may be considered: Al₂O₃, Ti₂O₃, Ti₃O₅ as well as complex oxide such as Al₂TiO₅ or liquid oxide. It has been a debate whether the complex oxides exist in liquid steel as inclusions or not, and whether these complex oxide inclusions may be responsible for the serious nozzle clogging of Ti-ULC or not. So called “inclusion stability diagram” in the Fe–Al–Ti–O was then introduced, first by Ruby-Mayer *et al.*,⁷⁾ subsequently by a number of researchers.^{2,8–10)} Recently, the present authors have paid attention to the interfacial reaction between

Ti-ULC steel and refractory of SEN.¹¹⁾ The refractory generates CO(g), which reacts with Ti-ULC steel at the interface between inner wall of the nozzle and the liquid steel. As a reaction product, it was found that liquid oxide formed along with solid alumina. Interpretation of this reaction also requires knowledge on thermodynamics and phase equilibria in the Fe–Al–Ti–O system. The oxide observed was not just an inclusion in liquid steel, therefore in the present note, phase diagram representing stability of various oxide phases in equilibrium with liquid steel is called “oxide stability diagram”.

The oxide stability diagram at 1 520°C reported by Ruby-Mayer *et al.*⁷⁾ is shown in Fig. 1. The diagram is governed by stable regions of Ti₂O₃, liquid oxide, Al₂TiO₅, and Al₂O₃. Liquid oxide and Al₂TiO₅ are seen to be stable between Ti₂O₃ and Al₂O₃. Jung *et al.*⁸⁾ proposed a new diagram calculated at 1 600°C using FactSage.¹²⁾ They reported that Ti₃O₅ should also be stable, by replacing some part of the stable region of Ti₂O₃, and liquid oxide was not to be stable. Later, they revised their diagram that the liquid oxide appears between Ti₃O₅ and Al₂O₃.¹⁰⁾ Matsuura *et al.*²⁾ proposed a different type of oxide stability diagram at 1 600°C where Al₂TiO₅ located between Ti₃O₅ and Al₂O₃. They did not consider liquid oxide phase due to limited thermodynamic information of liquid oxide.

Recently, Jo carried out a series of experiments in order to observe whether complex oxide (Al₂TiO₅, liquid oxide) is stable apart from Al₂O₃ and Ti₃O₅.¹³⁾ He equilibrated liquid Fe–Al–Ti alloy in an Al₂O₃ crucible at 1 600°C, and analyzed concentrations of Al and Ti in the liquid alloy using ICP, concentration of O using LECO, and interface between the liquid alloy and the crucible using SEM and EBSD. They confirmed that only Ti₃O₅ was newly formed between the liquid alloy and the Al₂O₃ crucible, when concentration of O in the liquid alloy was less than ~ 40 mass ppm. This means that only Ti₃O₅ and Al₂O₃ should appear in the oxide stability diagram in the range ([ppm O] < 40). This result does not conform to the previous thermodynamic calculations.^{2,7–10)} Matsuura and Tsukihashi also reported that no intermediate phase was found between Al₂O₃ and TiO_x solid phases in liquid Fe–Al–Ti alloys at 1 600°C, when concentration of O was less than ~ 60 ppm.¹⁴⁾ This also partly agrees with the result of Jo.¹³⁾ It can be inferred from these investigations that there is no phase between Ti₃O₅ and Al₂O₃ in the Fe–Al–Ti–O system when concentration of O in the liquid alloy is low (less than ~ 60 ppm).

The present authors’ recent investigation revealed that liquid oxide can form at relatively higher concentration of O, obtained by reaction with CO(g).¹¹⁾ Reaction between

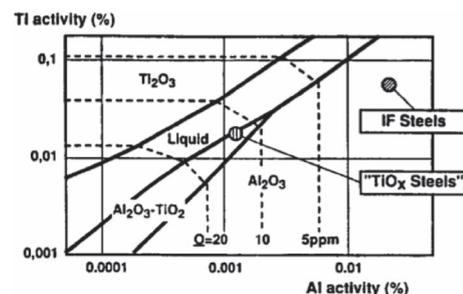


Fig. 1. Oxide stability diagram of the Fe–Al–Ti–O system at 1 520°C reported by Ruby-Mayer *et al.*⁷⁾

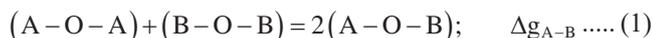
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liquid Fe and CO(g) would increase the concentration of O up to ~ 500 ppm. Therefore, in such high O region, the liquid oxide should appear in the oxide stability diagram. This is important to interpret interfacial reaction between Ti-ULC steel and nozzle refractory. So far, the oxide stability diagrams reported in literature^{2,7-10} do not explain recent experimental data consistently. In the present study, a new oxide stability diagram in the Fe–Al–Ti–O system is presented, by reassessing available thermodynamic modeling of the system.

2. Thermodynamic Model and Modification

In the present study, CALPHAD type thermodynamic calculation was carried out using FactSage.¹²⁾ The following phases were considered: liquid alloy (Fe–Al–Ti–O), liquid oxide (FeO–FeO_{1.5}–TiO_{1.5}–TiO₂–AlO_{1.5}), corundum (Al₂O₃ with limited solubility of Ti₂O₃), ilmenite (Ti₂O₃ with limited solubility of Al₂O₃), pseudobrookite (Ti₃O₅ with limited solubility of FeTi₂O₅), spinel (FeAl₂O₄ with limited solubility of Fe₃O₄), and Al₂TiO₅. Gibbs energies of these phases were initially taken from FactSage FTOxid and FTmisc databases. Formulation of Gibbs energies are described in previous reports.^{8,15-19)} Using these thermodynamic information, initially calculated oxide stability diagram of Fe–Al–Ti–O system at 1 600°C looks almost the same to that reported by Jung *et al.* in 2009.¹⁰⁾ In order to make the liquid oxide phase less stable to conform with the data of Jo¹³⁾ and that of Matsuura and Tsukihashi,¹⁴⁾ it was decided to reassess Gibbs energy of liquid Al₂O₃–TiO₂–Ti₂O₃ system.

Gibbs energy of the liquid oxide phase was modeled using the Modified Quasichemical Model in the pair approximation.²⁰⁾ In an AO–BO liquid oxide solution, the following pair exchange reactions are considered:



where (*i*-O-*j*) represents a Second-Nearest Neighbor (SNN) pair. Entropy of mixing is obtained by randomly distributing various SNN pairs in one-dimensional Ising approximation. The non-configurational Gibbs energy change for the formation of two moles of (A–O–B) pairs is Δg_{A-B} , which is used as model parameter in each binary system. Gibbs energy of ternary and higher order system is then estimated using appropriate interpolation method,²¹⁾ and a few of adjustable ternary model parameters can be added.

The previously estimated Gibbs energy of liquid Al₂O₃–TiO₂–Ti₂O₃ system by Jung *et al.*¹⁰⁾ was revised in the present study. The Gibbs energy of the ternary system was first estimated from that of sub-binary system using “Toop-like” interpolation method, with Al₂O₃ as an asymmetric component.²¹⁾ Since TiO₂–Ti₂O₃ binary liquid exhibits negative deviation¹⁶⁾ while Al₂O₃–TiO₂ and Al₂O₃–Ti₂O₃ exhibit positive deviation,¹⁰⁾ it is thought that choosing Al₂O₃ as the asymmetric component is reasonable. A small ternary adjustable parameter, 41 840 ($X_{\text{AlO}_{1.5}}/(X_{\text{AlO}_{1.5}} + X_{\text{TiO}_{1.5}} + (4/3)X_{\text{TiO}_2})$) (J/mol), was added to the $\Delta g_{\text{Ti}^{3+}-\text{Ti}^{4+}}$,¹⁶⁾ in order to reproduce the experimental data of Jo in the Fe–Al–Ti–O oxide stability diagram at 1 600°C.¹³⁾ This parameter represents an effect of Al³⁺ on the formation energy of (Ti³⁺-O-Ti⁴⁺), thereby making the (Ti³⁺-O-Ti⁴⁺) SNN pair less stable by Al³⁺ (TiO₂–Ti₂O₃ binary liquid exhibiting

less negative deviation). By changing the interpolation method as well as adding the positive ternary parameter, the Gibbs energy of Al₂O₃–TiO₂–Ti₂O₃ liquid oxide becomes relatively positive over entire composition, and the ternary liquid oxide could be less stable, compared to the previous assessment.¹⁰⁾ This resulted in narrowed liquid region in the ternary phase diagram.

Figure 2 shows a calculated liquidus surface of Al₂O₃–TiO₂–Ti₂O₃ system, which is slightly different to that proposed by Jung *et al.*¹⁰⁾ The minimum eutectic temperature was increased from 1 496°C¹⁰⁾ to 1 553°C, for a eutectic reaction Liquid→Ilmenite+Corundum+Ti₄O₇. The decreased stability of ternary liquid then contributes to the narrowed liquid oxide region in Fe–Al–Ti–O system.

Figure 3 shows a calculated oxide stability diagram in equilibrium with liquid alloy at 1 600°C in the Fe–Al–Ti–O system, extended to lower concentrations of Al and Ti. Thin lines are calculated iso-[ppm O] lines, and thick lines are phase boundaries. The stability diagram is mostly governed by Al₂O₃–corundum, (Ti,Fe)₃O₅–pseudobrookite, and liquid oxide (Fe₂O–TiO_x–Al₂O₃). Stability regions of FeAl₂O₄–spinel and (Ti,Al)₂O₃–ilmenite are also seen in limited regions. Open circles are experimentally determined concentrations of Al and Ti in the liquid alloys, which was in equilibrium with Ti₃O₅ and Al₂O₃.¹³⁾ The experimental method was described in Sec. 1. The experimental data were in good agreement with the present thermodynamic calculation, except for one datum at higher Al, Ti concentrations.

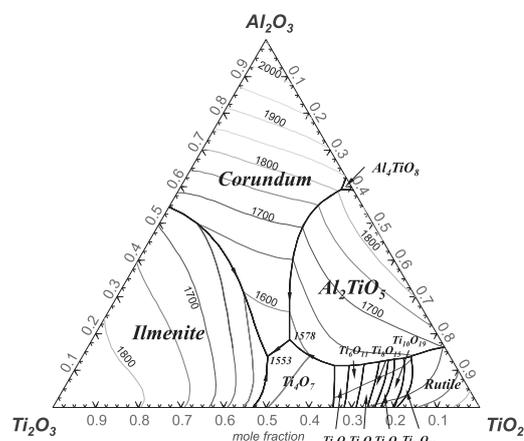


Fig. 2. Calculated liquidus surface of Al₂O₃–TiO₂–Ti₂O₃ system.

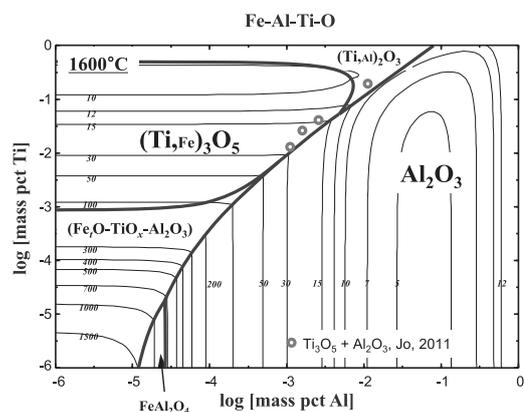


Fig. 3. Calculated oxide stability diagram of the Fe–Al–Ti–O system at 1 600°C in the present study. Thin lines are iso-[ppm O] lines. Open circles were taken from Jo.¹³⁾

Jo reported that there were no phases observed between Al_2O_3 and Ti_3O_5 , where [ppm O] was less than ~ 40 ppm. In the calculated diagram, liquid oxide becomes stable when [ppm O] is higher than ~ 50 ppm. Indeed, the size of ternary model parameter for the liquid oxide phase mentioned earlier was optimized in order to reproduce the experimental data of Jo,¹³⁾ but to be stable at high O content according to the present authors' investigation.¹¹⁾ It should be noted that the "50 ppm" (lower limit of O concentration where the liquid oxide becomes stable) is only an approximated value. Therefore, it should be understood that the liquid oxide is not stable when [ppm O] is less than ~ 40 ppm,^{13,14)} but it should be stable at relatively higher O concentration.¹¹⁾

3. Oxide Stability Diagram in Casting Condition

When the Ti-ULC steel passes through SEN connecting tundish and casting mold, the liquid steel is in contact with the nozzle refractory, which emits $\text{CO}(\text{g})$ according to Sasai and Mizukami.²²⁾ Temperature and O concentration at the interface between the liquid steel and the nozzle refractory are different to that in bulk liquid steel in RH. The temperature is about 1520°C – 1550°C . Equilibrium O concentration in liquid Fe was estimated in such a way that $\text{CO}(\text{g})$ dissolves into the liquid Fe by $\text{CO}(\text{g})=\underline{\text{C}}+\underline{\text{O}}$, and saturated concentration of O at this temperature range is about 500 ppm. This high O would consume Al and Ti in the liquid steel. Hence, concentrations of Al and Ti near the interface should be lower than those in the bulk. Similarly, concentration of O should be higher than that in the bulk.

Figure 4 shows a calculated (predicted) oxide stability diagram in the Fe–Al–Ti–O system at 1540°C in order to simulate condition at the interface during continuous casting. When concentrations of Al and Ti are in the range of a few hundred ppm, concentration of O is seen to be a few ppm (marked as "Region A"). This corresponds to the bulk steel. Equilibrium oxide phase is Al_2O_3 . This also tells that most stable inclusions in the bulk steel is alumina. On the other hand, when concentration of O in the liquid steel is high due to the dissolution of $\text{CO}(\text{g})$ from the refractory nozzle, it is reasonable to think that concentrations of Al and Ti are lower and concentration of O is higher than those in the Region A. This is marked as "Region B". It is clearly

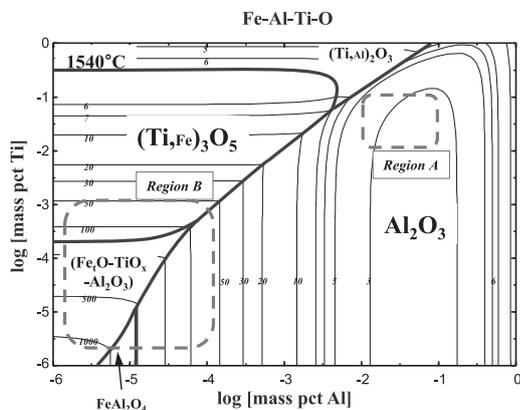


Fig. 4. Calculated oxide stability diagram of the Fe–Al–Ti–O system at 1540°C in the present study. "Region A" represents a condition in bulk liquid steel, and "Region B" represents another condition at interface between the liquid steel and the nozzle refractory.

seen that liquid oxide should form under this condition. This is also consistent with the present authors' experimental observation.¹¹⁾

4. Conclusions

Thermodynamic reassessment of the oxide stability diagram in the Fe–Al–Ti–O system was carried out. By decreasing thermodynamic stability of liquid Al_2O_3 – TiO_2 – Ti_2O_3 system, stable region of "liquid oxide" in the stability diagram could be refined. This reassessment is consistent with recent experimental investigations, regarding the stability of liquid oxide.^{11–13)} The thermodynamic reassessment and newly proposed oxide stability diagram can be used for figuring out what type of oxide phase including non-metallic inclusion and interfacial reaction product could form in Ti-ULC liquid steel.

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