Consideration of Phase Equilibria in Fe-Al-Ti-O System and Its Importance in Steel Cleanliness during Casting Process

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Phase diagram of oxide systems composed of Fe_tO-Al_2O_3-TiO_x was reviewed based on available experimental phase diagram data and CALPHAD thermodynamic database. Most recent updated thermodynamic database was used in order to predict phase equilibria of this oxide system under controlled oxygen partial pressure. In particular, phase equilibria of the oxide system in contact with liquid steel containing Al and Ti, with air, and with refractory for casting process were calculated. A series of experiments were carried out in order to validate the thermodynamic calculations. It was found that, apart from solid alumina, a liquid oxide composed of Fe_tO-Al_2O_3-TiO_x could be formed at the interface between the refractory and the steel, when the liquid steel contains very low C (ultra low C steel grade). The formation of liquid oxide seems to be responsible for clog materials during continuous casting of ultra low C steel. Moreover, this steel can be reoxidized in a tundish by entrapped air. This also generates a liquid oxide mixed with a solid oxide, which significantly affect cleanliness of the steel. Oxidation behavior of the Al-Ti containing steel in the tundish and in the nozzle refractory is comparably discussed.

KEYWORDS: CLEAN STEEL – FE-AL-TI-O – CLOGGING – PHASE EQUILIBRIA

INTRODUCTION

Ultra Low C (ULC) steel is one of typical steel grades that require high level cleanliness. This is partly due to susceptibleness of this steel to oxidation, as this steel contains extremely low C. In general, the ULC steel is deoxidized by Al. Once it is exposed to an oxidizing atmosphere, the steel is reoxidized and the oxidation product remains in the steel. Usually, the oxidation product is considered as non-metallic inclusion, and is known to be harmful to quality of the steel product and to continuous casting process by causing nozzle clogging. Therefore, cleanliness of ULC steel is seriously deteriorated by the reoxidation.

This becomes more serious when the ULC steel is further alloyed by Ti (Ti-ULC). Ti is added in order to bind interstitial elements such as C and N. This enhances formability of the Ti-ULC steel sheet and allows it to be shaped easily. The Ti-ULC steel is used for outer panel of automobiles. Therefore, cleanliness of the steel should be maintained. Unfortunately, Ti-ULC steel suffers difficulties in keeping its cleanliness. Defect on cast slab is often observed which is known to contain some portion of Al and Ti oxides (1). The defect might have been non-metallic inclusion in liquid steel during the process of RH degasser – tundish – continuous casting (CC). Or, it may be a separated portion of clog material during the CC of the steel. It is well known that nozzle clogging is extremely serious for the casting of Ti-ULC steel (1). In order to keep the cleanliness of the Ti-ULC steel and to minimize defect generation and nozzle clogging, it is necessary to understand how the Ti-ULC steel is reoxidized during the process.

Previous efforts have been focused on transient evolution of the non-metallic inclusions in the steel after Ti is added (2-6). Due to local inhomogeneity of the steel, composition, shape, and phase of inclusions vary during the alloying. This was suggested as a possible cause of defect generation and nozzle clogging. However, the root-cause is still unclear. Moreover, stable oxide phases which may form by deoxidation - reoxidation of Ti-ULC steel are controversial. As the understanding of the formation of various oxides is a key to understand the oxidation behavior of Ti-ULC steel, and further to resolve issues relevant cleanliness of the steel, it is necessary to look at phase equilibria of relevant oxide systems. In the present article, the system is confined in the Fe-Al-Ti-O system. In particular, as the oxides are mostly in contact with liquid steel, more attention was paid to the phase equilibria under reducing condition. The present article first reviews phase equilibria of the Fe-Al-Ti-O

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and its sub-system in order to know what kinds of phase are stable and may appear as non-metallic inclusion or clog material. Reoxidation product of Ti-ULC steel is then interpreted from the phase diagram information. Its consequences on steel cleanliness and nozzle clogging are discussed.

PHASE EQUILIBRIA OF FE-TI-AL-O AND ITS SUB-SYSTEM

Only one oxide, Al_2O_3 is known. It is most well-known inclusion in steel.

Ti-O System

Ti is one of representative transition metals. Ti presents as Ti^{2+}, Ti^{3+}, and Ti^{4+} in oxides depending on phase, temperature, and oxygen potential. Fig. 1 shows a part of Ti-O phase diagram (from Ti_2O_3 to TiO_2) (8). Apart from Ti_2O_3 and TiO_2, Ti_3O_5 and so-called Magneli phases (Ti_nO2_{n-1}, n > 3) are seen.

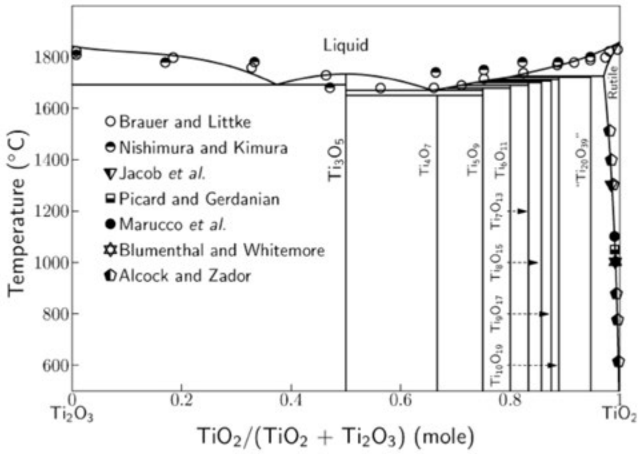

Fig. 1 – A part of Ti-O phase diagram, from Ti_2O_3 to TiO_2 (8).

Fe-Al-O System

Apart from Al_2O_3, $FeAl_2O_4$ is a stable oxide phase. This is known to form in liquid steel at very dilute Al concentration. Fig. 2(a) shows the Fe_tO-Al_2O_3 phase diagram at metallic Fe saturation (9). This is close to a condition of the oxides in steel of extremely dilute solutes. Fig. 2(b) shows a well-known Al deoxidation equilibria in liquid Fe, down to low Al concentration (10). It can be read from these diagrams that Al_2O_3 is a stable oxide phase in liquid steel, but at extremely low Al concentration (below 1 ppm), $FeAl_2O_4$ can form.

Fe-Ti-O System

Similar to the Fig. 2(a), the Fe_tO-TiO_x phase diagram section at metallic Fe saturation is shown in Fig. 3(a) (9). This phase diagram should be seen that the oxide phase is in equilibrium with steel of dilute solute concentration. Contrary to the Fig. 2(a), liquid oxide is likely to exist near steelmaking and casting temperature. Ti deoxidation equilibria is shown in Fig. 3(b) that is usually showing the deoxidation equilibrium with solid oxide phases (11). However, it is necessary to consider the equilibria at extremely low Ti concentration where liquid oxide should be stable (12).

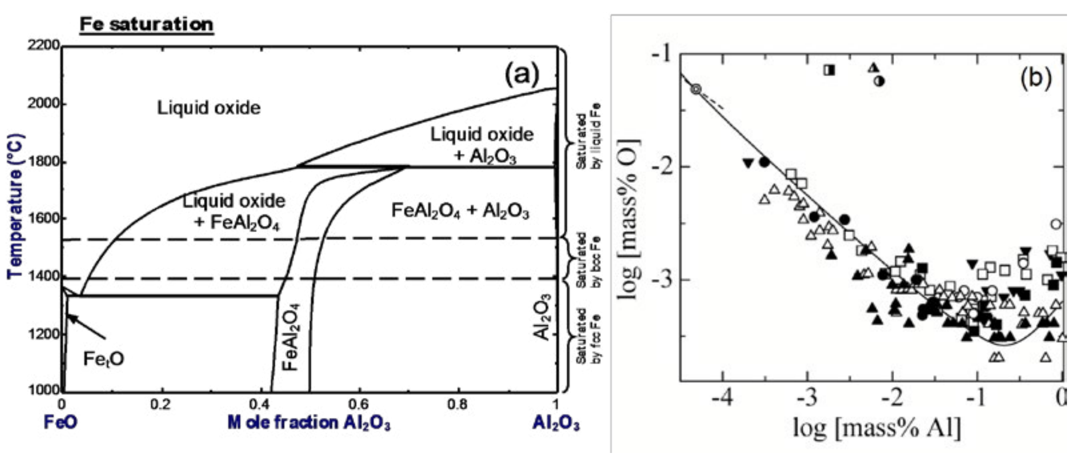

Fig. 2 – Fe-Al-O phase diagram: (a) Fe_tO-Al_2O_3 diagram section at metallic Fe saturation (9) and (b) Al deoxidation equilibria in liquid Fe (10). Double circle represents co-saturation of Al_2O_3 and $FeAl_2O_4$.

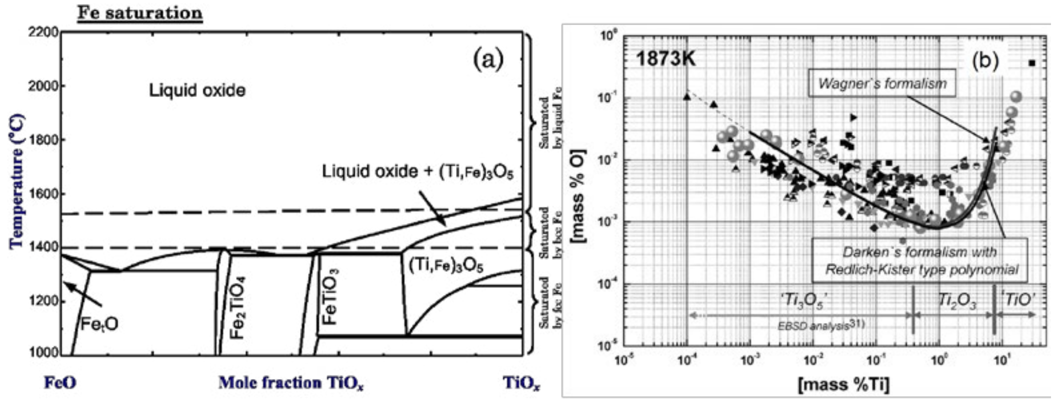

Fig. 3 – Fe-Ti-O phase diagram: (a) Fe_tO-TiO_x diagram section at metallic Fe saturation (9) and (b) Ti deoxidation equilibria in liquid Fe (11).

Fe-Al-Ti-O System

In order to know stable oxide phases in equilibrium with liquid steel containing both Al and Ti, an oxide stability diagram can be used. Fig. 4 shows one of the oxide stability diagrams of the present system reported so far (13). Similar to other versions, it can be seen that equilibrium oxide phase in general Ti-ULC steel that contain a few hundred ppm of Al and Ti is Al_2O_3. It has been controversial whether liquid oxide and/or Al-Ti complex oxide (Al_2TiO_5) exist in the steel or not (5,14-16). Nevertheless, it is agreed that the Al_2O_3 is final equilibrium inclusion phase in the steel. The liquid oxide and Al_2TiO_5 may appear under special condition (9). Kang and Lee pointed out that the liquid oxide is composed not only of Al_2O_3 and TiOx, but also Fe_tO (9).

Al-Ti-O System

Since Ti is a transition metal, stability of the Ti containing oxide depends strongly on oxygen potential. Fig. 5 shows phase diagram of Al-Ti-O (a) in air and (b) under reducing condition (16). Not only stable Ti oxide changes from TiO_2 to Ti_2O_3 at steelmaking temperature, but also stability of liquid oxide and Al_2TiO_5 change. This means that non-metallic inclusion and clog material in Ti-ULC steel are sensitive to local oxygen potential.

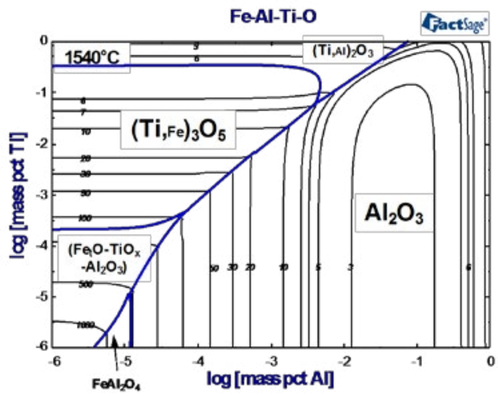

Fig. 4 – An Fe-Al-Ti-O oxide stability phase diagram (13)

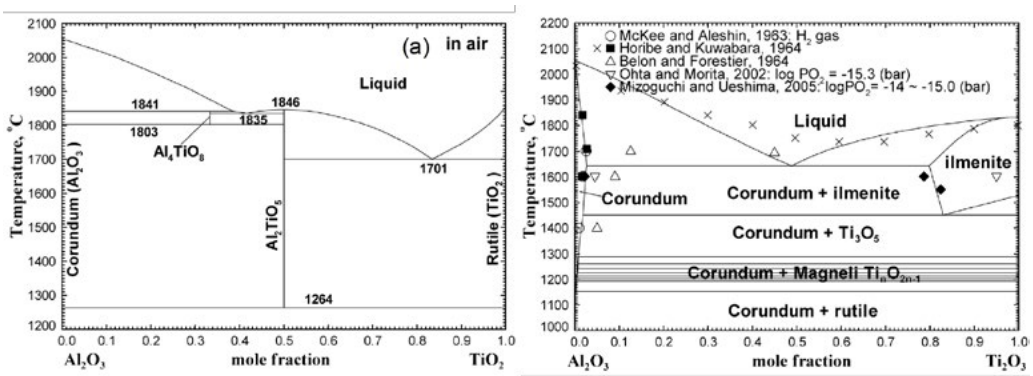

Fig. 5 – Al-Ti-O phase diagram (a) in air and (b) under reducing condition (16)

From the phase diagrams shown above, it is seen that stability of oxide phases depends on oxygen potential. Therefore, the oxygen potential relevant to liquid steel processing should be considered. Moreover, it is seen from Fig. 3(a) and Fig. 4 that a liquid oxide containing FetO can form when a liquid steel containing Ti is oxidized.

REOXIDATION OF TI-ULC STEEL AND ASSOCIATED OXIDE FORMATION

Reoxidation and inclusion formation in liquid steel

Regarding inclusion evolution in Ti-ULC steel relevant to steel cleanliness, a number of previous researches reported that stable inclusion in the steel is Al_2O_3. However, other inclusions that contain Ti could form as intermediate inclusion phase after Ti alloying (2-6). Composition and phase of these inclusions were not known accurately due to small size of the inclusion embedded in the steel matrix. Usually, Al and Ti concentrations in the inclusions were taken into account, but Fe is often neglected. However, under some condition where oxygen potential is higher than that in bulk liquid steel, oxidation of Fe can also occur simultaneously with Al/Ti oxidation. Sasai and Matsuzawa carried out a series of experiments by oxidizing Fe-0.15Ti, and Fe-0.1Al-0.15Ti steel using Ar-O_2 gas mixture (17). The oxygen partial pressure was varied from 0.04 to 0.23 bar, simulating reoxidation of ULC steel in tundish. This was an excessive oxidizing condition. They observed oxidized product on the surface of the steel, and reported that a liquid oxide formed when the steel contained Ti. By EPMA, it was found that the liquid oxide was composed of FeO-Al_2O_3-TiO_2. Once this liquid oxide enters into the liquid steel, it could be easily reduced by Al or Ti, then could be transformed to Al-Ti complex Fe-Al-Ti-O oxide. Further reduction by Al results in Al_2O_3 formation at equilibrium state, according to the oxide stability diagram (Fig. 4). Mizoguchi et al. analyzed alumina inclusions in 0.015Ti-0.03Al ULC steel (18). They reported that the alumina was often observed as clusters. They proposed that FeO suspended in the liquid steel works as a binder at the moment of collision of individual alumina inclusion. They also suggested possible sources of the FeO: oxygen contamination of ferroalloy additives, residual steel adhering to the refractory surfaces, and air entrapment. The experiment of Sasai and Matsuzawa would correspond to the case of air entrapment (18). The reoxidation of Ti-ULC in tundish by air can cause a formation of liquid oxide containing FeO (17). This liquid oxide may work as the binder to form the alumina clusters in liquid steel, as was proposed by Mizoguchi et al. (18).

Reoxidation and clog formation in SEN

Nozzle clogging during continuous casting of Ti-ULC steel is more serious than that of Ti-free ULC steel. Although there are various sources causing nozzle clogging (19), that of Ti-ULC steel is still unclear. This is because the clog material is not only alumina inclusion but also a mixture of skull and inclusions (1). Recently, the present authors proposed that reoxidation reaction between nozzle refractory and Ti-ULC at the interface may be a reason of the nozzle clogging (9). The reoxidation occurs due to CO(g) generated from the nozzle refractory. It was known that there is a carbothermic reaction between SiO_2 and graphite inside nozzle refractory. This results in formation of CO(g). The CO(g) moves at the surface of the nozzle through available pores. In an Al killed ULC steel, the CO oxidized Al to form Al_2O_3 that adheres on the surface (inner wall) of the nozzle. Schematic explanation of the adhesion mechanism by Matsui et al. is shown in Fig. 6 (20).

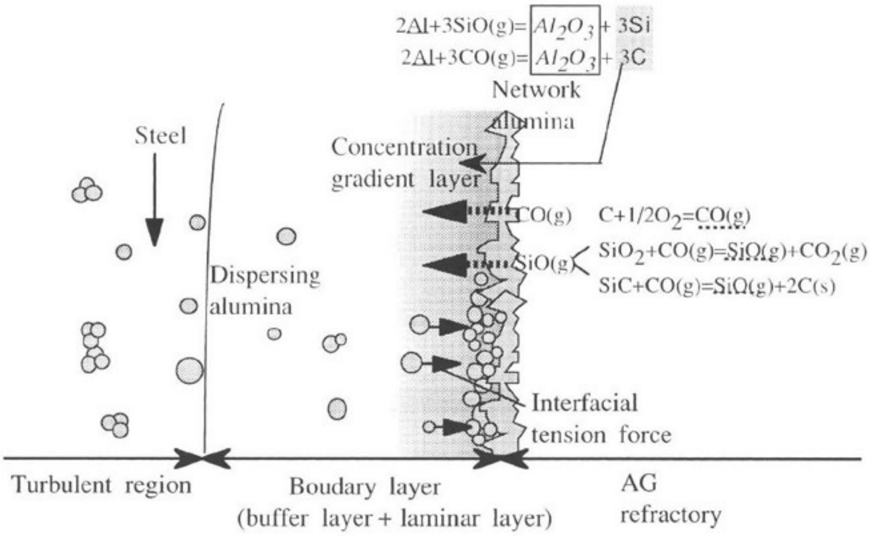

Fig. 6 – Adhesion mechanism of alumina inclusions on SEN surface (20)

However, if an ULC steel contains both Al and Ti, then the oxidation reaction product is not just Al_2O_3. A series of thermodynamic analyses including the phase diagram calculations shown in Fig. 4, the present authors proposed that a mixture of Al_2O_3 and Fe_tO-Al_2O_3-TiO_x form. The latter is a liquid at the casting temperature. It can also be seen in Fig. 4 that increasing O concentration due to the reoxidation by CO(g) lowers concentrations of Al and Ti near the interface between the nozzle and the liquid steel. According to the Fig. 4, the Fe_tO-Al_2O_3-TiO_x forms. The thermodynamic prediction was experimentally validated by oxidizing a number of Fe-Al-Ti alloys representing Ti-ULC steel (9). It was found that surface of the oxidized alloy was covered by Al_2O_3 and the liquid FetO-Al_2O_3-TiO_x. Fig. 7 shows an example of the oxidized surface, clearly showing the mixture of two phases. It was proposed that the liquid oxide may work as a precursor of the clog material in the SEN. The liquid oxide can work as a binder between the nozzle and the liquid steel, as a liquid oxide containing Fe_tO easily wets both to refractory and liquid steel. Once the mixture adheres to the nozzle refractory, Fe_tO in the liquid oxide would be reduced by Al/Ti in the liquid steel or by graphite in the refractory and leaves reduced Fe. Fig. 8 shows a schematic representation of the mechanism proposed by the present authors (9). Due to heat extraction through the nozzle wall, the reduced Fe may be solidified (9).

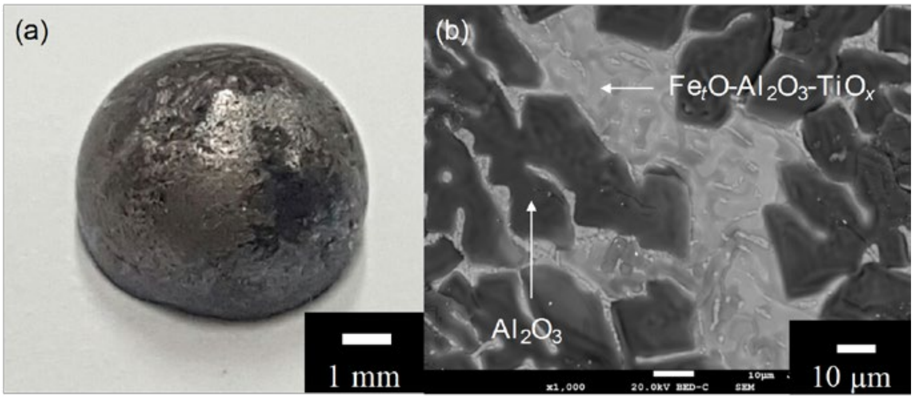

Fig. 7 – Oxidized surface of Fe-0.125Ti-0.05Al alloy by CO gas (9).

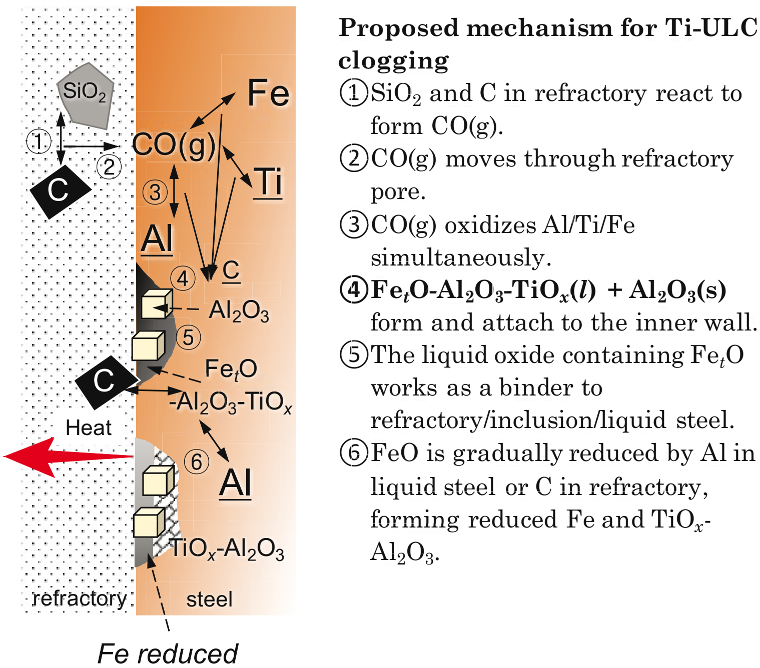

Fig. 8 – Schematic figure showing clogging mechanism of Ti-ULC steel casting (9).

SUMMARY
Phase diagrams of the Fe-Al-Ti-O and its sub-system were reviewed in order to identify what kinds of oxide phases can form in ULC steel containing Al and Ti. Depending on composition, temperature, and oxygen potential, stable phase in the liquid steel varies. In particular, Fe_tO containing liquid oxide can form during reoxidation when the liquid steel contains Ti. This is not the case when the liquid steel does not contain Ti.
Such reoxidation can occur in a tundish and in a SEN. Tundish reoxidation by air generates a Fe_tO containing liquid oxide. This would be entrapped into liquid steel, and cleanliness of the steel becomes low. The other reoxidation occurs at the interface between nozzle refractory. A mixture of Fe_tO containing liquid oxide and solid Al_2O_3 forms. This is thought to initiate deposition of clog material on inner wall of the SEN. It results in low productivity due to clogging, and bad product quality once the clog material is separated and enters into the liquid steel stream. It is necessary to minimize such reoxidation in order to keep cleanliness of the Ti-ULC steel. It was shown that phase diagram information can give us some insight to identify what is a reoxidation product, which is related to the steel cleanliness.

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