博士論文（要約）

Compositional and morphological evolution of Ti-bearing inclusions in Fe-based alloy during heating

(Fe 基合金の加熱中の Ti 系介在物の組成および形態変化)

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Chapter 1   Introduction

1.1 Introduction

The iron and steel industry has ushered in transformation in this age from two perspectives, enhancing properties and alleviating environmental burden.

The properties of steel product are largely affected by inclusions, i.e. the non-metallic phase except for the metallic matrix. Inclusions have been considered to deteriorate the strength, toughness, and fatigue characteristics because the larger size inclusions disrupt the continuity of metallic matrix. However, tiny size inclusions such as titanium oxide and nitrides can be utilized to enhance the properties of steel product, by grain refining or precipitation strengthening. Moreover, high strength steel manufactured by utilizing inclusions contributes to automobile weight reduction, thus improving fuel efficiency and reducing CO_2 emissions.

Plenty of research on inclusions in molten steel has been conducted. However, the final state of inclusion affects the properties of steel product. Therefore, research on evolution of inclusions in solid steel during heating is of significance.

Aluminum and titanium combined deoxidation is widely adopted in steelmaking process to improve yield rate of titanium. Ti-bearing oxide and nitride formed in deoxidation or casting can vary in the post heating process. However, research on inclusions, especially oxides in solid steel during heating is still insufficient.

In current research, compositional and morphological evolution of Ti-bearing oxide and nitride in Fe-Al-Ti-O-N alloy during heating at 1273 K and 1573 K is investigated. Furthermore, research on the evolution of complex inclusions of titanium nitride formed on oxide in Fe-16%Cr alloy during heating at 1573 K is conducted.

1.2 Literature review

1.2.1 Utilization of inclusions

The effect of inclusions on steel properties greatly depends on the size, deformability, elasticity of inclusion and the usage of steel.

Steels with high cycle fatigue properties such as bearing and spring steel are stringent on inclusion control. For instance, TiN in 7 μm size was found on a fracture structure of 2000 MPa low alloyed steel after milling by Focused Ion Beam (FIB) as shown in **Fig. 1-1.** It indicated TiN as the origin of crack due to its high hardness and low elasticity compared with matrix.[1]
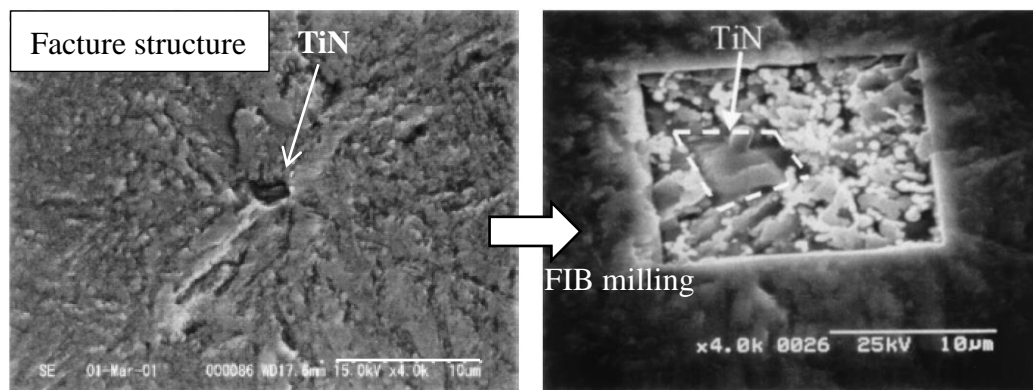
Fig. 1-1 TiN in 7 μm found after FIB milling in a fracture structure.[1]

However, it is possible to utilize certain types of inclusions in relatively small size to favor the properties of steel. The progress of utilization of inclusions is witnessed by the increasing demand for steel plates with high heat welding or with excellent weldability used in the field of shipbuilding, architectural construction, offshore structures, multi-purpose gas carriers and pipeline. In the fabrication of steels, the integrity and reliability of structures are greatly affected by the mechanical properties of the welded joints.[2] Weldments should normally exhibit at least similar properties to

the base steel to avoid the failure in service. However, as the welding heat input is greater than 100kJ/cm, even sometimes can range from 500kJ/cm to 1000kJ/cm, the structure of heat affected zone(HAZ) near fusion line is greatly coarsened, resulting in the decline of toughness of welded joints.[3] **Fig. 1-2** shows the coarse structure in HAZ.[4] The coarse grain boundary ferrite(GBF) and ferrite side plate(FSP) at the boundaries of prior austenite grain, while inside the grain, the mircro structure changes to upper bainite (Bu) including martensite-austenite constituent. The coarse GBF grain can act as the initiation and propagation route of crack.
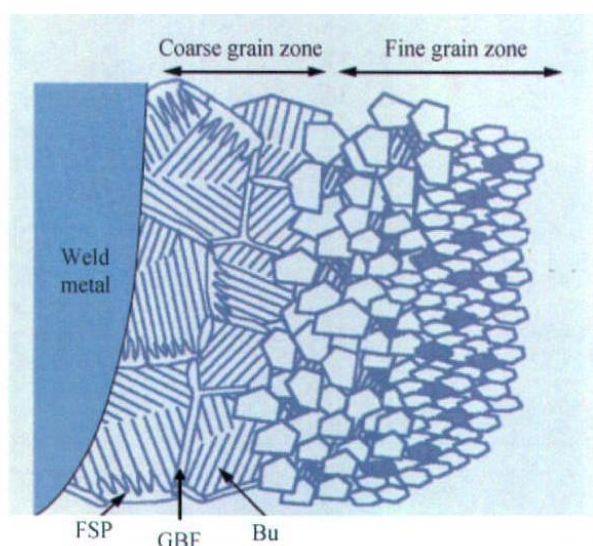
Fig. 1-2 Schematic view of structure in HAZ.[4]

As early as 1970s, the Nippon Steel Corporation(NSC) developed steel plate with high HAZ toughness by using fine TiN inclusions to prevent austenite grain growth, called by pining effect.[5] Since a great amount TiN dissolved into steel during heating, steel plate with improved toughness by using dispersed fine Ti_2O_3 were developed in their further research. The Ti_2O_3 were found to be more stable than TiN in the welding thermal cycle and promote the formation of intragranular ferrite (IGF).[6] In 1990, the concept of "oxide metallurgy" was first proposed by Takamura and Mizoguchi and the

basic concept is shown in **Fig. 1-3**.[7] It is noted utilization of deformable oxides to improve cutting performance is also included in the initial concept. The active oxides including titanium oxide is considered as active oxide to generate IGF due to the cation vacancy nature of oxide where anion vacancy type oxide as SiO_2 classified as inactive oxide.
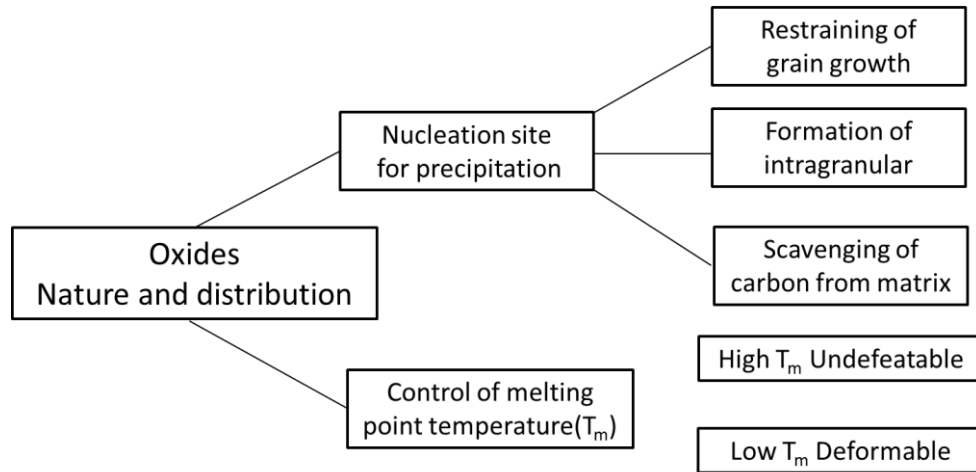
Fig. 1-3 The concept of oxide metallurgy.[7]

The novel third generation of oxide metallurgy proposed by NSC researchers is called HTUFF (high HAZ toughness technology with fine microstructure imparted by fine particles). As shown in **Fig. 1-4**, the oxides and sulfides of Mg and Ca ranges from tens to several hundreds of nanometer size with high thermal stability are utilized to exert strong pinning effect. The progress of oxide metallurgy is presented in **Fig. 1-5** and the growth of austenite grain is effectively restarted in HTUFF steel.[8]
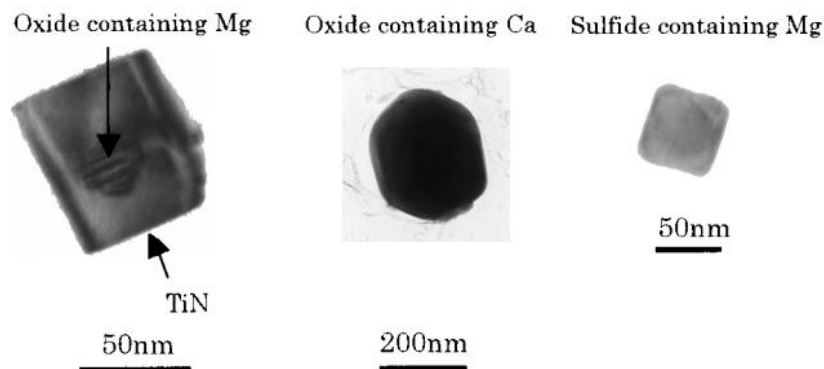
Fig. 1-4 Pinning inclusions in HTUFF steel.[8]
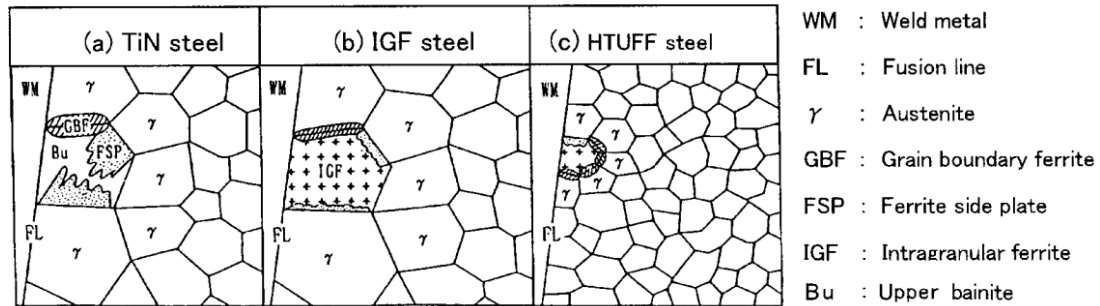
Fig. 1-5 Concept of HAZ microstructure in HTUFF steel.[8]

Therefore, Ti-bearing oxide and nitride can be utilized to enhance strength and toughness of steel based on the technology of oxide metallurgy.

Generally, Ti is added into molten steel as an alloying element after Al dexoidation in steel making process. Evolution of Ti-bearing oxide and TiN in both molten and solid Fe-Al-Ti-O-N fundamental alloy system should be clarified to fulfill the goal of oxide metallurgy.

1.2.2 Evolution of Ti-bearing oxide in liquid steel

1.2.2.1 Equilibrium oxide

To understand the formation of oxide inclusions and submerged entry nozzle clogging in Al and Ti deoxidized steel, access to the knowledge of thermodynamically equilibrium oxides is necessary.

Equilibrium phase diagram for the Fe-Al-Ti-O alloy system has been studied intensively at molten steel temperature. Nevertheless the discrepancies of available thermodynamic data of the Al-Ti-O system in molten iron still remain due to the following reasons: (1) Ti forms many types of oxide as it has more than one stable valence state. (2) The reciprocal solubility between Al_2O_3 and TiO_x results in the complexity of stable phase and available literature studies are not in agreement with each other. (3) Thermodynamic modeling is performed on the limited experimental

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data. Moreover, the existence of a liquid oxide phase in the Fe-Al-Ti-O system has remained an open question due to lack of phase equilibrium data for the Al-Ti-O ternary system, especially at low oxygen partial pressure.

Ruby-Meyer et al.[9] employed the multiphase equilibrium code CEQCSI based on the IRSID slag model to calculate Fe-Ti-Al-O equilibrium phase diagram at 1793 K assuming Ti_2O_3 as the stable oxide. The calculated diagram indicates the formation of Al_2O_3, Ti_2O_3, Al_2TiO_5 as well as Al_2O_3-TiO_x liquid oxide. On the other hand, Jung et al.[10] utilized FactSage database to calculate the same equilibrium phase diagram at 1873 K considering the existence of Ti_3O_5 solid phase as well as Ti_2O_3. Later, they revised the previous phase diagram in which Al_2O_3, Ti_2O_3 and Ti_3O_5 and a liquid oxide equilibrate with metal. They also pointed out that the existence of a liquid Al-Ti-O phase with unfixed Al/Ti molar ratio at 1873 K.[11] Kim et al. also calculated the phase diagram of oxides equilibrating with Fe-Al-Ti-O melt at 1873 K. Al_2O_3, Ti_2O_3 and Ti_3O_5 were considered as thermodynamic stable phase.[12] These reported phase diagrams are shown in **Fig. 1-6**.

(a)
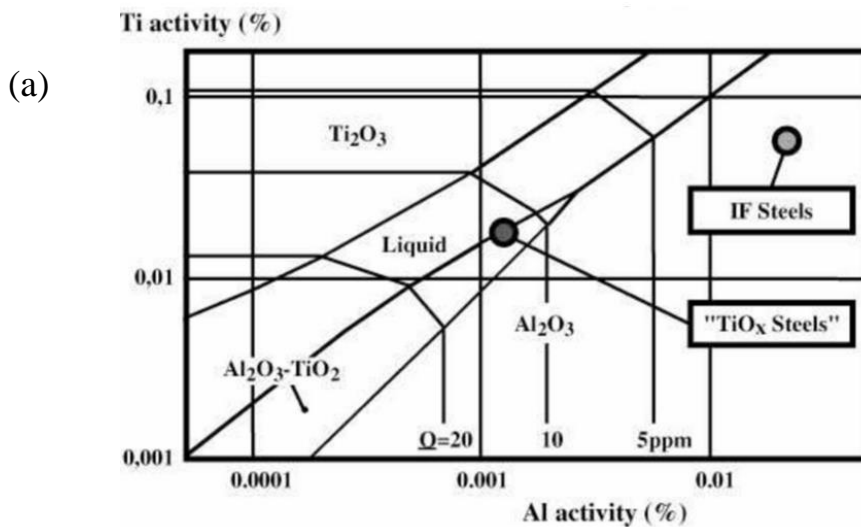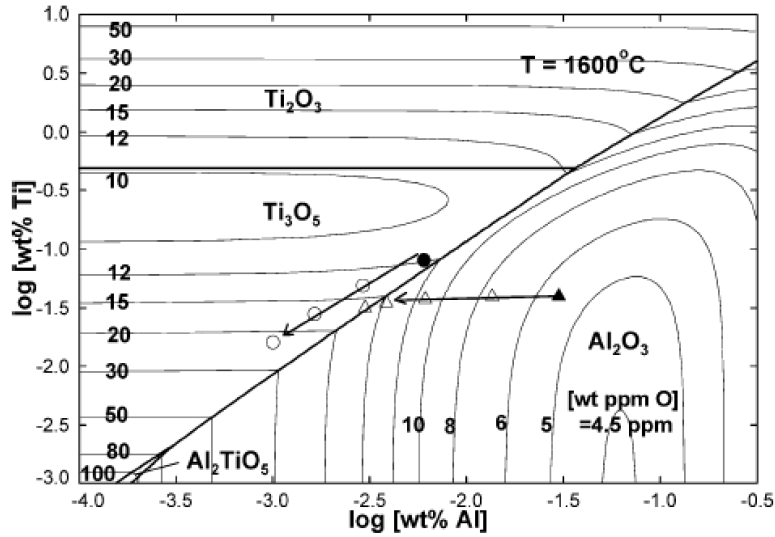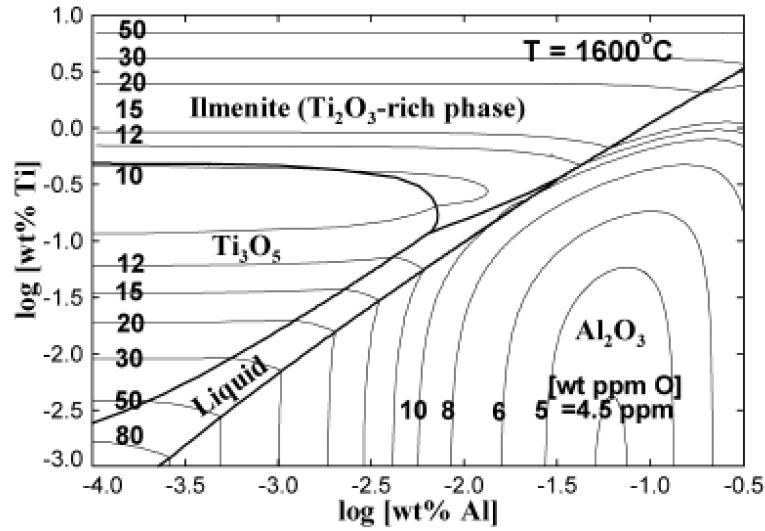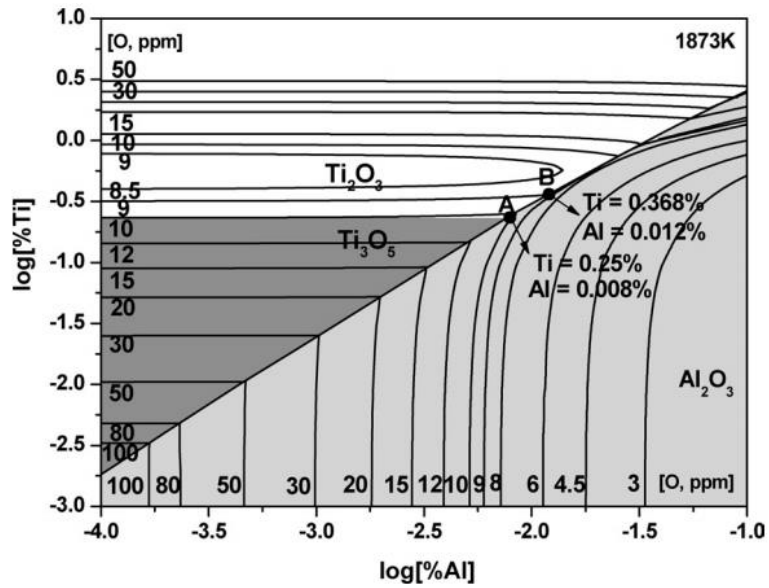
Fig. 1-6 Equilibrium diagram for alloy system of Fe-Al-Ti-O

at (a) 1793 K[9)] (b) 1873 K[10)] (c) 1873 K[11)] (d) 1873 K.[12)]

1.2.2.2 Transient oxide

The composition and morphology of oxide inclusions are greatly affected by Ti sources, order of Al and Ti addition, the amount ratio of Al to Ti, and the initial oxygen content prior to alloying on nonequilrium condition. Therefore, understanding transient evolution of Ti-bearing oxides in Al and Ti deoxidized steel is necessary.

The transient behavior of Ti-bearing oxide in liquid iron has also been investigated by many researchers using sampling technique.[13-18]

Matsuura *et al.*[13] investigated the evolution of oxides during Al and/or Ti additions into molten iron at 1873 K. They reported that Al_2O_3 inclusions were formed at first after Al and Ti additions, followed by Ti oxide formation on the existing particles. Ti oxides were reduced again by Al in liquid iron, however, resulting in the change of particle morphology from spherical to polygonal. The evolution of oxides by separate additions and simultaneous additions is shown in **Fig. 1-7**.
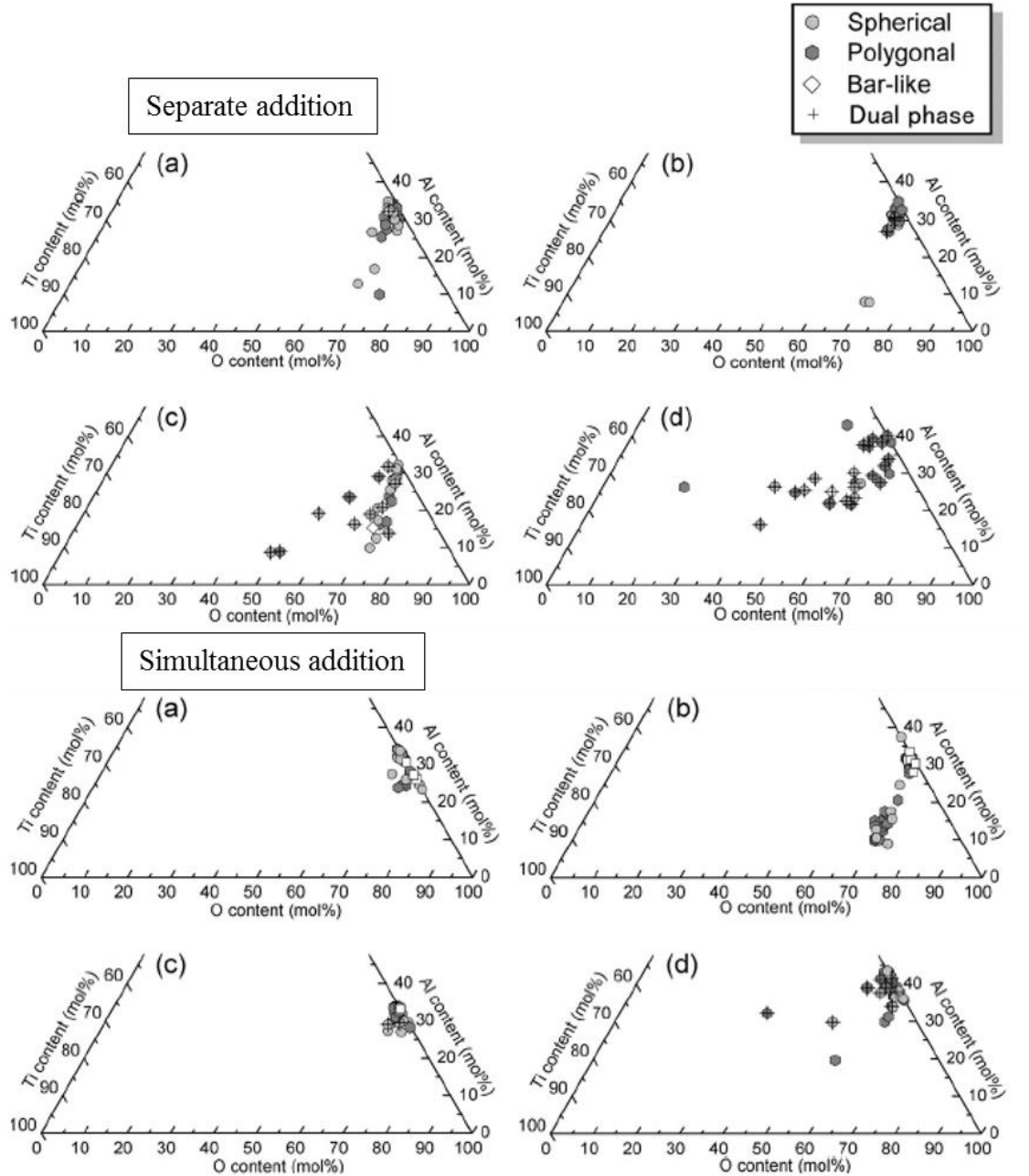
Fig. 1-7 Composition and morphology change of oxides during (a) 1min, (b) 2min, (c) 3min, (d) 4min in the case of separate addition and simultaneous addition.[13]

Wang *et al.*[14-16] studied the effect of Ti sources, order of Al and Ti addition, gradual increase in Ti transient behavior of oxide chemistry, shape and structure in Fe-Al-Ti-O melt employing sampling method. After Ti addition into melt, Al$_2$TiO$_5$, TiO and even Ti$_2$O were formed which were not considered as stable phase in the phase diagram mentioned above. The summary of evolution history of oxide is shown

in **Table1-1**.[15] The expectation path of formation of oxides with respect to soluble

oxygen and titanium is shown in **Fig. 1-7**.[16]

Table1-1 summary of evolution history of oxide in terms of compositional and

morphological information.[15]

Ti/Al Ratio	Stable Phase	Inclusion Evolution History
0	Al_2O_3	Al_2O_3 (spherical/irregular)
1/4		Al_2O_3 (spherical/irregular) $\rightarrow$ Al_2O_3 + Al_2TiO_5 (spherical/irregular) $\rightarrow$ Al_2O_3 (spherical/irregular)
1/1		Al_2O_3 (spherical/irregular) $\rightarrow$ Al_2O_3 + Al_2TiO_5 (irregular dominant) $\rightarrow$ Al_2O_3 (irregular-dominant)
15/1	Al_2TiO_5	Al_2O_3 (spherical/irregular) $\rightarrow$ Al_2TiO_5 (irregular dominant) $\rightarrow$ $Al_xTi_yO_z$ (irregular-dominant)
75/1	Ti_3O_5	Al_2O_3 (spherical/irregular) $\rightarrow$ Ti_xO + Ti_3O_5 (irregular dominant) $\rightarrow$ Ti_3O_5 (irregular-dominant)
∞		Ti_3O_5 (spherical/irregular) $\rightarrow$ Ti_xO + Ti_3O_5 (spherical/irregular)
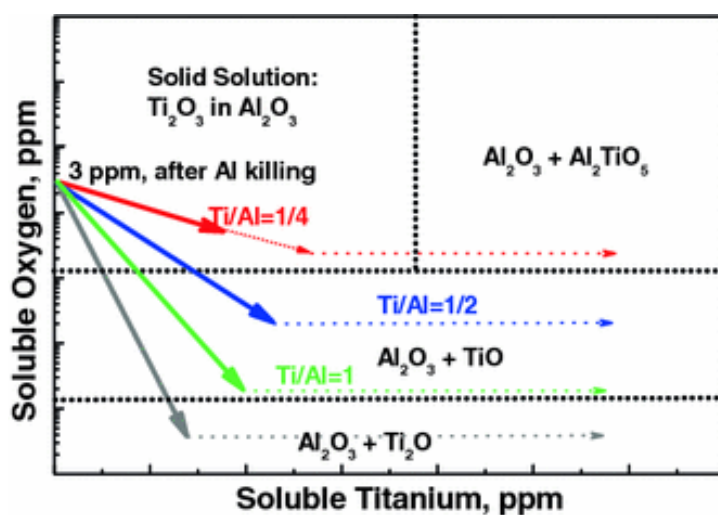
Fig. 1-7 Schematic illustration of possible formation paths of oxides.[16]

In their recent research concerning the reoxidation effect on transient oxide

evolution,[17] they suggested the formation of a liquid Al-Ti oxide phase with

nonstoichiometriy should be considered and the need of experimental data to prove its

existence.

Van Ende *et al.*[18] investigated the evolution of oxide in Fe-Al-Ti-O alloy

deoxidized by Al/Ti and Al/Ti/Al using sampling method, with temperature ranges

from 1873 K to 1923 K. **Fig. 1-8** presents evolution of [Ti] and [Al] in Al/Ti/Al

deoxidized alloy at 1893K. After Ti addition, metal composition entered the Al$_2$O$_3$•TiO$_2$ phase boundary (point D), and with the later Al addition, reduction of Al-Ti oxides with an increase of [Ti] occurred. Hence, the steel composition moved to the point E, where Al$_2$O$_3$ was stable. The reduction reaction proceeded with time by consuming [Al] and increasing [Ti] up to point F.

Based on the previous researches, it is possible for the existence of other Ti-bearing oxide as stable phase equilibrating with Fe-Al-Ti-O alloy at 1873 K. The composition and morphology of oxides in this liquid alloy varied a great extent with the practical deoxidation condition.

In present research, Ti is added into liquid alloy after Al deoxidation to simulate the industrial deoxidation process when producing Ti alloyed steels.

Fig. 1-8 Schematic illustration of possible formation paths of oxides.[18]

1.2.3 Evolution of TiN in solid steel

Making grain finer is the sole method to enhance strength and toughness of steel simultaneously. Inclusions can be utilized to prevent the growth of austenite grain through pinning effect durin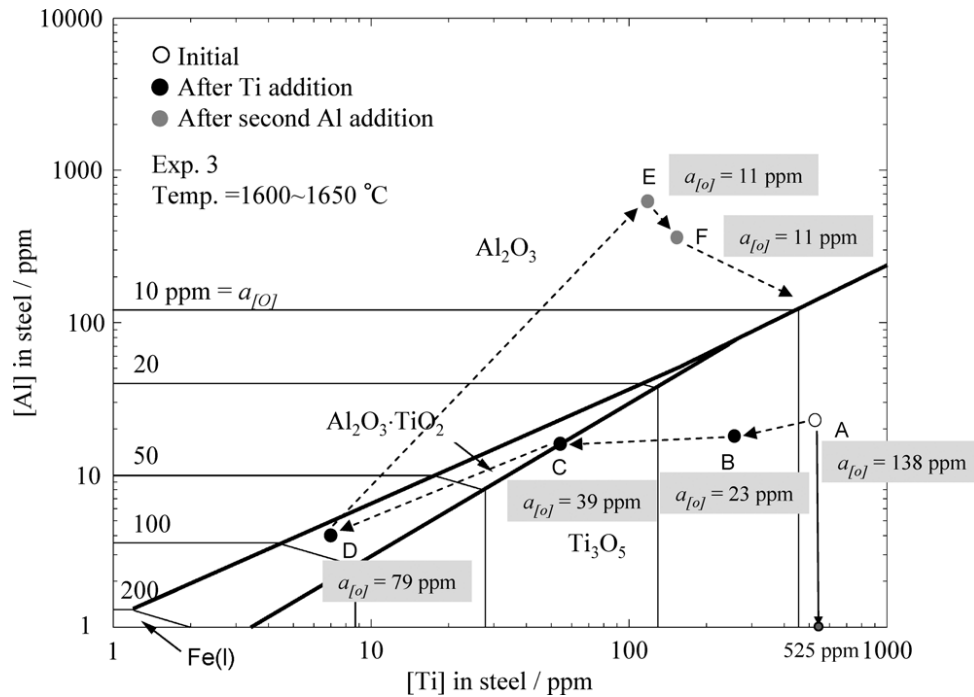g reheating process. The pinning effect generated by inclusions is expressed by Zener's equation as shown in **Eq. (1-1)**.[19]

$$R = (4/3) \cdot (r/f) \qquad (1\text{-}1)$$

Where, R is the radius of crystal grain, r is the radius of second phase particle, and f is the volume fraction of second phase particle. According to equation (1-1), it is necessary to minimize the value of r/f for retarding the growth of crystal grain.

TiN, precipitates during solidification most time, has been utilized to exert pinning effect during austenitization of steel due to high thermal stability. The reason is that the solubility of TiN in austenite is the lowest among carbides and nitrides of the microalloying elements. Moreover, the great change of TiN solubility in steel with variation of temperature renders the easy control of size and volume during heat treatment, thus, affecting the properties of Ti alloyed steel.

The solubility of TiN in liquid, δ, γ and α phase of iron measured by diffusion couple technique is presented in **Fig. 1-9** and expressed as **Eq. (1-2), Eq. (1-3)**, and **Eq. (1-4)**.[20]

$$\log[\text{mass\%Ti}]\,[\text{mass\%N}]_\gamma = 4.46 - \frac{13500}{T} \qquad (1\text{-}2)$$

$$\log[\text{mass\%Ti}]\,[\text{mass\%N}]_{\alpha(\delta)} = 4.65 - \frac{16310}{T} \qquad (1\text{-}3)$$

$$\log[\text{mass\%Ti}]\,[\text{mass\%N}]_{\text{liquid iron}} = 4.35 - \frac{14890}{T} \qquad (1\text{-}4)$$
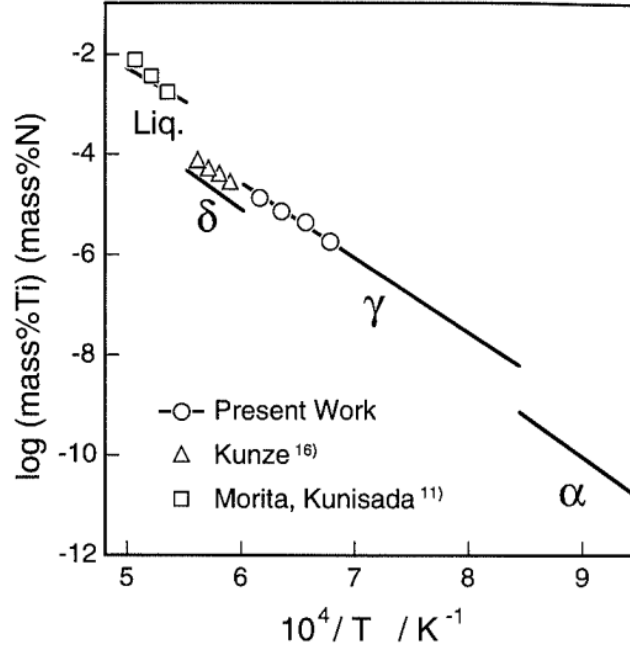
Fig. 1-9 Solubility of TiN in liquid, δ, γ and α phase of iron.[20]

However, during reheating, the pinning effect of TiN can be declined due to increase of solubility and Ostwald ripening, which involves dissolution of small particles and re-deposit onto larger particles shown in **Fig. 1-10**.[21] The particle coarsening is driven by the total surface energy minimization of the system. r_1 and r_2 are the radius of small and large particle, respectively. Cr_1 and Cr_2 are solute concentrations determined by the Gibbs-Thomson equation at the particle/matrix interface. C_m is the mean solute concentration in the matrix. The solute concentration at the small particle/matrix interface is higher than that of the large particle/matrix interface. Therefore, solute atoms detach into the matrix from a small particle and then attach onto a large particle until the small sized particle disappears. By this process, small particles are dissolved and large ones are coarsened.

Therefore, knowledge on the precipitation and Ostwald ripening of TiN during heating is needed. Matsuda *et al.*[22] investigated the evolution of TiN during heating and dispersion state of TiN on the austenite grain size of low carbon low alloy steel. It

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showed the growth of TiN during isothermal heating accorded with Lifshitz-Wagner equation, in which the mean size of TiN increased with heating time shown in **Fig. 1-11.** Austenite size was declined by decreasing the mean distance between TiN shown in **Fig. 1-12.** It indicated dispersion of TiN contributes greatly to grain refining.
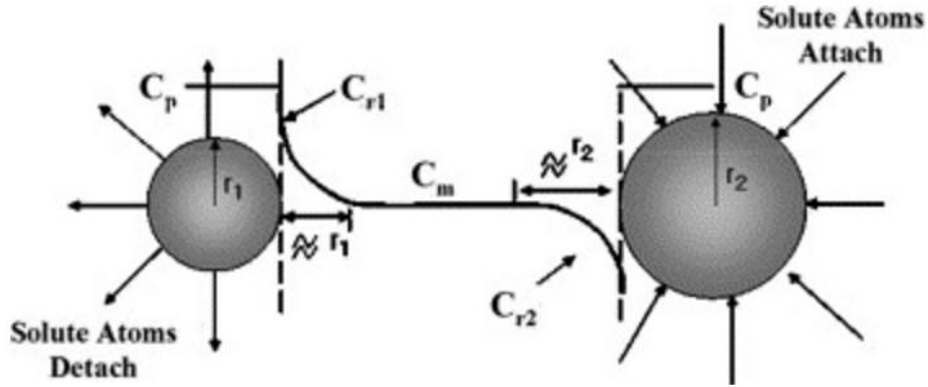
Fig. 1-10 Illustration of Ostwald ripening.[21]
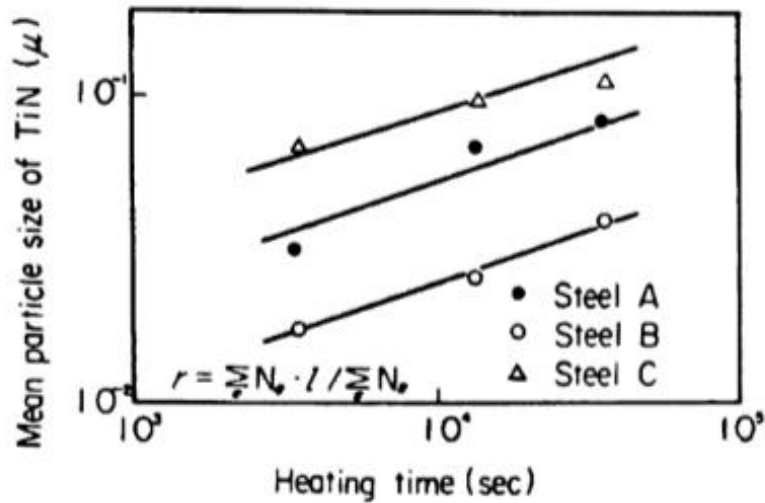
Fig. 1-11 Effect of heating time on mean size of TiN

during isothermal heating at 1623 K.[22]

S．F. Medina *et al.*[23] studied influence of Ti and N contents on austenite grain control and precipitate size in structural steel. The mass ratio Ti/N around 2 generated best pinning effect shown in **Fig. 1-13**. It is also noted the optimum mass ratio of Ti/N

in steel depends on several factors: the reheating temperature, the contents of other alloy elements, and the heat input during welding. Moreover, the size distribution of TiN expressed by relative frequency was measured in two size range at nm order and µm order as shown in **Fig. 1-14.** It is found both the distribution of fine and coarse particles follows lognormal law. TiN was coarser during heating at higher temperature.
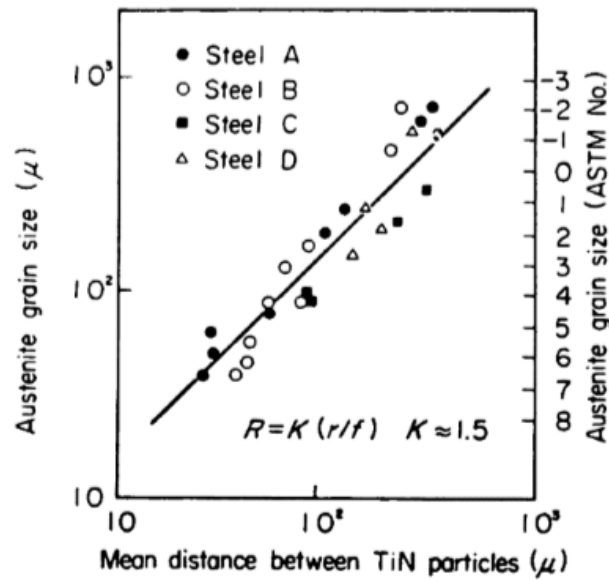
Fig. 1-12 Relation between mean distance of TiN particles and austenite size.[22]
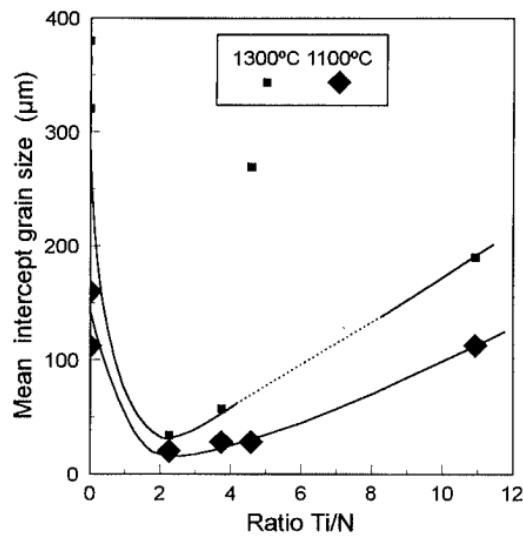
Fig. 1-13 Austenite grain size against the mass ratio Ti/N

after heating 1373K and 1573 K for 10 min.[23]

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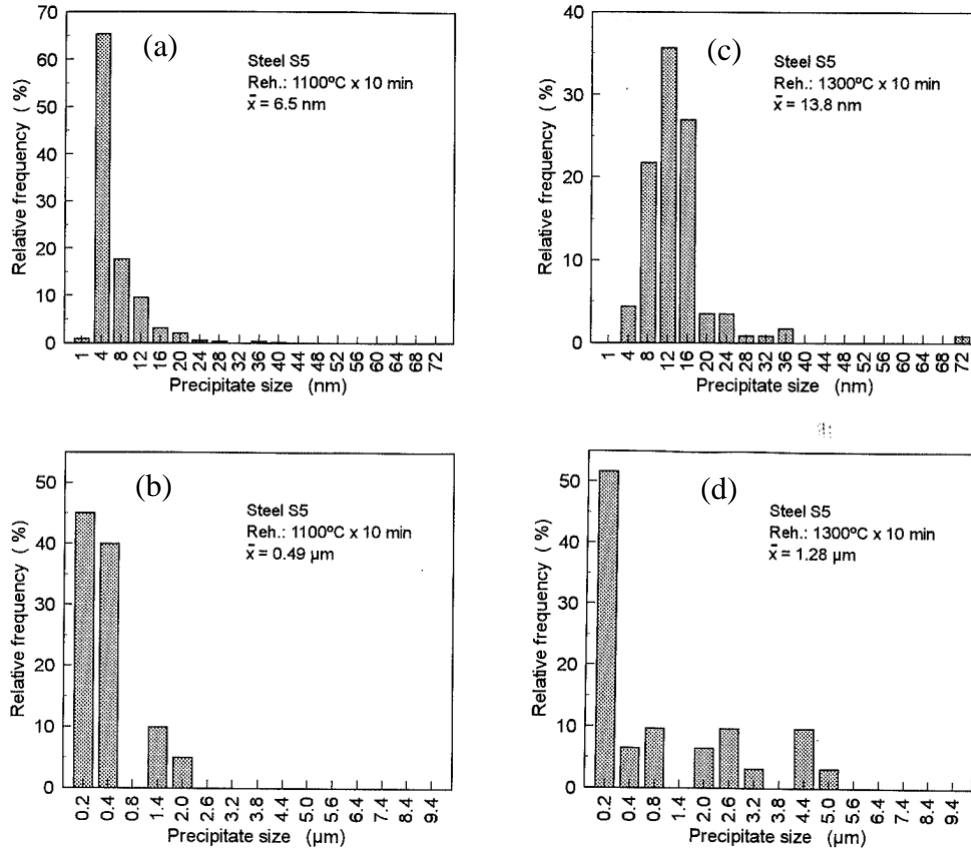
Fig. 1-14 Size distribution of TiN after heating at 1373 K (a) nm order, (b) μm order; and 1573 K (c) nm order, (d) μm order for 10min.[23]

Choi *et al.*[24,25] studied the effect of nitrogen on the behavior of inclusions in Fe-Al-Ti-O-N-S alloy during isothermal heating at 1473 K, TiN-based inclusions grew during heating. TiN-based inclusions retarded grain growth more effectively than TiS-based inclusions.

Besides pining effect, TiN is also effective serving as nucleation of IGF during phase transformation from austenite to ferrite in steel. Morikage *et al.*[26] proposed the ferrite nucleation model on different positions of rectangular TiN. The energy variation for various nucleation site models on TiN at constant driving force of transformation is shown in **Fig. 1-15**. The calculation revealed that a ferrite nucleates most easily on the facets of TiN rather than on its edges, corners, and austenite grain boundary and also indicated that the minimum size of TiN exists being influenced by

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the chemical driving force. Consequently, ferrite can be preferably formed on the facet of TiN shown in **Fig. 1-16**.
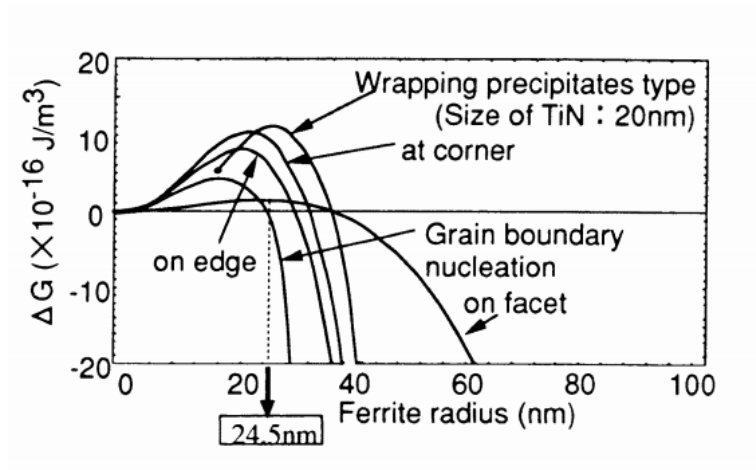
Fig. 1-15 Energy variation with ferrite radius for various nucleation site models on rectangular TiN precipitates.[26]
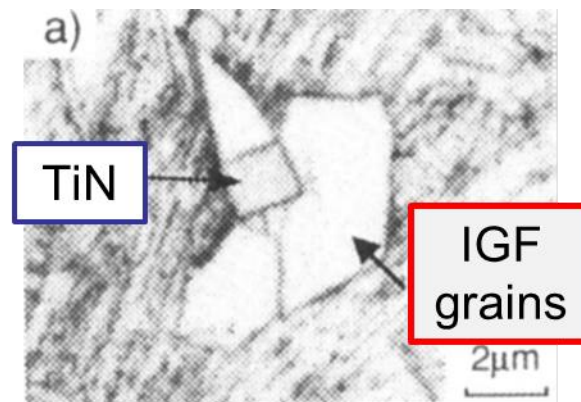
Fig. 1-16 nucleation of IGF on TiN by optical observation.[26]

Tomita *et al*.[27] reported that a 490 MPa class high strength steel used for offshore structure with superior toughness in HAZ was developed by utilizing TiN-MnS inclusion. This is probably attributable to pinning of austenite grains by TiN and the TiN-MnS precipitate that produces fine lGF structure. The mechanism is proposed as Mn depleted zone was formed around TiN. As Mn is austenite stabilizing

element, thus the driving force of formation of ferrite on TiN increases. The mechanism is shown in **Fig. 1-17**.[27]
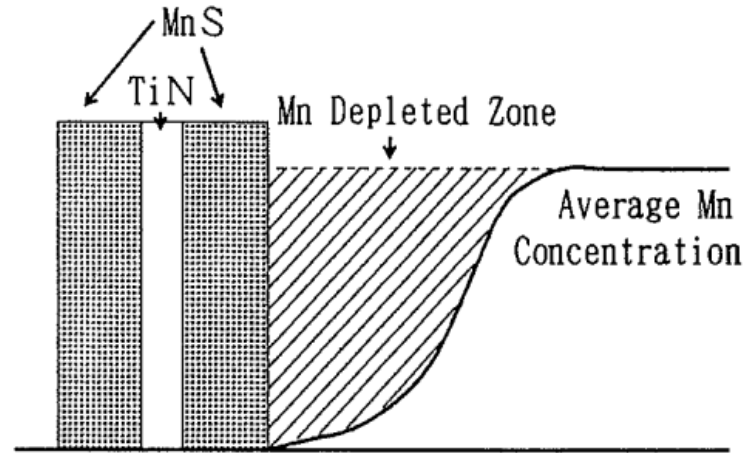
Fig. 1-17 Mechanism of formation of IGF on TiN-MnS.[27]

In the field of ferritic stainless steel, TiN can be utilized as nucleation agent for formation of ferrite to obtain fine structure. Fujimura *et al.*[28] studied the effect of oxide composition on equiaxed grain during solidification in ferritic steel. Mg-Al-O based oxide with Mg/Ti mass ratio range from 0.3 to 0.5 covered with TiN was found to be nucleation agent for formation of ferrite. The effect of Mg/Ti mass ratio oxide on solidification structure is shown in **Fig. 1-18**. The mechanism of formation of equiaxed structure is illustrated in **Fig. 1-19**.
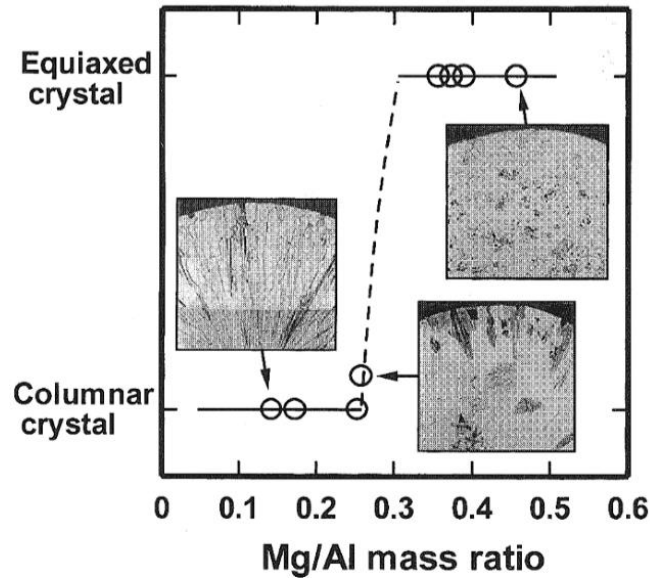
Fig. 1-18 Effect of oxide composition, Mg/A1 ratio, on solidification structure.[28)]
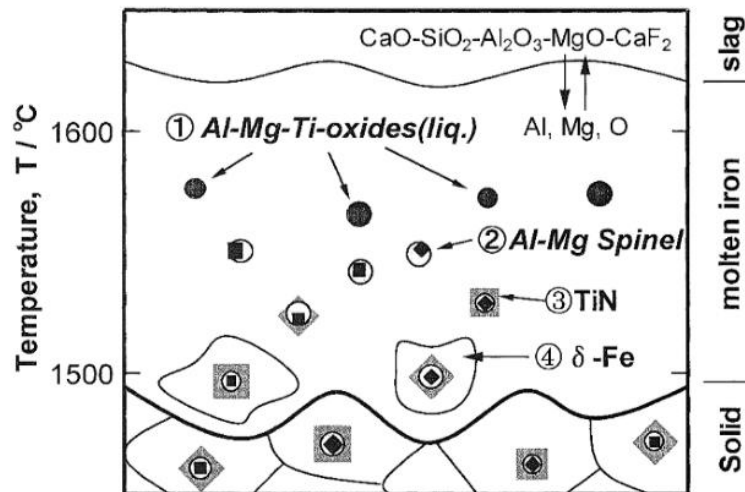
Fig. 1-19 Schematic illustration of equiaxed crystals solidification in 16% Cr ferritic

stainless steel assisted by inclusions.[28)]

Kimura *et al.*[29)] reported NSC has developed a ferritic stainless steel with excellent

formability. In this steel, Al-Mg-Ti oxides are dispersed in molten steel, where they

serve as the nuclei for the crystallization of TiN, and then, around the TiN crystals

thus formed, ferrite solidifies as small equiaxed grains as shown in **Fig. 1-20**. The use

of such multilayered compounds as the nuclei for ferrite solidification proved effective in obtaining a fine solidification structure with the addition of only a small amount of Ti. The formability increases as the structure is finer.
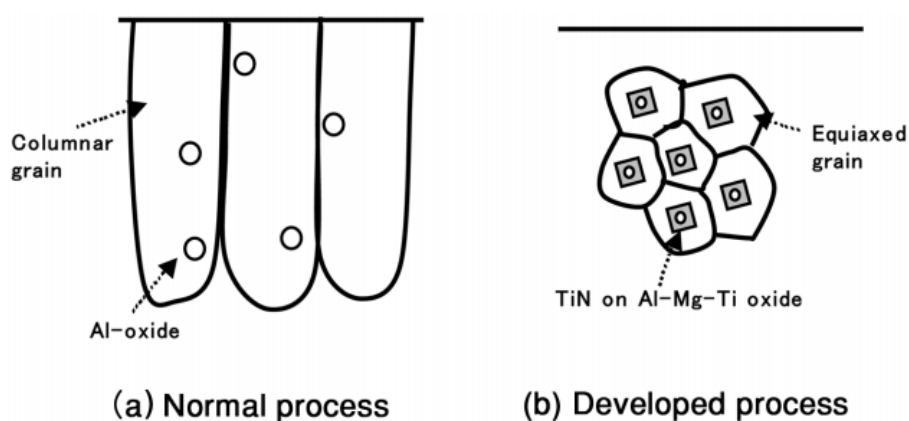
Fig. 1-20 Schematic figures showing relations between oxides and solidification structures.[29)]

In conclusion, TiN can be utilized to enhance strength and toughness of steel through pining effect and site of IGF formation. During reheating, the coarsening of TiN obeying Oswald ripening law occurs, resulting in loss of pining effect.

Therefore, the determination of precipitation-time-temperature (PTT) information without any deformation of austenite is of significance, and especially, would have an immediate application in near net shape casting.

However, most researches on evolution of TiN during heating were conducted in industrial steel which curtains considerate amount of alloying elements such as Mn, Si, and Cr. And these alloying elements can exert great effect on the evolution of TiN. Therefore, research concerning evolution of TiN in Fe-based alloy with basic compositions is needed.

1.2.4 Researches on oxide in solid steel

The evolution of oxide in solid steel is of interest of steelmakers since not only morphology but also composition of oxide inclusions can differ between slab and rolled steel product. The final state of inclusions affects greatly on steel properties. Moreover, the possible change of nature of Ti-bearing oxide during heating can exert different effect as site for formation of IGF.

However, compared with intensive researches on oxide inclusions in liquid steel, research on evolution of oxide in solid steel during heating is few. The possible reasons are as the followings:

(1) The change of oxide in solid steel is subtle compared with in liquid steel.

(2) Lack of quantification method of change of oxide in solid steel.

(3) Lack of thermodynamic data in solid steel.

Takahashi et al.[30] reported the evolution of the non-metallic inclusions in Fe-Cr-Ni alloys containing different contents of Si and Mn during heating at temperature range from 1073 K to 1473 K. MnO-SiO_2 inclusions were found to change to MnO-Cr_2O_3. The formed MnO-Cr_2O_3 changed back to MnO-SiO_2 after heating at 1573 K. Takano et al.[31] reported the same variation in austenite stainless steel after thermo-mechanical treatment as shown in **Fig. 1-21**. They concluded that the dissolution of MnO-SiO_2 and the precipitation of MnO-Cr_2O_3 had occurred. The newly formed MnO-Cr_2O_3 with a radius of 0.2μm can effectively restrain grain growth by pinning effect.
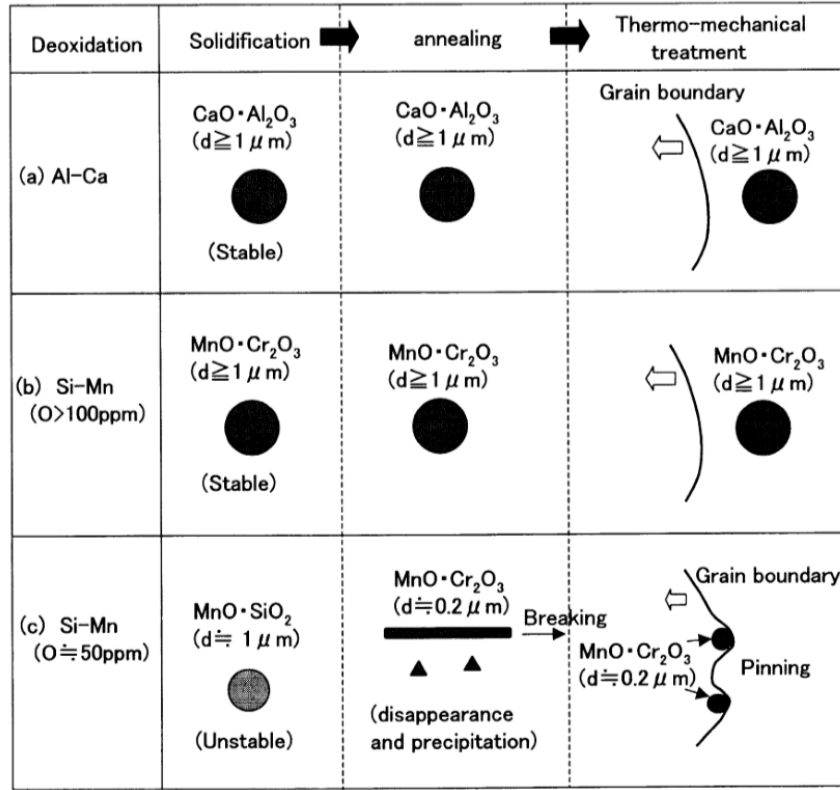
Fig. 1-21 Schematic illustration of the change in size and composition of oxides during thermo-mechanical treatment in (a) Al-Ca, (b) Si-Mn (O ≥ 100ppm), (c) Si-Mn (O ≈ 50ppm) deoxidized austenite stainless steels.[31]

Shibata *et al.*[32, 33] investigated the solid-state reaction at the interface between Fe-Cr steel and MnO-SiO$_2$ oxide created by heat treatment at 1473 K. The diffusion couple method was used to investigate the reaction between the oxide inclusions and the metal phase. It demonstrated that MnO-SiO$_2$-type inclusions changed to MnO-Cr$_2$O$_3$-type inclusions in the case of low Si content in the steel. On the other hand, in the case of high Si content, MnO-SiO$_2$-type inclusion was stable as shown in **Fig. 1-22**. Both the decrease in the solubility of Cr$_2$O$_3$ and the reaction at the interface are the main mechanisms that change the chemical composition of the oxides in the Fe–Cr alloys.

Sample \ Heating time		As cast	5 min.	10 min.	60 min.
Fe–10%Cr	Low-Si (0.08 mass%)	○	◐	◐	●
	High-Si (0.30 mass%)	○	○	○	○
Fe–5%Cr	Low-Si (0.03mass%)	○●	●	●	●
	Mid-Si (0.15mass%)	○	○	○	●
	High-Si (0.43mass%)	○	○	○	○
Fe–1%Cr	Low-Si (0.03mass%)	○	○	○	○
	High-Si (0.36mass%)	○	○	○	○

○ : MnO–SiO₂ type

◐ : MnO–SiO₂ type and MnO–Cr₂O₃ type

● : MnO–Cr₂O₃ type

Fig. 1-22 Summary of the change in the chemical composition of the oxide inclusions of Fe–Cr alloys before and after heat treatment at 1 473 K.[33]

Kim *et al.*[34, 35] investigated the solid-state reaction between Fe-Mn-Si alloy and MnO-SiO$_2$-FeO oxide under heat treatment at 1473 K employing the diffusion couple method. It was found that the Mn-depleted zone (MDZ) and particle precipitation zone (PPZ) were formed near the interface in the alloy. Because of the formation of fine metal particles near the interface in the oxide, they considered that the diffusion of oxygen from the oxide to the alloy occurred during heat treatment. The composition profile in interface is illustrated in **Fig. 1-23**.

23
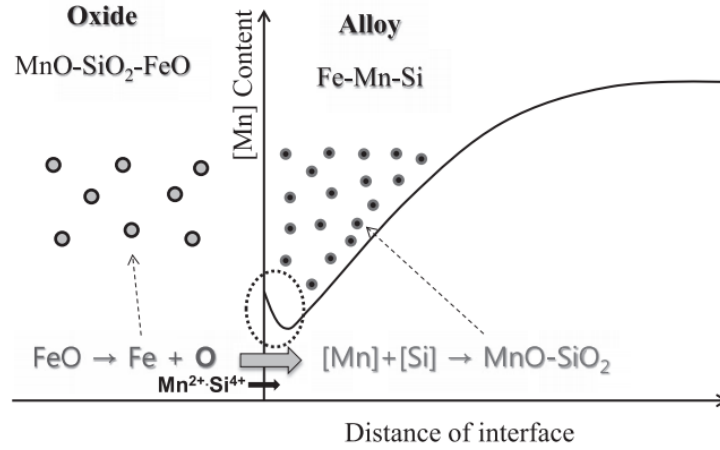
Fig. 1-23 Schematic diagram of the formation mechanism of concentration profile.[35]

Liu *et al.*[36] studied solid-state reaction between Fe-Al-Ca alloy and Al_2O_3-CaO-FeO oxide during heat treatment at 1473 K. Diffusion couple method is employed. Particle precipitation zone (PPZ) was formed near the interface, due to diffusion of oxygen into the alloy to react with Al, which caused decrease of Al content and the precipitation of Al_2O_3 particles in the alloy near the alloy–oxide interface. The mechanism is presented in **Fig. 1-24**. A dynamic model to calculate the width of the particle precipitation zone based on the Wagner model of internal oxidation of metal was proposed.
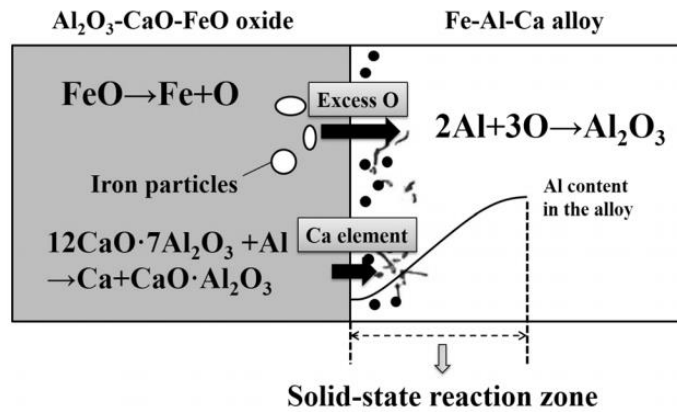
Fig. 1-24 Schematic of the formation mechanism of the particles and dendritic inclusions in the alloy near the interface.[36]

It should be noted the pressure between oxide and steel, which is an important parameter affecting reaction between oxide and steel can differ from that in diffusion couple. Therefore, research on evolution of oxide inside solid steel during heating should be conducted to reveal the mechanism.

Moreover, it is hard to guarantee the same type oxide inclusion being analyzed after heating by using the method mentioned above. Adoption of proper characterization method considering oxide type and possible reaction in solid steel during heating is essential. Different methods with regard to evolution of oxide in solid steel are compared in **Table.1-2**.

<p style="text-align:center">Table.1-2 Comparison of methods to study evolution of oxide in solid steel</p>

| Method	Advantage	Disadvantage
In situ observation of oxide on surface(without re-polishing)	The same type oxide is analyzed	Evolution is affected by surface energy
Diffusion couple	Easy characterization	Pressure in surface differs with that in steel
As cast-heating-re-polishing	Accurate information on evolution of oxide in solid steel	Identification of same type oxide is needed; Time consuming

Access to accurate information on evolution of oxide in solid steel during heating is most important. Therefore, identification of the same type oxide inside steel after heating is necessary in the method of as cast-heating-re-polishing.

There has not been any research concerning Ti-bearing oxide in solid steel during heating.

1.3 Objective and purpose of current study

The ultimate objective is utilization of Ti-bearing inclusions including oxide and nitride to improve strength and toughness of steel. It contains two parts: utilizing Ti-bearing oxide to induce IGF and TiN to make grain finer.

In order to achieve this goal, knowledge of evolution of Ti-bearing inclusions in solid steel during heating is a necessity, as the final state of inclusion affects the properties greatly. The present study aims to reveal evolution of Ti-bearing oxide and TiN in Fe-Al-Ti-O-N alloy during heating.

The Fe-Al-Ti-O-N alloy system is employed in this research for two reasons: (1) Al and Ti combined deoxidatoion process is widely adopted in industrial steelmaking process. (2) The possible effect of other alloying elements on the evolution of Ti-bearing inclusions during heating is erased. Two isothermal heating temperatures 1273 K and 1573 K are adopted to simulate the heating condition of reheating furnace in steelmaking process.

As an extension, evolution of oxide + TiN type inclusion in Fe-16% Cr ferritic alloy during heating at 1573 K is investigated to fulfill the goal of utilizing Ti-bearing inclusions to produce equiaxed structure in ferritic stainless steel.

1.4 Outline of thesis

Chapter1 is the overall review of utilization of Ti-bearing inclusions. Development of oxide metallurgy, previous researches on evolution of Ti-bearing oxide in liquid steel, TiN in solid steel and oxide in solid steel during heating are introduced.

Chapter2 presents experimental and characterization method adopted in current research. Different characterization methods are employed according to type of inclusions.

Chapter3 is evolution of Ti-bearing oxide in Fe-Al-Ti-O-N alloy during isothermal heating at 1273 K and 1573 K. The change of composition, morphology of two types of Ti-bearing oxides during heating is investigated. The mechanism is proposed.

Chapter4 is evolution of TiN in Fe-Al-Ti-O-N alloy during isothermal heating at 1273 K and 1573 K. The size distribution, morphology, coarsening behavior of TiN during heating is investigated.

Chapter5 is evolution of oxide + TiN type inclusion including Al_2TiO_4+TiN, Al_2(Mg, Ti)O_4 and Al_2(Mg, Ti)O_4+TiN in Fe-16%Cr alloy during heating at 1573 K. The size distribution of these inclusions during heating and the effect of inclusions on microstructure were studied. The effect of Mg addition on size distribution of inclusions is discussed.

Chapter6 presents conclusions of current study and directions of future work.

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Chapter 2　Experimental and characterization method

雑誌に投稿する予定のため第 2 章は公表できません。
Experimental and characterization method were determined to investigate evolution of Ti-bearing inclusions in solid alloy during heating.

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Chapter 3　Evolution of Ti-bearing oxides during heating

雑誌に投稿する予定のため第 3 章は公表できません。
Evolution of Ti-bearing oxides during heating was studied.

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Chapter 4　Evolution of TiN during heating

雑誌に投稿する予定のため第 4 章は公表できません。

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Chapter 5　Evolution of oxide + TiN during heating

雑誌に投稿する予定のため第 5 章は公表できません。

Evolution of oxide + TiN during heating was studied.

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Chapter 6   Conclusions and suggestions for future work

6.1 Conclusions

In current study, evolution of Ti-bearing oxide and TiN in Fe-Al-Ti-O-N alloy during heating at 1273 K and 1573 K is investigated. Furthermore, evolution of oxide + TiN in Fe-16%Cr ferritic alloy during heating at 1573 K is studied.

In Chapter 1, the importance to conduct research on Ti-bearing inclusions in solid steel during heating is proposed. The previous research on evolution of Ti-bearing oxide concerning equilibrium state and transient state in liquid steel, evolution of TiN and oxide in solid steel is proposed. Compared with intensive research on evolution of Ti-bearing inclusion in liquid steel, evolution in solid steel is still insufficient.

雑誌に投稿する予定のため、6.1 節の第 2 章の結論より以下の内容は公表できません。

6.2 Suggestions for future work

The future work can be conducted in the directions shown below:

(1) Variation of structure of Ti-bearing oxides in solid steel during heating should be clarified. Because induction of IGF structure can be affected by the structure of Ti-bearing oxides,[1-3] research on change in structure of different type Ti-bearing oxide inclusions in solid steel during heating should be conducted. Confirming the same type of oxide being analyzed in heated alloy with as cast alloy is of importance.

(2) Effect of alloying element such as Cr on evolution of oxide + TiN in ferritic alloy during heating should be studied to clarify the reason why the size distribution of oxide + TiN was maintained during heating at 1573 K in present research.

(3) Evolution of other types of inclusion in solid steel during heating is an interesting topic. The methodology and characterization method in current research can favor these researches.

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Acknowledgement

Take life into a long trip, the story was changed from May of 2014, when the offer of The University of Tokyo came. I chose to believe the future.

It was thunder and lightning the day I arrived at Kashiwanoha Campus of The University of Tokyo, it was so impressive and I did not realize I would fall into love with the place and people here soon. I met such lovely people here who I will never forget in life. It is about love and gratitude. The doctoral course study here, not only expanded my academic knowledge but also make me see the truth and grow.

Firstly, I would like to thank my family, especially my beloved parents, for your always understanding and support. I am proud to be your son.

I would like to express great appreciation to my supervisor Professor Fumitaka Tsukihashi, who offers lots of opportunities to broaden my vision and kind help to the life of my overseas study. Special appreciation to the support to my research, I gained a lot from the free academic atmosphere in my group.

I would like to thank my supervisor Associate Professor Hiroyuki Matsuura. Your patient instructions and wise suggestions help me get over the confusions in research. I benefit a lot from your hard work and modesty.

Great appreciation to the thesis evaluation committee members Prof. Kazuki Morita (Department of Material Engineering, The University of Tokyo), Prof. Kazuo Terashima (Graduate School of Frontier Sciences, The University of Tokyo), Prof. Masanobu Naito (Graduate School of Frontier Sciences, The University of Tokyo) for your valuable suggestions and comments to elevate my work.

I would like to express gratitude to Ms. Yuko Shoji for kind help on the daily life.

2017. June.8th