Research Article

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Effect of TiO_2 content in slag on Ti content in molten steel

<https://doi.org/10.1515/htmp-2021-0015>

received January 25, 2021; accepted February 22, 2021

Abstract: A calculation model of activity for $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-TiO}_2$ slag is established according to molecular-ion coexistence theory of slag structure to calculate the activities of Al_2O_3 , SiO_2 , and TiO_2 in the slag. The possibility of TiO_2 reduction in the slag during refining is analyzed by thermodynamics and verified by laboratory and industrial experiments. Both theoretical analysis and laboratory experimental results show that the content of TiO_2 in the ladle slag significantly influences the Ti content in molten steel. When the content of the dissolved aluminum in molten steel is 0.030–0.050%, the TiO_2 content in the ladle slag should be controlled below 0.3% to prevent TiO_2 reduction. The critical content of TiO_2 decreases with an increasing amount of the dissolved aluminum in molten steel. In addition, silicon should be used as a deoxidizer during diffused deoxidization because aluminum as a deoxidizer would lead to the reduction of TiO_2 . The industrial experiments confirm the results of the laboratory experiments and thermodynamics analysis.

Keywords: clean steel, Ti, TiO_2 , slag, coexistence theory

1 Introduction

Ti is a harmful element in special steel, such as bearing steel, spring steel, and wheel steel. Ti exerts a strong combining force with dissolved nitrogen in steel and

exists in the form of inclusions, such as Ti nitride and Ti carbonitride. These inclusions are hard and angular in shape and can severely affect the fatigue life of mechanical parts, such as bearings and wheels. Inclusions containing Ti are particularly harmful especially when the cleanliness is significantly improved, and there is very little oxide inclusion existing in steel. The effect of Ti nitride inclusions, with an average size of $6\text{ }\mu\text{m}$, on the fatigue property of steel is equivalent to the oxide inclusions, with an average size of $25\text{ }\mu\text{m}$ [1–5]. Therefore, the amount of Ti nitride inclusions should be strictly controlled in the production of high-quality steel.

The contents of Ti and N in steel must be decreased to prevent the formation of TiN inclusions. Bearing and wheel steel with severe service conditions are generally treated by vacuuming to decrease the dissolved nitrogen content to as low as 0.004%. Further reducing the dissolved nitrogen content is extremely difficult; in this case, Ti content in the steel should be controlled.

The source of Ti should be first analyzed to control Ti content in molten steel. Based on the literature and production practices, Ti content in molten steel mainly originates from the following: (1) residual Ti in molten steel at the end of the converter or electric arc furnace smelting; (2) Ti as an impurity element from ferroalloy during alloying; (3) and reduction of TiO_2 in the ladle slag into molten steel during refining [6–8]. According to the author's surveys, oxidation smelting leads to be very low [Ti] content (approximately 0.0002–0.0005%) in molten steel at the end of converter or electric arc furnace smelting. Most Ti in ferroalloys are incorporated into molten steel during alloying. In general, low Ti content in the ferroalloy results in low [Ti] content in molten steel. However, ferroalloys with low [Ti] content are very expensive. Therefore, the [Ti] content in the ferroalloy should not be necessarily too low for the control of the cost of steel. Thus far, the appropriate amount of [Ti] in ferroalloys remains unknown. The [Ti] content in the product is determined by the customer before steelmaking and is generally determined at the end of the converter or electric arc furnace smelting. The [Ti] content in the ferroalloy can be determined if the [Ti] content from reducing

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TiO₂ in the ladle slag is determined. To investigate TiO₂ reduction and reduction in its amount, the reduction rule of TiO₂ in ladle slag during the refining process is analyzed by thermodynamics calculation and is verified through laboratory experiment and industrial production.

2 Thermodynamic analysis

2.1 Reduction thermodynamics of TiO₂ in the ladle slag

During the refining of bearing and wheel steels, a certain amount of dissolved aluminum exists in molten steel. Under suitable thermodynamic conditions, the dissolved aluminum can react with TiO₂ in the ladle slag, thereby increasing the [Ti] content in molten steel. The reaction is given by equation (1) [8–11]:

$$\begin{aligned} \frac{2}{3}[\text{Al}] + \frac{1}{2}(\text{TiO}_2) &= \frac{1}{3}(\text{Al}_2\text{O}_3) + \frac{1}{2}[\text{Ti}] \\ \Delta G_1^\theta &= -71,653 + 17.72T \quad (\text{J/mol}) \\ \Delta G_{[\text{Al}]} &= \Delta G_1^\theta + RT \ln \frac{a_{\text{Al}_2\text{O}_3}^{1/3} \cdot a_{[\text{Ti}]}^{1/2}}{a_{[\text{Al}]}^{2/3} \cdot a_{\text{TiO}_2}^{1/2}} \quad (\text{J/mol}), \end{aligned} \quad (1)$$

where $a_{\text{Al}_2\text{O}_3}$ is the activity of Al₂O₃ in the ladle slag; a_{TiO_2} is the activity of TiO₂ in the ladle slag; and $a_{[\text{Al}]}$, $a_{[\text{Ti}]}$ are the activities of dissolved aluminum and [Ti] in molten steel. Activity is calculated using 1% solution as the reference state.

In a very empirical manner, it is assumed that the activity coefficient is equal to unity when the concentration of element is very low, as occurs in the present steels studied. Therefore, $a_{[\text{Al}]}$, $a_{[\text{Ti}]}$ are defined as the concentration (wt%) of the Al, Ti in the steel.

When $\Delta G_{[\text{Al}]}$ is less than zero, TiO₂ in the ladle slag will be reduced by the dissolved aluminum in molten steel.

A diffusion deoxidizer for slag deoxidation is added to the ladle slag for rapid deoxidation to create a reducing atmosphere during refining. The most commonly used diffusion deoxidizers are Al and SiFe. The diffusion deoxidizer can possibly reduce TiO₂. The thermodynamics equation of the reaction between Al deoxidizer and TiO₂ is given by equation (2) [8–11].

$$\begin{aligned} \frac{2}{3}\text{Al} + \frac{1}{2}(\text{TiO}_2) &= \frac{1}{3}(\text{Al}_2\text{O}_3) + \frac{1}{2}\text{Ti} \\ \Delta G_2^\theta &= -94,083 + 13.95T \quad (\text{J/mol}) \\ \Delta G_{\text{Al}} &= \Delta G_2^\theta + RT \ln \frac{a_{\text{Al}_2\text{O}_3}^{1/3} \cdot a_{\text{Ti}}^{1/2}}{a_{\text{Al}}^{2/3} \cdot a_{\text{TiO}_2}^{1/2}} \quad (\text{J/mol}), \end{aligned} \quad (2)$$

where the activities of Al and Ti in molten steel are calculated using pure substance as the reference state,

$a_{\text{Al}} = 1$, $a_{\text{Ti}} = 1$; and the activities of the other components are as same as equation (1).

The thermodynamic equation of the reaction between Si deoxidizer and TiO₂ is given by equation (3) [8–11].

$$\begin{aligned} \text{Si} + (\text{TiO}_2) &= (\text{SiO}_2) + \text{Ti} \\ \Delta G_3^\theta &= -40,730 + 11.32T \quad (\text{J/mol}) \\ \Delta G_{\text{Si}} &= \Delta G_3^\theta + RT \ln \frac{a_{\text{SiO}_2} \cdot a_{\text{Ti}}}{a_{\text{Si}} \cdot a_{\text{TiO}_2}} \quad (\text{J/mol}), \end{aligned} \quad (3)$$

where activities of Si and Ti in molten steel are calculated using pure substance as the reference state, $a_{\text{Si}} = 1$, $a_{\text{Ti}} = 1$; a_{SiO_2} is the activity of SiO₂ in the ladle slag; and a_{TiO_2} is the activity of TiO₂ in the ladle slag.

When ΔG_{Al} and ΔG_{Si} are less than zero, TiO₂ in the ladle slag can be reduced by Al or Si.

Based on equations (1)–(3), the activities of different components in the ladle slag should be calculated first to determine whether TiO₂ can be reduced.

2.2 Calculation model of activity for slag component

The structure of the high-temperature solution is very complicated. Directly determining the internal structure of liquid slag by experiments is difficult because of limitations of research and experimental methods. According to empirical and theoretical analyses, the following structures are proposed: molecular structure, ion structure theory, and molecular-ion coexistence theory model. Molecular and ion structure models exhibit limitations, but molecular-ion coexistence theory has achieved satisfactory results [12–15]. Molecular-ion coexistence theory is originally proposed by Chuiko [16] and amended by Zhang to become a complete set of model systems [17]. In this paper, molecular-ion coexistence theory is used to calculate the activity of slag component.

2.2.1 Hypothesis

- (1) The structural units in CaO–SiO₂–Al₂O₃–MgO–TiO₂ molten slags are composed of simple ions, simple molecules, and complex molecules. Each structural unit is independent in slags.
- (2) The forming of complex molecules is confirmed by reactions of chemical dynamic equilibrium.
- (3) The chemical reactions of forming complex molecules obey the mass action law.
- (4) The structural units in slags obey the law of conservation of mass.

2.2.2 Structural Units in CaO–SiO₂–Al₂O₃–MgO–TiO₂ Slag System

According to the molecular-ion coexistence theory, the structural units in the slag at 1,873 K are as follows:

- Simple ions: Ca²⁺, O²⁻, Mg²⁺
- Simple molecules: SiO₂, Al₂O₃, TiO₂
- Complex molecules: (1) 3CaO·Al₂O₃, (2) 12CaO·7Al₂O₃, (3) CaO·Al₂O₃, (4) CaO·2Al₂O₃, (5) CaO·6Al₂O₃, (6) CaO·SiO₂, (7) 2CaO·SiO₂, (8) 3CaO·SiO₂, (9) CaO·MgO·2SiO₂, (10) 2CaO·MgO·2SiO₂, (11) CaO·MgO·SiO₂, (12) 3CaO·MgO·2SiO₂, (13) CaO·TiO₂, (14) 3CaO·2TiO₂, (15) 4CaO·3TiO₂, (16) Al₂O₃·TiO₂, (17) CaO·SiO₂·TiO₂, (18) 3Al₂O₃·2SiO₂, (19) 2CaO·Al₂O₃·SiO₂, (20) CaO·Al₂O₃·2SiO₂, (21) MgO·Al₂O₃, (22) 2MgO·SiO₂, (23) MgO·SiO₂, (24) MgO·2TiO₂, (25) MgO·TiO₂, (26) 2MgO·TiO₂.

Let $m_1 = n_{\text{CaO}}$, $m_2 = n_{\text{SiO}_2}$, $m_3 = n_{\text{Al}_2\text{O}_3}$, $m_4 = n_{\text{MgO}}$, $m_5 = n_{\text{TiO}_2}$, $N_1 = N_{\text{CaO}}$, $N_2 = N_{\text{MgO}}$, $N_3 = N_{\text{Al}_2\text{O}_3}$, $N_4 = N_{\text{SiO}_2}$, $N_5 =$

N_{TiO_2} , $N_6 = N_{3\text{CaO}\cdot\text{Al}_2\text{O}_3}$, $N_7 = N_{12\text{CaO}\cdot 7\text{Al}_2\text{O}_3}$, ..., and $N_{31} = N_{2\text{MgO}\cdot\text{TiO}_2}$. The $\sum X$ is the sum of the amounts of substance of each structural unit. m_1, m_2, m_3, m_4 , and m_5 represent the mole percentages of CaO, SiO₂, Al₂O₃, MgO, and TiO₂ in the CaO–SiO₂–Al₂O₃–MgO–TiO₂ slag system, respectively. N_i ($i = 1, 2, 3, \dots, 31$) represents the mole percentages of different structural units, that is, the activity of each structural unit.

According to the coexistence theory, the main reactions involved in the model are presented in Table 1 [10,16].

According to the law of conservation of mass, the equations (30–34) are listed as follows:

$$\sum_{i=1}^{31} N_i = 1, \quad (30)$$

$$\begin{aligned} \sum n_{\text{CaO}} = & (N_1 + 3N_6 + 12N_7 + N_8 + N_9 + N_{10} + N_{11} \\ & + 2N_{12} + 3N_{13} + N_{14} + 2N_{15} + N_{16} + 3N_{17} \\ & + N_{18} + 3N_{19} + 4N_{20} + 4N_{22} + 2N_{24} + N_{25}) \sum X, \end{aligned} \quad (31)$$

Table 1: Chemical reactions in CaO–SiO₂–Al₂O₃–MgO–TiO₂ slag system

Chemical reactions	Standard Gibbs free energy (J/mol)	Balanced relationships
$3(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{Al}_2\text{O}_3)_{(\text{s})} = (3\text{CaO}\cdot\text{Al}_2\text{O}_3)_{(\text{s})}$	$-12,600 - 24.69 T$	$N_6 = K_1 N_1^3 N_3$ (4)
$12(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + 7(\text{Al}_2\text{O}_3)_{(\text{s})} = (12\text{CaO}\cdot 7\text{Al}_2\text{O}_3)_{(\text{s})}$	$-47,279 - 180.46 T$	$N_7 = K_2 N_1^{12} N_3^7$ (5)
$(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{Al}_2\text{O}_3)_{(\text{s})} = (\text{CaO}\cdot\text{Al}_2\text{O}_3)_{(\text{s})}$	$-18,000 - 18.83 T$	$N_8 = K_3 N_1 N_3$ (6)
$(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + 2(\text{Al}_2\text{O}_3)_{(\text{s})} = (\text{CaO}\cdot 2\text{Al}_2\text{O}_3)_{(\text{s})}$	$-16,700 - 25.52 T$	$N_9 = K_4 N_1 N_3^2$ (7)
$(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + 6(\text{Al}_2\text{O}_3)_{(\text{s})} = (\text{CaO}\cdot 6\text{Al}_2\text{O}_3)_{(\text{s})}$	$-16,380 - 37.58 T$	$N_{10} = K_5 N_1 N_3^6$ (8)
$(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{SiO}_2)_{(\text{s})} = (\text{CaO}\cdot\text{SiO}_2)_{(\text{s})}$	$-81,416 - 10.50 T$	$N_{11} = K_6 N_1 N_4$ (9)
$2(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{SiO}_2)_{(\text{s})} = (2\text{CaO}\cdot\text{SiO}_2)_{(\text{s})}$	$-16,043 + 4.106 T$	$N_{12} = K_7 N_1^2 N_4$ (10)
$3(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{SiO}_2)_{(\text{s})} = (3\text{CaO}\cdot\text{SiO}_2)_{(\text{s})}$	$-93,366 - 23.03 T$	$N_{13} = K_8 N_1^3 N_4$ (11)
$(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{Mg}^{2+} + \text{O}^{2-})_{(\text{s})} + 2(\text{SiO}_2)_{(\text{s})} = (\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2)_{(\text{s})}$	$-162,758 - 18.83 T$	$N_{14} = K_9 N_1 N_2 N_4^2$ (12)
$2(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{Mg}^{2+} + \text{O}^{2-})_{(\text{s})} + 2(\text{SiO}_2)_{(\text{s})} = (2\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2)_{(\text{s})}$	$-73,688 - 63.64 T$	$N_{15} = K_{10} N_1^2 N_2 N_4^2$ (13)
$(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{Mg}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{SiO}_2)_{(\text{s})} = (\text{CaO}\cdot\text{MgO}\cdot\text{SiO}_2)_{(\text{s})}$	$-124,683 + 3.77 T$	$N_{16} = K_{11} N_1 N_2 N_4$ (14)
$(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{Mg}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{SiO}_2)_{(\text{s})} = (\text{CaO}\cdot\text{MgO}\cdot\text{SiO}_2)_{(\text{s})}$	$-315,469 + 24.786 T$	$N_{17} = K_{12} N_1^3 N_2 N_4^2$ (15)
$(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{TiO}_2)_{(\text{s})} = (\text{CaO}\cdot\text{TiO}_2)_{(\text{s})}$	$-79,900 - 3.35 T$	$N_{18} = K_{13} N_1 N_5$ (16)
$3(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + 2(\text{TiO}_2)_{(\text{s})} = (3\text{CaO}\cdot 2\text{TiO}_2)_{(\text{s})}$	$-206,690 - 17.03 T$	$N_{19} = K_{14} N_1^3 N_5^2$ (17)
$4(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + 3(\text{TiO}_2)_{(\text{s})} = (4\text{CaO}\cdot 3\text{TiO}_2)_{(\text{s})}$	$-292,900 - 17.57 T$	$N_{20} = K_{15} N_1^4 N_5^3$ (18)
$(\text{Al}_2\text{O}_3)_{(\text{s})} + (\text{TiO}_2)_{(\text{s})} = (\text{Al}_2\text{O}_3\cdot\text{TiO}_2)_{(\text{s})}$	$-25,300 + 3.93 T$	$N_{21} = K_{16} N_3 N_5$ (19)
$(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{SiO}_2)_{(\text{s})} + (\text{TiO}_2)_{(\text{s})} = (\text{CaO}\cdot\text{SiO}_2\cdot\text{TiO}_2)_{(\text{s})}$	$-122,591 + 10.88 T$	$N_{22} = K_{17} N_1 N_4 N_5$ (20)
$3(\text{Al}_2\text{O}_3)_{(\text{s})} + 2(\text{SiO}_2)_{(\text{s})} = (3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2)_{(\text{s})}$	$-8,600 - 17.41 T$	$N_{23} = K_{18} N_3^3 N_4^2$ (21)
$2(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{Al}_2\text{O}_3)_{(\text{s})} + (\text{SiO}_2)_{(\text{s})} = (2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2)_{(\text{s})}$	$-171125.6 + 8.79 T$	$N_{24} = K_{19} N_1^2 N_3 N_4$ (22)
$(\text{Ca}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{Al}_2\text{O}_3)_{(\text{s})} + 2(\text{SiO}_2)_{(\text{s})} = (\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2)_{(\text{s})}$	$138,969 + 17.15 T$	$N_{25} = K_{20} N_1 N_3 N_4^2$ (23)
$(\text{Al}_2\text{O}_3)_{(\text{s})} + (\text{Mg}^{2+} + \text{O}^{2-})_{(\text{s})} = (\text{MgO}\cdot\text{Al}_2\text{O}_3)_{(\text{s})}$	$-35,530 - 2.09 T$	$N_{26} = K_{21} N_2 N_3$ (24)
$2(\text{Mg}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{SiO}_2)_{(\text{s})} = (2\text{MgO}\cdot\text{SiO}_2)_{(\text{s})}$	$-67,200 + 4.13 T$	$N_{27} = K_{22} N_2^2 N_4$ (25)
$(\text{Mg}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{SiO}_2)_{(\text{s})} = (\text{MgO}\cdot\text{SiO}_2)_{(\text{s})}$	$-41,100 + 6.1 T$	$N_{28} = K_{23} N_2 N_4$ (26)
$(\text{Mg}^{2+} + \text{O}^{2-})_{(\text{s})} + 2(\text{TiO}_2)_{(\text{s})} = (\text{MgO}\cdot 2\text{TiO}_2)_{(\text{s})}$	$-27,600 + 0.63 T$	$N_{29} = K_{22} N_2 N_5^2$ (27)
$(\text{Mg}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{TiO}_2)_{(\text{s})} = (\text{MgO}\cdot\text{TiO}_2)_{(\text{s})}$	$-26,400 + 3.14 T$	$N_{30} = K_{22} N_2 N_4$ (28)
$2(\text{Mg}^{2+} + \text{O}^{2-})_{(\text{s})} + (\text{TiO}_2)_{(\text{s})} = (2\text{MgO}\cdot\text{TiO}_2)_{(\text{s})}$	$-25,500 + 1.26 T$	$N_{31} = K_{26} N_2^2 N_5$ (29)

$$\sum n_{\text{MgO}} = (N_2 + N_{14} + N_{15} + N_{16} + N_{17} + N_{26} + 2N_{27} + N_{28} + N_{29} + N_{30} + 2N_{31}) \sum X, \quad (32)$$

$$\sum n_{\text{Al}_2\text{O}_3} = (N_3 + N_6 + 7N_7 + N_8 + 2N_9 + 6N_{10} + N_{21} + 3N_{23} + N_{24} + N_{25} + N_{26}) \sum X, \quad (33)$$

$$\sum n_{\text{SiO}_2} = (N_4 + N_{11} + N_{12} + N_{13} + 2N_{14} + 2N_{15} + N_{16} + 2N_{17} + N_{22} + 2N_{29} + N_{30} + N_{31}) \sum X. \quad (34)$$

Equations (4)–(34) comprise the calculation models for CaO–SiO₂–Al₂O₃–MgO–TiO₂ slags. The calculating model is a system of nonlinear multivariable equations. Programming by MATLAB, the calculation model is solved.

2.3 Analysis

Under the actual production conditions, refining slags with different TiO₂ contents are designed, as presented in Table 2.

According to molecular-ion coexistence theory, the activities of Al₂O₃, TiO₂, and SiO₂ are calculated, as presented in Table 3.

According to Table 3 and equation (1), when the [Ti] content in the molten steel is 0.001% and the dissolved

aluminum is 0.02–0.09%, $\Delta G_{[\text{Al}]}$ varies with the change in TiO₂ in the ladle slag (Figure 1). When the dissolved aluminum in molten steel is less than 0.05% and the TiO₂ content in the ladle slag is less than 0.3%, $\Delta G_{[\text{Al}]}$ is greater than zero, that is, the dissolved aluminum in molten steel could not reduce TiO₂. However, $\Delta G_{[\text{Al}]}$ would be less than zero with increasing TiO₂ content in the ladle slag, indicating that the dissolved aluminum in steel could reduce TiO₂ in the slag. When the dissolved aluminum in molten steel is larger than 0.07%, $\Delta G_{[\text{Al}]}$ remains less than zero even if the TiO₂ content in the ladle slag is 0.2%. With increasing [Al], the critical content of TiO₂ reduces markedly.

According to equations (2)–(3) and Table 3, ΔG_{Al} and ΔG_{Si} vary with the change in TiO₂ in the ladle slag when different deoxidizers are used in slag deoxidation (Figure 2). As shown in Figure 2(a), even if the TiO₂ content in the slag is 0.1%, ΔG_{Al} will remain less than zero. That is, Al could still possibly reduce the TiO₂ in the slag. With increasing TiO₂ content in the ladle slag, the tendency of Al reducing TiO₂ is promoted. Figure 2(b) shows that even if the TiO₂ content in the slag reaches 0.7%, ΔG_{Si} is still greater than zero, that is, Si could not reduce TiO₂ in the slag.

Table 2: Mass percentage of different components in the refining slag, %

Scheme	Component				
	CaO	SiO ₂	MgO	Al ₂ O ₃	TiO ₂
1	55	11	5	28.9	0.1
2	55	11	5	28.8	0.2
3	55	11	5	28.7	0.3
4	55	11	5	28.6	0.4
5	55	11	5	28.5	0.5
6	55	11	5	28.4	0.6
7	55	11	5	28.3	0.7

Figure 1: Variation in Gibbs free energy of the reaction between [Al] and TiO₂ in the slag at 1,873 K.

Table 3: The activities of Al₂O₃, TiO₂, and SiO₂ in the different refining slag

Component	Scheme						
	1	2	3	4	5	6	7
Al ₂ O ₃	0.0111536	0.0111101	0.0110845	0.0110518	0.0110197	0.0109885	0.0109578
TiO ₂	0.0000086	0.0000164	0.0000235	0.0000302	0.0000364	0.0000423	0.0000479
SiO ₂	0.0000324	0.0000324	0.0000325	0.0000325	0.0000325	0.0000326	0.0000326

Figure 2: Variation in Gibbs free energy with different diffusion deoxidizer. (a) Al as diffusion deoxidizer; (b) Si as diffusion deoxidizer.

3 Laboratory experiment

3.1 Experimental materials and device

The diagram of experimental devices is shown in Figure 3. The main experimental equipment was a self-control style electronic high-temperature furnace with silicon molybdenum rods as a heating element, and an alumina crucible with the experimental sample was closed in a corundum tube within the furnace. To avoid the oxidation of molten steel, the Ar (600 mL/min) was injected into the furnace by corundum tube. The slag was the mixture of CaO , SiO_2 , MgO , Al_2O_3 , and TiO_2 , all of which were analytically pure grade. The amount of metal and slag in each heat is 1,000 and 100 g, respectively.

Figure 3: Diagram of experimental devices.

3.2 Experimental scheme and process

The experiment was divided into two parts: the reaction between the dissolved aluminum and TiO_2 in slag, and the reaction between the diffusion deoxidizer (Al or Si) and TiO_2 in slag. The chemical composition of steel was as follows (wt%): C: 0.5–0.6, Si: 0.3–0.4, and Mn: 1.0–1.2.

- (1) Reaction between the dissolved aluminum and TiO_2 in slag

After industrial pure iron in the alumina crucible was melted at 1,873 K, the carbon, metallic silicon, manganese, and pure aluminum were added to molten steel. A sample was obtained from molten steel to analyze initial [Ti] content. After sampling, refining slag with different TiO_2 contents was added to molten steel. The sample was obtained after 10 and 15 min to analyze [Ti] and [Al] content through ARL-4460 photoelectric direct reading spectrometry analysis. According to the calculation results in Figure 1, the dissolved aluminum in molten steel was divided into two ranges: 0.03–0.050% and 0.07–0.09%. The composition of the refining slag and [Al] content in the steel is presented in Table 4.

- (2) Reaction between the diffusion deoxidizer (Al or Si) and TiO_2 in slag

After the alloying was finished and the initial [Ti] content in the sample was determined, refining slag with different TiO_2 contents was added to molten steel. The refining slag was melted and added with 1.0 g metallic aluminum with a diameter of 2–4 mm or 2.0 g metallic silicon with a diameter of 0.5–1 mm. After 2 and 7 min, the [Ti] content in the sample was analyzed. The experimental schemes are presented in Table 5.

Table 4: The component of refining slag with different TiO_2 and Al content in steel, %

Experimental schemes	Refining slag					Al content in steel	
	CaO	SiO_2	MgO	Al_2O_3	TiO_2	0.03–0.050 Al	0.07–0.090 Al
1	55	11	5	28.90	0.10	0.042	0.077
2	55	11	5	28.80	0.20	0.035	0.075
3	55	11	5	28.75	0.25	0.041	0.082
4	55	11	5	28.70	0.30	0.047	0.083
5	55	11	5	28.60	0.40	0.039	0.074
6	55	11	5	28.55	0.45	0.044	0.080
7	55	11	5	28.50	0.50	0.047	0.085
8	55	11	5	28.30	0.70	0.044	0.077

Table 5: Experiment schemes

Experimental schemes	Refining slag, %					Diffusion deoxidizer
	CaO	SiO_2	MgO	Al_2O_3	TiO_2	
1	55	11	5	28.9	0.1	Aluminum
2	55	11	5	28.7	0.3	Aluminum
3	55	11	5	28.5	0.5	Aluminum
4	55	11	5	28.3	0.7	Aluminum
5	55	11	5	28.7	0.3	Silicon
6	55	11	5	28.5	0.5	Silicon

3.3 Experimental results

When the dissolved aluminum in molten steel was 0.030–0.050%, [Ti] content in the molten steel varied with different TiO_2 contents in the slag (Figure 4(a)). As shown in Figure 4(a), the initial [Ti] content in molten steel after

alloying was between 0.0011 and 0.0015%. When the TiO_2 content in the slag was less than 0.3%, the [Ti] content in the steel was almost unchanged. That is, the dissolved aluminum almost did not reduce TiO_2 in the slag. When the TiO_2 content in the slag was more than 0.3%, the [Ti] content increased obviously. For example, when the TiO_2 content in the slag was 0.4%, the initial Ti content was 0.0012% and the [Ti] content increased to 0.0020% after 10 min. In addition, the [Ti] content was almost the same at 10 and 15 min, indicating that the reaction between [Al] and TiO_2 reached the equilibrium at 10 min.

When the dissolved aluminum was 0.070–0.09%, the [Ti] content in the molten steel varied with different TiO_2 contents in the slag (Figure 4(b)). As shown in Figure 4(b), the dissolved aluminum (less than 0.2%) almost could not reduce TiO_2 . When the TiO_2 content was greater than 0.2%, TiO_2 was rapidly reduced by dissolved aluminum, thereby significantly increasing the

Figure 4: Content of [Ti] in steel varying with the content of TiO_2 in slag. (a) 0.030–0.05% [Al]; (b) 0.070–0.09% [Al].

[Ti] content in steel. For example, when the TiO_2 content in the slag was 0.3%, the initial [Ti] content was 0.0012% and the [Ti] content increased to 0.0022% at 10 min. When the TiO_2 content was 0.7%, the [Ti] content increased from the initial 0.0013 to 0.0046%. Comparison of Figure 4(a) and (b) shows that the critical TiO_2 content of the reaction between TiO_2 and dissolved aluminum obviously decreased with increasing dissolved aluminum content. The increase in the [Ti] content was more obvious when the content of dissolved aluminum in steel was higher.

Figure 5 shows that the amount of [Ti] changed when the aluminum or silicon was added to the refining slag for diffused deoxidation. When using aluminum as a deoxidizer, the [Ti] content in the molten steel increased even if the TiO_2 content in the slag was 0.1%. The [Ti] content in the molten steel increased rapidly with increasing TiO_2 content in the slag. When silicon was used as the diffusion deoxidizer, the [Ti] content was almost unchanged even if the TiO_2 in the slag increased to 0.5%. Therefore, TiO_2 was not reduced when using silicon for diffusion deoxidation.

Based on Figures 1, 2, 4, and 5, the experimental results are consistent with the thermodynamics calculation. Therefore, the TiO_2 content in the ladle slag significantly influences the [Ti] content in molten steel during refining. To prevent the reduction of TiO_2 , this work suggests the following: the amount of the dissolved aluminum in steel should not exceed 0.05%, the TiO_2 content in the refining slag should be controlled below 0.3%, and ferrosilicon or silicon carbide should be used for diffusion deoxidation.

4 Industrial experiments

Laboratory experiments were small crucible experiments, whereas actual industrial refining was in a large steel ladle, which can provide a better kinetic condition for steel/slag reaction. The bottom blow system in industrial production was also beneficial for steel/slag reaction. Therefore, the slag/steel equilibrium in industrial production can realize within 80–90 min ladle refining [18], and the production of the steel with refining slags of low TiO_2 content was carried out based on the thermodynamic calculation and laboratory experimental results.

The steel composition was the same as that shown in Section 3.2, and the dissolved aluminum was determined as 0.01–0.04%. The 80-t EAF-LF-RH-LF-CCM process was used in the production in a domestic steel company, and 10 heats melted. The roughing slag amount during EAF tapping was less than 0.35 kg per ton of steel and LF refining time was 1 h. The weight of refining slag accounted for 2% of the weight of liquid steel. Liquid steel samples were obtained during refining and used to determine [Ti] content through ARL-4460 photoelectric direct reading spectrometry analysis. The specific sampling schemes were as follows:

- (i) At the end of EAF smelting, sample 1 was obtained before tapping when the composition and temperature met the requirement.
- (ii) During tapping, alloys, such as Al, Si, Mn, and C, and two-third of the refined slag were added to the ladle. The ladle was transferred to LF. Sample 2 was obtained at this time.

Figure 5: Variation in [Ti] content by adding different deoxidizer in refining slag. (a) Al as diffusion deoxidizer; (b) Si as diffusion deoxidizer.

- (iii) Heating and soft stirring were conducted to homogenize molten steel and the slag. According to component requirements, ferroalloys and the rest of the refined slag were added to molten steel. Sample 3 was then obtained.
- (iv) During subsequent LF refining, samples 4 and 5 were obtained at 15–20 min intervals.
- (v) After LF refining was completed, the ladle was transferred to RH vacuum degassing for 25 min. Samples 6 and 7 were obtained before and after vacuuming, respectively.
- (vi) After RH refining was completed, the soft stirring lasted for 10 min and the steel was transferred to the tundish where the sample 8 was taken.

During the refining process, 1.5 kg SiC per ton of steel was added for diffusion deoxidization. At the end of the refining, slag samples were obtained to determine TiO_2 content through X-ray fluorescence spectrometry analysis (ARLAdvant[™]X Intellipower[™] 3600). The TiO_2 content in the slag was determined to be 0.01–0.03%. The variation in the [Ti] content in molten steel in all heats is shown in Figure 6.

As shown in Figure 6, at the end of EAF, the [Ti] content was $\sim 0.0003\%$ (average Ti content in 10 heats) and then rapidly increased to $\sim 0.0007\%$ (sample 2) because of deoxidation and alloying process during tapping process. The ferroalloys were continuously added to the liquid steel to adjust the composition from sample 2 to sample 3 during LF refining process, which leads to the increase in Ti content. Therefore, the [Ti] content in sample 3 further increased to $\sim 0.0011\%$ after alloying. After sample 3, the alloying of molten steel was complete and no additional ferroalloys were added to the liquid

steel. During the alloying process, the Ti content in the steel increased from ~ 0.0003 to $\sim 0.0011\%$. The [Ti] content varied slightly from samples 3 to 8, indicating that TiO_2 could not be reduced. The industrial experiments confirm the accuracy of the results of the laboratory experiments and thermodynamics analysis.

5 Conclusion

1. Molecular-ion coexistence theory is adopted to calculate the activities of the slag components. According to calculation results, the possibility of the reaction between aluminum and TiO_2 is analyzed from a thermodynamics point of view. The results show that TiO_2 can be reduced by the dissolved aluminum when the TiO_2 content in the refining slag and the dissolved aluminum in the molten steel are kept at a suitable level at 1,873 K.
2. Laboratory experiments show that the Ti content in the molten steel almost does not increase when the aluminum content is 0.03–0.50%, and the TiO_2 content in the ladle slag is less than 0.3% at 1,873 K. However, even if the TiO_2 content in the ladle slag is 0.2%, it can be reduced by 0.07–0.09% dissolved aluminum. When the aluminum is used as a diffusion deoxidizer, TiO_2 is easily reduced. Opposite results are obtained when using silicon as a deoxidizer. The industrial experimental results are consistent with that of the laboratory experimental results.
3. The reduction of TiO_2 can be prevented through the following: the dissolved aluminum in steel should not exceed 0.05%, the TiO_2 content in the refining slag should be controlled below 0.3%, and ferrosilicon or silicon carbide should be used for diffusion deoxidation.

Figure 6: Variation in [Ti] content in molten steel during the smelting process.

Acknowledgments: The authors gratefully acknowledge financial support from the National Nature Science Foundations of China (Grant No. 51974002).

Funding information: This study was funded by the National Nature Science Foundations of China (Grant No. 51974002).

Author contributions: Gang Gao: experiment and data. Xiaofang Shi: writing and funding. Zhenghai Zhu: experiment. Lizhong Chang: revision.

Conflict of interest: Authors state no conflict of interest.

Data availability statement: All authors can confirm that all data used in this article can be published the Journal “High Temperature Materials and Processes”.

References

- [1] Fu, J., J. Zhu, and L. Di. Study on the precipitation behavior of TiN in the microalloyed steels. *Acta Metallurgica Sinica*, Vol. 36, No. 8, 2000, pp. 801–804.
- [2] Yin, X., Y. Sun, Y. Yang, X. Deng, M. Barati, and A. Mclean. Effect of alloy addition on inclusion evolution in stainless steels. *Ironmaking and Steelmaking*, Vol. 26, No. 5, 2016, pp. 1–7.
- [3] Toshikazu, U. Production of high-carbon chromium steel in vertical type continuous caster. *Transactions of the Iron and Steel Institute of Japan*, Vol. 26, No. 7, 1986, pp. 614–620.
- [4] Orihashi, H., K. Doi, Y. Matsushima, S. Yasuki, Y. Fukuzaki, and S. Nakajima. Development of long fatigue-life steel for bearings. *KOBELCO Technology Review*, Vol. 25, 2002, pp. 44–48.
- [5] Ma, W. J., Y. P. Bao, L. H. Zhao, and M. Wang. Control of the precipitation of TiN inclusions in gear steels. *International Journal of Minerals, Metallurgy and Materials*, Vol. 21, No. 3, 2014, pp. 234–239.
- [6] Tian, X. Z., R. Z. Liu, C. F. Zhou, Z. X. Xue, and B. J. Zhong. Control of titanium nitride in bearing steel. *Journal of University of Science and Technology Beijing*, Vol. 31, No. 1, 2009, pp. 150–153.
- [7] Zhang, F. and G. Q. Li. Control of ultra low Ti in ultra low carbon Al-Si killed steel. *Journal of Iron and Steel Research, International*, Vol. 20, No. 4, 2013, pp. 20–25.
- [8] Chen, L. F., L. F. Zhang, Y. Ren, M. Li, W. Fang, J. B. Zhu, et al. Source of titanium in silicon steel during manufacturing process. *AISTech 2016 – Proceedings of the Iron and Steel Technology Conference*, Pittsburgh, PA, United states, 2016, pp. 1117–1122.
- [9] Pak, J. J., Y. S. Jeong, I. K. Hong, W. Y. Cha, D. S. Kim, and Y. Y. Lee. Thermodynamics of TiN formation in Fe–Cr melts. *ISIJ International*, Vol. 45, No. 8, 2005, pp. 1106–1111.
- [10] Liang, Y. J. and Y. C. Che. *Handbook of inorganic substance thermodynamics data*. Northeastern University Press, Shenyang, 1993.
- [11] Huang, X. H. *Principles of iron and steel metallurgy*. Metallurgical Industry Press, Beijing, 2008.
- [12] Xue, M. Y., Z. Meng, J. L. Zhang, P. C. Li, J. Y. Li, and J. Zhang. Representation of oxidation ability for metallurgical slags based on the ion and molecule coexistence theory. *Steel Research International*, Vol. 85, No. 3, 2014, pp. 347–375.
- [13] Zuo, Z. L., Q. B. Yu, J. X. Liu, Q. Qin, H. Q. Xie, F. Yang, et al. Effects of CaO on reduction of copper slag by biomass based on ion and molecule coexistence theory and thermogravimetric experiments. *ISIJ International*, Vol. 57, No. 2, 2017, pp. 220–227.
- [14] Yang, X. M., J. Y. Li, M. Zhang, and J. Zhang. Prediction model of sulphur distribution ratio between CaO–FeO–Fe₂O₃–Al₂O₃–P₂O₅ slags and liquid iron over large variation range of oxygen potential during secondary refining process of molten steel based on ion and molecule coexistence theory. *Ironmaking and Steelmaking*, Vol. 43, No. 1, 2016, pp. 39–55.
- [15] Zhang, B., M. F. Jiang, J. Qi, and C. J. Liu. Activity calculation model for a slag system consisting of CaO–SiO₂–Al₂O₃–FeO–CaF₂–La₂O₃–Nb₂O₅–TiO₂. *Journal of Northeastern University (Natural Science)*, Vol. 32, No. 4, 2011, pp. 524–528.
- [16] Chuiko, N. M. On the structural theory of metallurgical slags. *Ferrous Metallurgy*, Vol. 5, 1959, pp. 3–10.
- [17] Zhang, J. *Computational thermodynamics of metallurgical melts and Solutions*. Metallurgical Industry Press, Beijing, 2007.
- [18] Chen, S. S., M. Jiang, X. F. He, and X. H. Wang. Top slag refining for inclusion composition transform control in tire cord steel. *International Journal of Minerals, Metallurgy and Materials*, Vol. 19, No. 6, 2012, pp. 490–498.