Thermodynamic Research on the Precipitation of Ti₂O₃, TiN and TiC in Continuous Casting of Titanium Microalloyed Steel

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Abstract: The composite precipitation of Ti₂O₃ + TiN during continuous casting has an important influence on the microstructure and properties of the slab. In order to study the precipitation conditions of Ti₂O₃, TiN and TiC second phase in titanium microalloyed steel, the solid-liquid phase line temperature, the initial precipitation temperature of different second phase, the equilibrium and actual solubility product of Ti₂O₃, TiN and TiC at different temperatures are calculated, and the precipitation rules of titanium microalloyed steel in liquid steel and two-phase region are analyzed. The results show that: Ti₂O₃ and TiN can precipitate in molten steel, and the precipitation order of Ti₂O₃ is prior to that of TiN, while TiC does not precipitate. Due to the enrichment of Ti, O, C and N in the liquid phase during solidification, the equilibrium precipitation conditions of Ti₂O₃ and TiN are reached when the temperature is lower than 1469 °C of the liquidus, and the precipitation begins at the initial stage of solidification. When the temperature in the two-phase region is lower than 1332 °C, the precipitation of TiC begins.

1. Introduction
In the process of continuous casting, microalloyed steel undergoes the transformation from liquid-solid-liquid coexistence to solid state with the decrease of temperature, and the solubility and interaction of microalloyed solute elements in steel also change during this transformation [1-2]. Ti in microalloyed steel can combine with a small amount of dissolved O, N and C in steel to form different second phases (Ti₂O₃, TiN, TiC or Ti(C, N)), which can improve the microstructure and properties of microalloyed steel [3-5]. The precipitation amount of different second phases in microalloyed steel has always been a hot research issue at home and abroad [6]. Based on the basic thermodynamic data, the possibility of precipitation of Ti₂O₃, TiN and TiC in titanium microalloyed steel can be judged; the thermodynamic model of precipitation of Ti₂O₃, TiN and TiC is established. The initial precipitation temperature of Ti₂O₃, TiN and TiC in molten steel and two-phase region, the equilibrium precipitation amount and the equilibrium content of solute elements at different temperatures are calculated by using MATLAB engineering software. The Origin-Lab is used to plot and analyze the precipitation rules of each precipitate at different temperatures.

2. Research objects and related parameters
The steel studied in this paper is 321 stainless steel containing Ti, the chemical composition is shown in table 1, in which w[Ti] = 0.18%, w[N] = 0.01%, w[C] = 0.02%, w[O] = 0.0008%. The solidus and
liquidus temperatures of titanium microalloyed steel can be calculated according to the formula in reference [7], the liquidus temperature \( T_l = 1469^\circ C \), that is 1742K; the solidus temperature \( T_s = 1318^\circ C \), that is 1591K. The calculation formulas are as follows:

\[
T_l = 1536 + 273 - \{90[\%C] + 6.2[\%Si] + 1.7[\%Mn] + 28[\%P] + 40[\%S] + 2.6[\%Cu] + 2.9[\%Ni] + 1.8[\%Cr] + 5.1[\%Al]\},
\]

\[
T_s = 1536 + 273 - \{175[\%C] + 30[\%Mn] + 20[\%Si] + 280[\%P] + 575[\%S] + 6.5[\%Cr] + 4[\%V] + 4.75[\%Ni] + 7.5[\%Al] + 2.5[\%W] + 40[\%Ti] + 5[\%Mo] + 60[\%Nb] + 160[\%O]\}.
\]

The relevant parameters used in thermodynamic calculation are shown in table 2 [8].

### Table 2. Values of thermodynamic calculation parameters.

| Parameters                          | Value | Notes         |
|-------------------------------------|-------|---------------|
| Melting point of pure iron / K      | 1809  |               |
| Temperature / K                     |       |               |
| Liquidus                           | 1742  | 321 stainless steel |
| Solidus                            | 1591  |               |
| Equilibrium solute partition factor |       |               |
| C                                   | 0.17  | Upper limit   |
| N                                   | 0.25  |               |
| O                                   | 0.022 |               |
| Ti                                  | 0.14  | Upper limit   |

Because the basic conditions of test or derivation of each solubility product formula are not the same, the solubility product of the same second phase obtained sometimes has numerical difference [9-12]. In the following thermodynamic calculation, the solubility product data of liquid steel and liquid phase in two-phase region are compiled by Jiaxiang Chen, and the applicable temperature is 1500K ~ 2000K, which is corresponding with the research conditions of this paper [13-14]. The solubility product formulas of all selected different second phases in liquid steel and liquid phase in two-phase region are shown in table 3.

### Table 3. Solubility product of second phase in liquid steel and liquid phase in two phase region.

| Second phase   | Equilibrium solubility product (lgK) | Actual solubility product (lgQ) |
|----------------|--------------------------------------|---------------------------------|
| TiN            | \(5.9 - 16580 T^{-1}\)               | \(\lg([\%Ti] \cdot [\%N])\)     |
| TiC            | \(5.317 - 9393 T^{-1}\)              | \(\lg([\%Ti] \cdot [\%C])\)     |
| \(\text{Ti}_2\text{O}_3\) | \(18.08 - 56060 T^{-1}\)           | \(\lg([\%Ti]^2 \cdot [\%O]^3])\) |

### 3. Details of thermodynamic model

According to the equilibrium solubility product formula of the binary second phase: \( \lg([\%M] \cdot [\%X]) = B - T^{-1} A \), whether the second phase can precipitate or not can be judged [15-16]. Where, \([\%M]\) and \([\%X]\) are the mass fraction of metal and non-metal elements in steel respectively; \(A\) and \(B\) are the product constants of solid solubility. The actual solubility product and equilibrium solubility product of different second phases can be expressed by the following equation.

The actual concentration product \( Q_{Ti_2O_3} \) of oxygen and titanium forming \( Ti_2O_3 \) in molten steel can be expressed as:

\[
Q_{Ti_2O_3} = [\%Ti]^2 \cdot [\%O]^3
\] (1)

The equilibrium concentration product \( K_{Ti_2O_3} \) of oxygen and titanium forming \( Ti_2O_3 \) in molten
steel can be expressed as:

\[ K_{N_2O_3} = a_{Ti}^2 \cdot a_{O}^3 = 10^{\left( \frac{56060-18.08}{T} \right)} \]  

(2)

The actual concentration product \( Q_{TiC} \) of carbon and titanium in molten steel can be expressed as follow:

\[ Q_{TiC} = [\%Ti] \cdot [\%C] \]  

(3)

The equilibrium concentration product \( K_{TiC} \) of carbon and titanium in molten steel can be expressed as:

\[ K_{TiC} = a_{Ti} \cdot a_{C} = 10^{\left( \frac{9393}{T}+5.317 \right)} \]  

(4)

The actual concentration product \( Q_{TiN} \) of nitrogen and titanium in molten steel can be expressed as:

\[ Q_{TiN} = [\%Ti] \cdot [\%N] \]  

(5)

The equilibrium concentration product \( K_{TiN} \) of nitrogen and titanium in molten steel can be expressed as:

\[ K_{TiN} = a_{Ti} \cdot a_{N} = 10^{\left( \frac{-16580}{T}+5.9 \right)} \]  

(6)

When the temperature of liquid steel decreases to the solid-liquid two-phase region, the oxygen, carbon, nitrogen and titanium in the steel are segregated, and the content of non-metallic element X (oxygen, carbon, nitrogen) and metallic element Ti can be expressed as equations (7) and (8) [17-18].

\[ [\%X] = \frac{[\%X]_0}{f_x(k_x-1)+1} \]  

(7)

\[ [\%Ti] = [\%Ti]_0 \cdot (1 - f_x)^{k_{Ti}-1} \]  

(8)

Where, \([\%X]\) - mass percentage of oxygen, carbon and nitrogen in liquid phase during solidification process. \([\%X]_0\) - the mass percentage of oxygen, carbon and nitrogen in the initial liquid phase. \([\%Ti]\) - mass percentage of titanium in liquid phase during solidification. \([\%Ti]_0\) - mass percent of titanium in the initial liquid phase. \(f_x\) - solid fraction. \(k_x\) and \(k_{Ti}\) are the equilibrium solute partition factors of nonmetallic elements and titanium respectively.

The relationship between temperature \( T \) and solid fraction \( f_x \) is expressed by formula (9) [19]:

\[ f_x = \frac{(T_m - T_s)(T_i - T)}{(T_i - T_s)(T_m - T)} \]  

(9)

Notes of the (9), \( T \): liquid temperature (K) during solidification. \( T_m \): melting point of pure iron (1809K) [20]. \( T_i \): liquidus temperature (1742K). \( T_s \): solidus temperature (1591K).

According to the above formula of solubility product of the second phase, when the actual solubility product is higher than the equilibrium solubility product, the thermodynamic equations of precipitation of Ti2O3, TiN and TiC in liquid phase of molten steel and two-phase region are established, and the precipitation amount of Ti2O3, TiN and TiC and the equilibrium residual content of each element can be calculated.

Thermodynamic model of Ti2O3 precipitation [21]:

\[ \log([\%Ti] \cdot [\%O]) = A - \frac{B}{T} \]  

(10)
\[
\begin{align*}
[\%Ti]_0 - [\%Ti] &= \frac{2A_{Ti}}{A_{Ti_2O_3}} [\%Ti_2O_3] \\
[\%O]_0 - [\%O] &= \frac{3A_{O}}{A_{Ti_2O_3}} [\%Ti_2O_3] \\

\text{Thermodynamic model of TiN precipitation [21]:} \\
\lg([\%Ti] - [\%N]) &= A - \frac{B}{T} \\
[\%Ti]_0 - [\%Ti] &= \frac{A_{Ti}}{A_{TiN}} [\%TiN] \\
[\%N]_0 - [\%N] &= \frac{A_{N}}{A_{TiN}} [\%TiN] \\

\text{Thermodynamic model of TiC precipitation [21]:} \\
\lg([\%Ti] - [\%C]) &= A - \frac{B}{T} \\
[\%Ti]_0 - [\%Ti] &= \frac{A_{Ti}}{A_{TiC}} [\%TiC] \\
[\%C]_0 - [\%C] &= \frac{A_{C}}{A_{TiC}} [\%TiC]
\end{align*}
\]

Where, \( A \) and \( B \) are the corresponding constants in the formula of solid solubility product. \( A_{Ti}, A_{O}, A_{N}, A_{C}, A_{Ti_2O_3}, A_{TiN} \) and \( A_{TiC} \) are the atomic weight of Ti, O, N and C and the molecular weight of Ti\(_2\)O\(_3\), TiN and TiC respectively. \( A_{Ti} = 47.9, A_{O} = 16, A_{N} = 14, A_{C} = 12, A_{Ti_2O_3} = 143.8, A_{TiN} = 61.9, A_{TiC} = 59.9 \). \( [\%Ti]_0, [\%O]_0, [\%N]_0, [\%C]_0 \) is the initial mass percentage of Ti, O, N and C respectively. \( [\%Ti], [\%O], [\%N] \) and \( [\%C] \) are the equilibrium mass percentages of Ti, O, N and C respectively, \( [\%Ti_2O_3], [\%TiN] \) and \( [\%TiC] \) are the equilibrium precipitation amounts.

The mass percentage of Ti, O, N, C and Ti\(_2\)O\(_3\), TiN, TiC in molten steel at different temperatures can be calculated by the above equations, and the variation of Ti, O, N, C and Ti\(_2\)O\(_3\), TiN, TiC with temperature in a certain temperature range can be obtained. Note that the above equations belong to nonlinear equations, and analytical solutions cannot be obtained. By using Newton iteration method and substituting appropriate initial values, a set of solutions can be obtained at each determined temperature [22-24].

In the solidification process, the volume fraction of the solidified liquid steel in the initial liquid phase should also be considered when using the above formula, and the following formula should be used for calculation [1, 25].

\[
f_s = \left( f_s^* - f_s' \right) \cdot (1 - f_s')^{-1}
\]

Notes of the (19), \( f_s^* \): The difference between the solid fraction at temperature \( T^\prime \) and the solid fraction at temperature \( T' \) accounts for the specific gravity of molten steel at temperature \( T' \), \( (T^\prime < T') \). \( f_s' \): The solid fraction at temperature \( T' \). \( f_s^* \): The solid fraction at temperature \( T' \).

It should be noted that the absolute amount of the liquid phase is different at different temperatures, and the percentage content of the second phase or element calculated at a certain temperature is obtained from the liquid phase at that temperature. So equation (20) is also used to calculate the mass
percentage of the second phase or element in the sum of the liquid phase and the solid phase \([1, 26]\).

\[ [W]_0 = [W] \cdot (1 - f_p') \quad (20) \]

Notes of the (20), \([W]_0\): The mass percentage of W element (liquid phase + solid phase) in the steel at temperature \(T'\). \([W]\): The mass percentage of W in the liquid phase at \(T'\) is determined.

The precipitation amount of \(\text{Ti}_2\text{O}_3\), \(\text{TiN}\) and \(\text{TiC}\) and the change of the contents of Ti, O, N and C during solidification can be calculated by equations (10) to (20).

4. Thermodynamic calculation results and analysis

4.1. Calculation results of liquid steel

With the decrease of molten steel temperature, the solubility of \(\text{Ti}_2\text{O}_3\), \(\text{TiN}\) and \(\text{TiC}\) in molten steel decreases gradually. When the actual solubility product of \(\text{Ti}_2\text{O}_3\), \(\text{TiN}\) and \(\text{TiC}\) is greater than its equilibrium solubility product and precipitation reaction can occur \([27-29]\). According to the solubility product formula of different second phases in molten steel, the relationship between equilibrium concentration product and actual concentration product of \(\text{Ti}_2\text{O}_3\), \(\text{TiN}\) and \(\text{TiC}\) at different temperatures can be obtained, so as to judge whether \(\text{Ti}_2\text{O}_3\), \(\text{TiN}\) and \(\text{TiC}\) can precipitate in molten steel \([30-32]\). The figure 1 shows the relationship between the equilibrium concentration product of each second phase and the actual concentration product of the liquid steel. It can be seen from the figure that when the initial titanium content is 0.18%, carbon content is 0.02%, nitrogen content is 0.01%, and oxygen content is 0.0008%, \(\text{Ti}_2\text{O}_3\) begins to precipitate in the liquid phase before \(\text{TiN}\) during the cooling process of the liquid steel. It can be seen from the figure that the equilibrium precipitation temperature of \(\text{Ti}_2\text{O}_3\) is 1670 °C, and the equilibrium precipitation temperature of \(\text{TiN}\) is 1645°C. However, the actual concentration product of \(\text{TiC}\) is always less than the equilibrium concentration product during the cooling process to the liquidus, so \(\text{TiC}\) can not be precipitated in the liquid steel.

Because \(\text{Ti}_2\text{O}_3\) precipitates first in molten steel, the concentration of titanium in molten steel is bound to be affected. However, the mass fraction of oxygen in steel is very low, so the content of
titanium is unlikely to be greatly reduced. Through further calculation, it is concluded that 1644°C is the equilibrium precipitation temperature of TiN. It is known that the equilibrium precipitation point of TiN is reached when the temperature of molten steel is 1644°C. Therefore, according to the above thermodynamic equations (10) ~ (15) of Ti2O3 and TiN precipitation, the equilibrium contents of [%O], [%N], [%Ti], [%TiN] and [%Ti2O3] in molten steel can be obtained when Ti2O3 + TiN composite precipitation occurs in the temperature range of 1469°C ~ 1644°C. Considering that Ti2O3 precipitates first at 1645°C ~ 1670°C, the contents of [%O], [%N], [%Ti], [%TiN] and [%Ti2O3] in molten steel at different temperatures can be obtained.

Figures 2 and 3 show the content changes of [%O], [%N], [%C], [%Ti], [%TiN], and [%Ti2O3] in molten steel. Due to the precipitation of Ti2O3 before, the titanium element in the figure below exists excessive changes in 1644°C ~ 1670°C. In this range, the decrease of titanium content is due to the influence of Ti2O3 precipitation first, while in the range of 1469°C ~ 1644°C, the decrease of titanium content is due to the influence of TiN and Ti2O3 precipitation together, the decrease of oxygen content is due to the precipitation of Ti2O3, and the decrease of nitrogen content is due to the precipitation of TiN. However, TiC does not precipitate in molten steel, so the carbon content remains unchanged.

When the temperature of molten steel drops to liquidus 1469°C, the contents of elements and second phase in molten steel are: [%C] = 0.02%, [%O] = 0.0007054449%, [%N] = 0.001609022%, [%Ti] = 0.1498349%, [%TiN] = 0.037100105%, [%Ti2O3] = 0.002185371%.

![Figure 2. The content of each element and the second phase in steel.](image-url)
4.2. Calculation results of two phase region

According to the calculation results of liquid steel, when the temperature of liquid steel drops to 1469°C, the content of each element in liquid steel is: [%C] = 0.02%, [%O] = 0.00007054449%, [%N] = 0.001609022%, [%Ti] = 0.1498349%. By substituting the above elements into formula (7) and formula (8) as the initial contents and related thermodynamic parameters, the enrichment of elements in the liquid phase of the two-phase region at different temperatures is obtained. After substituting formulas (7) ~ (9) into formula (1), formula (3), formula (5) respectively, and substituting different temperature $T(K)$ into formula (2), formula (4), formula (6) respectively, the curves of $\lg Q_{TiO_2} - T$, $\lg K_{TiO_2} - T$, $\lg Q_{TiN} - T$, $\lg K_{TiN} - T$, $\lg Q_{TiC} - T$ and $\lg K_{TiC} - T$ are obtained, and calculate the initial precipitation points of Ti$_2$O$_3$, TiN and TiC. The figure 4 shows the precipitation of Ti$_2$O$_3$, TiN and TiC in the liquid phase of 321 stainless steel. It can be seen from the figure that in the initial liquidus, when the titanium content is 0.1498349%, the carbon content is 0.02%, the nitrogen content is 0.001609022%, and the oxygen content is 0.00007054449%, TiN, Ti$_2$O$_3$ and TiC reach the precipitation condition in the liquid phase during solidification. It can be seen from the figure 4 that TiN and Ti$_2$O$_3$ are at the equilibrium precipitation point at the liquidus temperature of 1469°C ($f_s = 0$), while the equilibrium precipitation temperature of TiC is about 1333°C.
In the solidification process of molten steel, Ti$_2$O$_3$ and TiN meet the thermodynamic precipitation conditions, so the precipitation amount of Ti$_2$O$_3$ and TiN and the equilibrium content of each element at each node temperature from 1333°C to 1469°C can be calculated first. Because of the precipitation of Ti$_2$O$_3$ and TiN, the content of titanium in liquid can also decrease, which may affect the actual concentration product of TiC. Therefore, it is necessary to find out the equilibrium precipitation temperature point of TiC in liquid phase again, and determine the influence of simultaneous precipitation of Ti$_2$O$_3$ and TiN on the possibility of TiC precipitation in the liquid phase. After further calculation and verification, 1332°C (\(f_s = 0.97\)) is the equilibrium precipitation temperature of TiC, which is only 1°C different from the initial precipitation temperature of 1333°C, indicating that the simultaneous precipitation of Ti$_2$O$_3$ and TiN has little effect on the actual concentration of titanium and carbon in the liquid phase of the two-phase region.

It is known that TiC reaches the equilibrium precipitation point at 1332°C. So according to the above thermodynamic equations (10) ~ (20), the contents of [%Ti], [%O], [%N], [%C] in liquid phase and [%Ti], [%O], [%N], [%C], [%Ti$_2$O$_3$], [%TiN], [%TiC] in steel can be obtained, when Ti$_2$O$_3$ + TiN + TiC simultaneously precipitates at 1332°C ~ 1319°C. Based on the previous simultaneous precipitation of Ti$_2$O$_3$ + TiN, the contents of each element in the liquid phase at 1319°C ~ 1469°C and the contents of each element and the second phase in the steel can be obtained. The results are shown in the figure below.

It can be seen from figure 5 and figure 6 that the change of element content in the liquid phase of the two-phase region: the content of titanium increases, the content of oxygen and nitrogen decreases, and the content of carbon increases first and then decreases. In the initial liquidus, the content of oxygen and nitrogen is low and the content of titanium is high. During solidification, the concentration of titanium is much higher than that of oxygen and nitrogen. Therefore, Ti$_2$O$_3$ and TiN precipitate simultaneously in the liquid phase, only a small amount of titanium is taken away, and oxygen and nitrogen are greatly reduced. When the temperature is lower than 1332°C, Ti$_2$O$_3$, TiN and TiC precipitate simultaneously in the liquid phase. At this time, the oxygen and nitrogen elements in the
liquid phase decrease continuously, and the precipitation amount of Ti$_2$O$_3$ and TiN also slows down. Due to the large enrichment of titanium and the high content of carbon, the content of TiC increases rapidly, which accelerates the consumption of carbon.

![Graph showing element content changes](image)

**Figure 5.** Change of element content in steel (liquid phase)

![Graph showing element content changes](image)

**Figure 6.** Change of element content in steel (liquid phase)

It can be seen in figure 7 and figure 8 that the content changes of each element and the second phase in the steel. Due to the simultaneous precipitation of Ti$_2$O$_3$ + TiN at the beginning, the content of titanium, oxygen and nitrogen in the steel gradually decreases, while the content of Ti$_2$O$_3$ and TiN
increases. When the temperature range is between 1319 ℃ ~ 1332 ℃, due to the simultaneous precipitation of Ti₂O₃, TiN and TiC, with the decrease of temperature, the content of titanium and carbon in the steel decreases rapidly, and the content of oxygen and nitrogen decreases slowly. At the end of solidification, the content of TiC increases rapidly, while the content of Ti₂O₃ and TiN increases slowly. When the temperature of molten steel drops to 1319 ℃, the contents of elements and second phase in molten steel are: [%C] = 0.01724409%, [%O] = 0.00000007%, [%N] = 0.000168%, [%Ti] = 0.1337645%, [%TiC] = 0.01375658%, [%TiN] = 0.00637132%, [%Ti₂O₃] = 0.000209%.

![Figure 7. Changes of elements and second phase content in steel (liquid phase + solid phase).](image1)

![Figure 8. Changes of elements and second phase content in steel (liquid phase + solid phase).](image2)
5. Conclusions
(1) Ti$_2$O$_3$ and TiN can be precipitated in molten steel, but TiC does not precipitate in molten steel. The precipitation temperature of Ti$_2$O$_3$ is higher than the precipitation temperature of TiN, which provides a medium for the heterogeneous nucleation and precipitation of TiN in molten steel.

(2) The continuous precipitation of Ti$_2$O$_3$ and TiN in the liquid phase of the two-phase region can effectively promote each other's nucleation and increase the number of nucleation. However, the TiC begins to precipitate at 1332°C ($f_s = 0.97$) at the end of solidification, and the content increases rapidly, which indicates that the enrichment of carbon is large at the end of solidification, the concentration product of titanium and carbon increases sharply, and the precipitation strength also increases.

(3) The precipitation amount of Ti$_2$O$_3$ and TiN in liquid steel and two-phase region is compared. It is found that the content of Ti$_2$O$_3$ and TiN in liquid steel is higher than that in two-phase region. The precipitation trend of Ti$_2$O$_3$ and TiN in the two-phase region gradually slows down, which indicates that the content of elements has a great influence on the precipitation amount. The consumption of nitrogen and oxygen in the steel makes it accumulate slowly in the liquid phase during solidification. With the consumption of nitrogen and oxygen during solidification, the content of Ti$_2$O$_3$ and TiN tends to be stable at the end of solidification.

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