Thermodynamic Calculation among Cerium, Oxygen, and Sulfur in Liquid Iron

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Thermodynamic calculation has been applied to predict the inclusion formation in molten SS400 steel. When the Cerium addition in liquid iron is 70 ppm and the initial Oxygen and Sulphur are both 110 ppm, the formation of oxides containing Cerium would experience the transformation from Ce2O3 to CeO2 and also the formation of sulfides containing Cerium would experience the transformation from CeS to Ce2S3 and then to Ce3S4. Below 2000 K the most thermodynamic stable matter is CeO2 and the less thermodynamic stable inclusion is CeS. Only when the amount of [O] is extremely low and the amount of [S] and [Ce] is relatively high, Ce2S3 has the possibility to form.

Rare earth (RE) metals have many applications1–5 and their addition to molten iron has attracted increasing research attention6. Such addition affects inclusion structures7 and can be used to purify steel8. The conjugation between oxygen and RE metals9 and between sulfur and RE metals10 is very strong. A lot of research11–13 has been done on the equilibrium relation between O, S, and RE metals. It has been found that extremely low oxygen and sulfur concentrations in steel can be achieved via the addition of an RE metal14. A lot of research15–18 has also been done on steel deoxidization and desulfurization via titanium and magnesium. RE metals can be used to deoxidize and desulfurize steel to control inclusion size and chemical composition. Few studies have performed thermodynamic calculations on the use of cerium to modify inclusions.

This paper focuses on the thermodynamic calculations of the cerium-oxygen-sulfur system in molten SS400 steel. The formation conditions of CeS, Ce2S3, Ce3S4, CeO2, and Ce2O3 in molten steel are examined using Wagner’s relation and Lupis’s relation based on the Gibbs free energy change. The transformation mechanism is analyzed by determining the thermodynamic conditions of Ce-desulfurized and Ce-deoxidized steel. The segregation of Ce2O3 in molten iron is also analyzed. In addition, a model for predicting the formation of various inclusions is established for SS400 steel with cerium addition.

Calculations
The thermodynamic calculations of the Ce-O-S system are based on Wagner’s relation19 and Lupis’ relation20. These calculations were implemented in C++9. The segregation of Ce2O3 in molten SS400 steel, whose chemical composition is shown in Table 1, was calculated in Matlab 2015a.

The Ce-O-S system is the thermodynamic relation between the dissolved Oxygen, Sulphur and Cerium in liquid iron to explore the formations of inclusions containing Cerium. The first stage for thermodynamic calculation is to derive the thermodynamic equations for the inclusion formations by Wagner’s relation19 and Lupis’ relation20. Then the second stage is to use C++ programming software to derive the unknown chemical composition values for every equation.

Results and Discussion
For the addition of cerium into molten SS400 steel, the reactions of [O], [S], and [Ce] are of interest because Ce has strong affinity with S and O. As reported previously21, when w(RE)/(w(O) + w(S)) = 3.9, the function of
cerium is optimal. To determine the separation sequence for various oxides and sulfides of cerium, the amount of cerium in the calculations was set as 1 mol to compare the Gibbs free energy of formation for various inclusions, which can be derived as:

\[ \Delta G = \Delta G^\theta + RT \ln J \] (1)

\[ \Delta G^\theta = -RT \ln K \] (2)

where \( J \) denotes the reaction quotient (unitless), \( \Delta G \) is the Gibbs free energy change of reaction (J/mol), \( \Delta G^\theta \) denotes the Gibbs free energy change of reaction for unmixed reactants and products at standard conditions (J/mol), \( R \) is the gas constant (J·mol\(^{-1}\)·K\(^{-1}\)), \( T \) is temperature (K), and \( K \) is the equilibrium constant (unitless).

The Gibbs free energy of oxides, sulfides and oxysulfides of cerium are shown in Table 2\(^{14,21-26}\). Below 2000 K, the most thermodynamically stable inclusion was CeO\(_2\), as shown in Fig. 1. Therefore, CeO\(_2\) likely formed in the molten iron when the temperature reached the simulated steelmaking temperature of 1873 K. In Fig. 1, it could be read that the least thermodynamic stable inclusion is CeS and the thermodynamic stable sequence of the possible inclusion formed in liquid steel is CeO\(_2\) > Ce\(_2\)O\(_3\) > Ce\(_2\)O\(_2\)S > Ce\(_2\)S\(_3\) > Ce\(_3\)S\(_4\) > CeS. However, the most thermodynamically stable matter does not guarantee the formation of CeO\(_2\), because the formation of oxides containing cerium are controlled not only by the equilibrium constant but also by the concentrations of cerium and oxygen in the molten iron. That is to say, the formation of CeO\(_2\) at 1873 K is also determined by the solubility product of CeO\(_2\) and the concentration of cerium and oxygen, even though the Gibbs Free Energy of CeO\(_2\) is the lowest at 1873 K.

The activities and activity coefficient of Ce, O and S can be written as Eqs (9) and (10) from Wagner’s relation\(^7\) and Lupis’ relation\(^8\) as follow,

\[ \alpha_i = f_i \cdot w_i \] (9)

| C  | Si | Mn | P | S | O |
|----|----|----|---|---|---|
| 0.14 | 0.26 | 0.90 | 0.02 | 0.03 | 0.018 |

Table 1. Chemical composition of SS400 steel (wt. %).

| Reaction | Standard Gibbs Free Energy, J/mol | No. |
|----------|---------------------------------|-----|
| [Ce] + 2[O] = CeO\(_2\) | \( \Delta G^\theta = -854270 + 250T \) | (3) |
| [Ce] + 3/2[O] = 1/2Ce\(_2\)O\(_3\) | \( \Delta G^\theta = -715560 + 180T \) | (4) |
| [Ce] + [S] = CeS | \( \Delta G^\theta = -2311390 + 60.5T \) | (5) |
| [Ce] + 3/2[S] = 1/2Ce\(_2\)S\(_3\) | \( \Delta G^\theta = -537290 + 164T \) | (6) |
| [Ce] + 4/3[S] = 1/3Ce\(_3\)S\(_4\) | \( \Delta G^\theta = -498480 + 146.3T \) | (7) |
| [Ce] + [O] + 1/2[S] = 1/2Ce\(_2\)O\(_2\)S | \( \Delta G^\theta = -676795 + 166T \) | (8) |

Table 2. Formation equations and Gibbs free energy of oxides, sulfides and oxysulfides of cerium\(^{14,21-26}\).
\[
\sum_{i} e_i \gamma_{ij}^{\text{lg}}(10)
\]

where \(f_i\) is the Henrian activity coefficient of component \(i\) relative to the dilute solution and \(e_i^{\text{lg}}\) is the first-order interaction parameter of \(i\) on \(j\) in molten iron; \(w[i]\) and \(w[j]\) are the mass percentages of elements \(i\) and \(j\), respectively (Table 3); \(\alpha_{ij}\) is the activity of element \(i\).

By using data from Tables 2 and 3, the following curves for Ce-S and Ce-O in Fig. 2 can be calculated. The key to derive every line in Fig. 2 is the relation of equilibrium constant, Gibbs free energy and the amount of the chemical compositions for every possible inclusion according to Wagner's relation and Lupis' relation. When the equilibrium constant is linked to the amount of the chemical compositions for every possible inclusion, equations for Fig. 2 can be obtained. When the weight percentage of cerium, oxygen and sulphur are known in the molten iron at 1873 K, the main inclusion formed would be found in Fig. 2. As shown in Fig. 2, if the cerium addition in liquid iron is 70 ppm and the initial oxygen and sulphur are both 110 ppm, the formation of oxides containing cerium would experience the transformation from \(\text{Ce}_2\text{O}_3\) to \(\text{CeO}_2\) and also the formation of sulfides containing cerium would experience the transformation from \(\text{CeS}\) to \(\text{Ce}_2\text{S}_3\) and then to \(\text{Ce}_3\text{S}_4\). From Fig. 2, when the temperature of molten iron reached 1873 K, \(\text{Ce}_3\text{S}_4\) is the main product, as the amount of cerium in molten iron is high and the amount of sulphur is relatively lower compared to the formation of \(\text{CeS}\) and \(\text{Ce}_2\text{S}_3\).

In order to investigate the formation conditions of \(\text{Ce}_2\text{O}_3\), \(\text{Ce}_2\text{O}_2\text{S}\) and \(\text{Ce}_2\text{O}_2\text{S}\), the doubly saturated curve with \(\text{Ce}_2\text{O}_3/\text{Ce}_2\text{O}_2\text{S}\) and \(\text{Ce}_2\text{S}_3/\text{Ce}_2\text{O}_2\text{S}\) are calculated, using the thermodynamic data derived in Tables 2 and Equation 1–2.

In molten iron, it is assumed that \(K_{\text{Ce}_2\text{O}_3,1873\text{K}} = [%\text{Ce}]^3 \cdot [%\text{O}]^3 = 10^{-11}\) and \(K_{\text{Ce}_2\text{S}_3,1873\text{K}} = [%\text{Ce}]^3 \cdot [%\text{S}]^3 = 10^{-9}\). Based on the reaction \(\text{Ce}_2\text{O}_3 + [O] = \text{Ce}_2\text{O}_2 + [S]\), it is found that [%S] = 100[%O] when \(\text{Ce}_2\text{O}_3\) and \(\text{Ce}_2\text{O}_2\) coexist in molten iron, it is derived that [%S] = 100[%O], based on the thermodynamic calculation of the reaction \(\text{Ce}_2\text{S}_3 + 2[O] = \text{Ce}_2\text{O}_2 + 2[S]\). Figure 3 was derived from the above calculations. In Fig. 3, it can be concluded that \(\text{Ce}_2\text{O}_3\) and \(\text{Ce}_2\text{O}_2\text{S}\) can exist in molten iron in a wide amount range of [Ce], [O] and [S]. More importantly, only when the amount of [O] is extremely low and the amount of [S] and [Ce] is relatively high, \(\text{Ce}_3\text{S}_4\) has the possibility to form.

Cerium is a perfect deoxidizer and desulfurizer for steel purification. Compared with other elements, for example Aluminum, Titanium, Magnesium and Calcium, which can also deoxidize and desulfurize, cerium can form a complex compound \(\text{Ce}_2\text{O}_3\) which contains Oxygen and Sulphur together. The formation possibility of \(\text{Ce}_2\text{O}_3\) has been verified by Hu’s research when they studied the effect of Ce addition on the C-Mn steel microstructure. It is reported by Wang that \(\text{Ce}_2\text{O}_3\) is easier to form in molten iron when the iron molten temperature is 1873 K. However, the thermodynamic conditions were changed when the temperature decreases from 1873 K to solidus temperature. On the other hand, when the temperature of molten iron decreases to that at which solid steel starts to form, the cerium and oxygen in the molten iron begin to segregate. Their amounts are respectively:

\[
W_{\text{CeO}} = W_{\text{Co}} (1 - f) \kappa \alpha^{-1}
\]
where $W_{(Ce)}$ and $W_{(O)}$ are the percentage amounts of cerium and oxygen of molten iron during the molten iron solidification, respectively; $W_{(Ce)}$ and $W_{(O)_b}$ are the initial percentage amounts of cerium and oxygen in the liquid phase, respectively; $k_{Ce}$ (=0.005) and $k_{O}$ (=0.022) are the solvent partition coefficients at equilibrium for cerium and oxygen, respectively; $f_s$ is the solid fraction.

The solidus temperature of SS400 is 1777 K. The solubility product of the Ce$_2$O$_3$ formed in molten iron can be expressed as:
The solubility product of the $\text{Ce}_2\text{O}_3$ formed in molten iron at equilibrium can be expressed as:

$$Q_{\text{Ce}_2\text{O}_3} = W_{\text{Ce}}^2 \cdot W_{\text{O}}^3$$

From Eqs (11) to (14), the solubility products versus solidification ratio ($f_s$) are plotted in Fig. 4. In Fig. 4(a), where the simulated oxygen concentration in liquid steel is 10 ppm and the cerium concentration varies from 0.1% to 0.5%, the solubility products versus solidification ratio ($f_s$) are plotted with the varying cerium concentration (shown in the colorful lines of Fig. 4(a)) and the equilibrium constant of $\text{Ce}_2\text{O}_3$ ($K_{\text{Ce}_2\text{O}_3}$) versus solidification ratio $f_s$ is curved as the black solid line in Fig. 4(a). It is read in Fig. 4(a) that the colorful lines are all in the above of the black solid line, which means $\text{Ce}_2\text{O}_3$ prefers to segregate in liquid phase with the 10 ppm Oxygen concentration in liquid iron. Moreover, the same conclusion can be drawn from the similar Fig. 4(b–d) with 50 ppm, 100 ppm, 200 ppm oxygen concentration in liquid iron. The inset red diagrams in Fig. 4(a–d) are the detailed solid black curves appeared in Fig. 4(a–d). Figure 4 shows that when the oxygen concentration in molten iron was increased from 10 to 200 ppm and the cerium concentration was in the range of 0.1% to 0.5%, $\text{Ce}_2\text{O}_3$ preferred to segregate in the liquid phase.

Conclusion

By the addition of cerium in molten SS400 steel, when the temperature of molten iron reached 1873 K, at the same time that the cerium addition in liquid iron is 70 ppm and the initial Oxygen and Sulphur are both 110 ppm, the formation of oxides containing Cerium would experience the transformation from $\text{Ce}_2\text{O}_3$ to $\text{CeO}_2$ and also the formation of sulfides containing Cerium would experience the transformation from $\text{CeS}$ to $\text{Ce}_2\text{S}_3$ and then to $\text{Ce}_3\text{S}_4$. Below 2000 K the most thermodynamic stable matter $\text{CeO}_2$ and the least thermodynamic stable inclusion is $\text{CeS}$. And the thermodynamic stable sequence of the possible inclusions formed in liquid steel is $\text{CeO}_2 > \text{Ce}_2\text{O}_3 > \text{Ce}_3\text{S}_4 > \text{Ce}_2\text{S}_3 > \text{CE}_2\text{S}_3 > \text{CeS}$. Only when the amount of [O] is extremely low and the amount of [S] and [Ce] is relatively high, $\text{Ce}_2\text{S}_3$ has the possibility to form. With the amount of oxygen in molten iron increasing from 10 ppm to 200 ppm and the amount range of cerium increasing from 0.1% to 0.5%, $\text{Ce}_2\text{O}_3$ prefers to segregate in liquid phase all the time.

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**Author Contributions**

This paper was proposed by W.-S.H., F.P. and J.Z. contributed to this article equally. This manuscript was written by F.P. The thermodynamic calculations were carried out by F.P. and J.Z. H.-L.C. and Y.-H.S. contributed to data analysis. Y.-H.S. gave us a lot of suggestions to promote our research. All authors reviewed the manuscript.

**Additional Information**

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