Abstract

To understand the precipitation behavior and solidification process of micro-alloyed steel, abundant thermodynamic data of pure substances were incorporated in the coupled thermodynamic model of inclusions precipitation and solutes micro-segregation during the solidification of heat-resistant steel containing cerium. The liquid inclusions $\text{Ce}_2\text{Al}_x\text{Si}_{1-x-y}\text{O}_z$ where $0 < x < 1$, $0 < y < 1 - x$ and $z = 1 - x - y$ and their generation Gibbs free energy were first introduced to the inclusions reactions according to the Al$_2$O$_3$-SiO$_2$-Ce$_2$O$_3$ phase diagram. Then plant trials, lab experiments and published work in the literature were taken account to valid the established model. Also, the difference of calculated results between FactSage and this model were argued. Finally, the liquid inclusions were found in the samples from experiments in the tube furnace based on the calculations by this model.

Keywords: liquid inclusions, thermodynamic model, rare earth, heat-resistant steel

1. Introduction

The heat resistant steels containing rare earth elements (RE) have absolute advantages in mechanical properties and corrosion resistance [1–4]. The oxidation resistance of 253MA steel at high temperature is dramatically enhanced as alloyed with cerium element. However, the rare earth elements are used as deoxidizing and desulfurizing agents in the earlier ages owing to the strong oxidation property [5]. As a result, a large number of inclusions such as Ce$_2$O$_3$ and Ce$_2$O$_2$S with high melting temperature and small size are generated in the molten steel. During the continuous casting process these inclusions are easily captured by the submerged nozzle. Then the accumulated inclusions with frozen steel lead to nozzle blocking and the production process is interrupted [6–9]. As one of the effectual solutions to nozzle blocking calcium treatment can modify the solid alumina clusters to liquid inclusions which have weak affinity force with the nozzle inner wall [10–13]. Inspired by the above method, the high
melting point inclusions containing rare earth elements may be modified to liquid phase by some alloys to solve the nozzle clogging issue of heat resistant steel.

Many prediction models of inclusions formation and evolution are reported in the previous reports. However, the released self-built model mainly involve a few equilibrium reactions of alloy elements with oxygen or sulfur at 1600°C [14, 15]. And the thermodynamic properties of complex liquid inclusions, such as Mn-Si-Al-O, Ca-Al-O, Ca-Al-Mg-O, are calculated by the commercial software [15–19]. Harada assessed the CaO-Al2O3 liquid inclusions formation setting the fixed ratio of CaO to Al2O3 instead of the whole liquid region [20, 21]. FactSage as the common software in metallurgical field is strong at the equilibrium calculations of multi phases, but the FToxide database is short of solution thermodynamic data containing rare earth and the solidification model is not thoroughly optimized. Liu released one coupling model of micro-segregation and inclusion formation during solidification process in silicon steels [22]. However, the number of reactions was restricted and the solution phase was not considered. Fang proposed a thermodynamic model which includes plenty of formation reactions of rare earth inclusions except the liquid inclusions as a pity [23]. To make up for the deficiency of previous models [24], the more ampler generation reactions of inclusions especially the liquid phase coupling with the solute micro-segregation are introduced in the present model. Then the coupled model was validated by various methods, such as plant trials, lab scale experiments and released experimental data. Finally, the formation regions of liquid phases in the predominance diagrams were given. Moreover, the liquid inclusions with sphere shape and large size were found in the exploitative experiments of lab scale.

2. Modeling process

The coupling model is composed of two parts: the thermodynamic model of inclusions precipitation both in liquid and solid and the dynamic model of solute micro-segregation model in the liquid–solid interface during solidification. The schematic diagram of coupling process is shown in Figure 1. Considering the kinetic factors such as diffusion rate and atomic size, the inclusions with large size are formed in the residual liquid phase above the solidus temperature and the small-size carbonitrides are precipitated in the solidified steel under the liquidus temperature. All the relevant reactions of inclusions generation both in liquid and solidified steel are listed in Table 1 [26–33] and Table 2 [34–37], respectively. The activity standard state of solute elements and inclusions was 1 mass% infinite dilute solution and the pure substance, respectively. The activity coefficients of solute elements were arranged by Wagner’s relations expanded to second order interaction coefficient. The solute segregation at liquid–solid interface during solidification was calculated form the Brody-Flemings micro-segregation model modified by Clyne-Kurz [25]. The more details including the mathematic expressions and thermodynamic properties of solutes can be consulted from the previous works [24].

The generated liquid inclusions whose activity is 1 can be identified as one isolated phase (pure liquid phase) out of the solid inclusions (pure solid phase) and solute elements (solute in the infinite dilute solution) in the system. As the same as listed in Table 1, the liquid inclusion in the form of Ce2xAl2ySi1–x–yOz (l, 0 < x < 1, 0 < y < 1–x and z = 1–x–y) is introduced
according to the phase diagram of Al₂O₃-SiO₂-Ce₂O₃ system. The hard task is the calculation of standard Gibbs free energy of Ce₂xAl₂ySi1−x−yOz generation as the following reaction:

\[ x\text{Ce}^{\frac{1}{2}} + 2y\text{Al}^{\frac{1}{2}} + (1 - x - y)\text{Si} + z\text{O} = \text{Ce}_{2x}\text{Al}_{2y}\text{Si}_{1-x-y}\text{O}_{z} \]  

(1)

The chemical reaction of Eq. 1 can be derived from the following reactions:

\[ 2\text{Ce} + 3\text{O} = \text{Ce}_{2}\text{O}_{3} \]  

(2)

\[ 2\text{Al} + 3\text{O} = \text{Al}_{2}\text{O}_{3} \]  

(3)

\[ \text{Si} + 2\text{O} = \text{SiO}_{2} \]  

(4)

\[ \text{Ce}_{2}\text{O}_{3} = \text{Ce}_{2}\text{O}_{3} \quad \Delta G^0 = 63086.4 - 25.1T \quad J \cdot mol^{-1} \]  

(5)

\[ \text{Al}_{2}\text{O}_{3} = \text{Al}_{2}\text{O}_{3} \quad \Delta G^0 = 110756.7 - 46.8T \quad J \cdot mol^{-1} \]  

(6)
| Reaction equations in molten steel | $\Delta G^0 = A + B \times T, \text{J} \cdot \text{mol}^{-1}$ |
|------------------------------------|-----------------------------------------------|
| **A**                              | **B**                                     |
| 2[Ce] + 3[O] = Ce$_2$O$_3$(s)       | −1,431,090                                 |
| [Ce] + 2[O] = CeO$_2$(s)            | −854,274.7                                 |
| [Ce] + [S] = CeS(s)                | −422,783                                   |
| [Ce] + 2[S] = Ce$_2$S$_2$(s)        | −131,000                                   |
| 2[Ce] + 3[S] = Ce$_2$S$_3$(s)       | −1,074,584                                 |
| 3[Ce] + 4[S] = Ce$_3$S$_4$(s)       | −1,493,010                                 |
| 2[Ce] + 2[O] + [S] = Ce$_2$O$_2$S(s) | −135,3592.4                                |
| [Ce] + [Al] + 3[O] = CeAlO$_3$(s)   | −1,366,460                                 |
| [Ce] + 11[Al] + 3[O] = CeAl$_{11}$O$_{18}$(s) | −726,1120.00.00                            |
| 2[Ce] + 5[Si] + 5[O] = Ce$_2$SiO$_5$(s) | −207,7830.00.00                           |
| 4.67[Ce] + 3[Si] + 13[O] = Ce$_{4.67}$Si$_2$O$_{13}$(s) | −529,9450.00.00                           |
| 2[Ce] + 2[Si] + 7[O] = Ce$_2$Si$_2$O$_7$(s) | −280,0700.00.00                           |
| 2x[Ce] + 2y[Al] + (1-x-y)[Si] + z[O] = Ce$_2$Al$_2$Si$_{1-x-y}$O$_z$(l) | −401,200                                    |
| [Ce] + [N] = CeN(s)                | −202,790                                   |
| [Ce] + 2[C] = CeC$_2$(s)            | −224,000                                   |
| 2[Ce] + 3[C] = Ce$_2$C$_3$(s)       | −1,205,090                                 |
| [Al] + [N] = AlN(s)                | −172,676.1                                 |
| [Mn] + [S] = MnS(s)                | −284,420                                   |
| [Si] + 2[O] = SiO$_2$(s)            | −580,550                                   |
| 6[Al] + 2[Si] + 13[O] = Al$_6$Si$_2$O$_{13}$(s) | −4,758,434                                 |
| 4[Cr] + [C] = Cr$_2$C$_2$(s)        | −195,790                                   |
| 23[Cr] + 6[C] = Cr$_{23}$C$_6$(s)   | −887,889.7                                 |
| 7[Cr] + 3[C] = Cr$_3$C$_3$(s)       | −356,120.1                                 |
| 3[Cr] + 2[C] = Cr$_5$C$_2$(s)       | −182,030.1                                 |
| 2[Cr] + 3[O] = Cr$_2$O$_3$(s)       | −797,190                                   |
| 3[Cr] + 4[O] = Cr$_3$O$_4$(s)       | −944,399.9                                 |
| [Cr] + [O] = CrO(s)                | −236,320                                   |
| 2[Cr] + [N] = Cr$_2$N(s)            | −141,300                                   |
| [Cr] + [N] = CrN(s)                | −136,250                                   |
| [Ni] + [O] = NiO(s)                | −125,000                                   |

Table 1. The possible reactions and standard Gibbs free energy in liquid.
\[ \Delta G^0 = A + B \times T, \text{ J mol}^{-1} \]

| Reaction equations in solid phase(γ) | \( \Delta G^0 \) |
|-------------------------------------|-----------------|
| \([\text{Al}] + [\text{N}] = \text{AlN(s)}\) | \(-137536.1\)   |
| \([\text{Mn}] + [\text{S}] = \text{MnS(s)}\) | \(-176,782\)    |
| \([\text{Ti}] + [\text{N}] = \text{TiN(s)}\) | \(-153158.23\)  |
| \([\text{Ti}] + [\text{C}] = \text{TiC(s)}\) | \(-143585.84\)  |
| \([\text{Nb}] + [\text{N}] = \text{NbN(s)}\) | \(-162730.62\)  |
| \([\text{Nb}] + [\text{C}] = \text{NbC(s)}\) | \(-143585.84\)  |
| \([\text{V}] + [\text{N}] = \text{VN(s)}\) | \(-182030.1\)   |
| \([\text{V}] + [\text{C}] = \text{VC(s)}\) | \(-797,190\)    |

Table 2. The possible reactions and standard Gibbs free energy in solid.

where the standard Gibbs free energy of reactions 2, 3, 4 are listed in Table 1. And the CALPHAD technique was used to optimize the Gibbs free energy change of reaction 8. The Redlich-Kister (R-K) expression was adopted to describe the excess Gibbs free energy of solution phases in \(\text{Al}_2\text{O}_3-\text{SiO}_2\), \(\text{Al}_2\text{O}_3-\text{Ce}_2\text{O}_3\) and \(\text{Ce}_2\text{O}_3-\text{SiO}_2\) binary systems. The R-K expression is written as Eq. 9.

\[
G^E = x_1 x_2 \sum_{j=0}^{n} L_j (x_1 - x_2)^j
= x_1 x_2 L_0
+ x_1 x_2 L_1 (x_1 - x_2)
+ x_1 x_2 L_2 (x_1 - x_2)^2
+ \ldots
\]

where \(G^E\) is the excess Gibbs free energy of binary system; \(x_1, x_2\) are the mole fraction of end members in the binary system; \(L_j (j = 0, 1, 2, \ldots)\) are the interaction parameters of components in the binary system. And \(L_j\) in Table 3 were obtained by the phase diagram optimization when the restricted experimental points from literature were employed.

The excess Gibbs free energy of \(\text{Ce}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2\) ternary system was derived by the following geometric Kohler method [38].
The Gibbs free energy was further modified by the solidification energy of reaction 8 is written as:

$$G_{extra}^E = (x_1 + x_2)^2 G_{12}^E \left( \frac{x_1}{x_1 + x_2}, \frac{x_2}{x_1 + x_2} \right)$$

$$+ (x_2 + x_3)^2 G_{23}^E \left( \frac{x_2}{x_2 + x_3}, \frac{x_3}{x_2 + x_3} \right)$$

$$+ (x_1 + x_3)^2 G_{13}^E \left( \frac{x_1}{x_1 + x_3}, \frac{x_3}{x_1 + x_3} \right)$$  \tag{10}$$

where the first term $G_{12}^E \left( \frac{x_1}{x_1 + x_2}, \frac{x_2}{x_1 + x_2} \right)$ is the excess Gibbs free energy at $(\frac{x_1}{x_1 + x_2}, \frac{x_2}{x_1 + x_2})$ point in the 1–2 binary system. The following two terms in Eq. 10 have similar representation as the first term. In order to exactly describe the thermodynamic properties of Ce$_2$O$_3$–Al$_2$O$_3$–SiO$_2$ system, the Gibbs free energy was further modified by the $G_{ternary}^E$ term with the value of $-825000x_{Ce_2O_3}x_{Al_2O_3}x_{SiO_2}$. After the interaction coefficients in Table 3 are imported, the standard Gibbs free energy of reaction 8 is written as:

$$\Delta G_{1}^0 = G_{idea}^E + G^E = G_{idea}^E + G_{extra}^E + G_{ternary}^E$$

$$= -825000xy(1 - x - y)^2 + 42569.73xy + 19570.28y(1 - y) - 140979.96x(1 - x)$$

$$\quad + \frac{y(1 - x - y)(1 - x - 2y)}{1 - x} \left( 14875.48 + 5640.02 \frac{1 - x - 2y}{1 - x} \right)$$

$$\quad + \frac{x(1 - x - y)(1 - 2x - y)}{1 - y} \left[ 215301.91 + 547791.07 \frac{1 - 2x - y}{1 - y} + 398115.65 \left( \frac{1 - 2x - y}{1 - y} \right)^2 \right]$$

$$\quad + \left\{ \begin{array}{l}
-98.65xy - 10.49y(1 - y) + 78.91x(1 - x) \\
\quad + \frac{y(1 - x - y)(1 - x - 2y)}{1 - x} \left[ -0.71 + 1.21 \frac{1 - x - 2y}{1 - x} \right] \\
\quad + \frac{x(1 - x - y)(1 - 2x - y)}{1 - y} \left[ 23.6 - 202.71 \frac{1 - 2x - y}{1 - y} - 155.94 \left( \frac{1 - 2x - y}{1 - y} \right)^2 \right] \\
\quad + 8.314[x \ln x + y \ln y + (1 - x - y) \ln (1 - x - y)] \\
\end{array} \right\} T$$  \tag{11}$$

Table 3. The optimized coefficients of the binary systems.

| System               | $L_1$ | $L_0$ | $L_1$ | $L_2$ | $L_3$ |
|----------------------|-------|-------|-------|-------|-------|
| Al$_2$O$_3$–SiO$_2$  | $a$   | 19570.28 | 14875.48 | 5640.02 | –     |
|                      | $b$   | –10.49 | –0.71 | 1.21  | –     |
| Ce$_2$O$_3$–Al$_2$O$_3$ | $a$ | –78839.95 | –     | –     | –     |
|                      | $b$   | –30.23 | –     | –     | –     |
| Ce$_2$O$_3$–SiO$_2$  | $a$   | –140979.96 | 215301.91 | 547791.07 | 398115.65 |
|                      | $b$   | 78.91  | 23.60 | –202.71 | –155.94 |
When the Gibbs free energy of Eqs. (2)–(8) are introduced, the standard Gibbs free energy of Eq. (1) is finally written as follows:

$$\Delta G^0_L = -825000xy(1 - x - y)^2 + 42569.73xy + 19570.28y(1 - y) - 140979.96x(1 - x)$$

$$-1368003.6x - 1094333.3y - 570968.7(1 - x - y)$$

$$+ \frac{y(1 - x - y)(1 - x - 2y)}{1 - x} \left(14875.48 + 5640.02 \frac{1 - x - 2y}{1 - x}\right)$$

$$+ \frac{x(1 - x - y)(1 - 2x - y)}{1 - y} \left[215301.91 + 547791.07 \frac{1 - 2x - y}{1 - y} + 398115.65 \left(\frac{1 - 2x - y}{1 - y}\right)^2\right]$$

$$+ \left\{\begin{array}{c}
-98.65xy - 10.49y(1 - y) + 78.91x(1 - x) + 334.96x + 340.92y + 216.23(1 - x - y) \\
+ \frac{y(1 - x - y)(1 - x - 2y)}{1 - x} \left[-0.71 + 1.21 \frac{1 - x - 2y}{1 - x}\right] \\
+ \frac{x(1 - x - y)(1 - 2x - y)}{1 - y} \left[23.6 - 202.71 \frac{1 - 2x - y}{1 - y} - 155.94 \left(\frac{1 - 2x - y}{1 - y}\right)^2\right] \\
+ 8.314[x \ln x + y \ln y + (1 - x - y) \ln (1 - x - y)]
\end{array}\right\}^T$$

(12)

After the standard Gibbs free energy $\Delta G^0_L$ of liquid inclusions formation was worked out, the inclusions compositions (certain $x$, $y$ values, $z = 1-x-y$) can be calculated according to the minimum of Gibbs free energy $\Delta G_L$. At the equilibrium status in the molten steel, the Gibbs free energies of chemical reactions in Table 1 are greater than or equal to zero.

### 3. Modeling validation

The constructed model was validated by plant trial, lab scale experiments and experimental data from others work. Moreover, the calculated results by this model were compared with the popular commercial software FactSage.

The standard chemical compositions of 253MA steel were shown in Table 4. And the industrial samples of 253MA steel were obtained after EAF → AOD → LF → CC process in one stainless steel plant of China. The obtained samples were machined into column of $\Phi = 4$ mm

| C   | Si  | Mn  | S   | P   | N   | Ni  | Cr  | Ce  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0.05–0.10 | 1.40–2.0 | ≤0.80 | ≤0.030 | ≤0.040 | 0.14–0.20 | 10.00–12.00 | 20.00–22.00 | 0.03–0.08 |

**Table 4.** The chemical compositions of 253MA steel (mass fraction, %).
and then polished by emery paper and polishing cloth to make metallographic specimen. Then the field emission scanning electron microscope (FE-SEM) and energy dispersive spectrometer (EDS) were employed to observe the morphology and analyze the compositions of inclusions, as shown in Figure 2. It can be seen that the inclusions with the size of 1-2 μm in the solidification structure of 253 MA steel are mainly Ce₂O₂S and Ce₂O₃. CeN maybe exist as the element N was detected as shown in Figure 2(b). The peaks without labels are matrix elements Fe, Cr and Ni.

The experiments in laboratory that carefully follows the industrial operations were carried out in the Si-Mo rod heating furnace protected by argon flow at 1873 K, as shown in Figure 3. Firstly, the Fe-Cr-Ni alloys with fixed ratio as in the 253MA steel were loaded in the MgO crucible until completely melted. Then the mass fraction of Si was calculated and added into the crucible after the oxygen content was first determined. After Si was totally melted, the oxygen content was determined for the second time and then the melt was alloyed by Ce. The molten steel was drawn using quartz tube (inner Φ = 4 mm) and immediately quenched into ice water at 30 min after Ce addition. Therefore, the inclusions formed at 1873 K can be preserved since the extremely cooling rate of quenching. The quenched samples were processed and observed as the same as that of industrial samples. It is explicit that the inclusions are Ce₂O₂S and Ce₂O₃ with the size smaller than 2 μm as the analysis results shown in Figure 4.

Figure 2. SEM images and EDS analysis of inclusions in the solidification structure.

Figure 3. The flow chart of technological process of lab scale experiment.
The types and amounts of inclusions formed during the solidification of 253MA steel was calculated by the present model and the results are drawn in Figure 5 which (b) is the zoom view of the liquid–solid two-phase region \( (T_{L} = 1713 \text{ K}) \). It can be seen that the inclusions types are mainly Ce\(_2\)O\(_2\)S, Ce\(_2\)O\(_3\), CeN and Ce\(_2\)SiO\(_5\). And the calculation results are in agreement with the industrial experiments except Ce\(_2\)SiO\(_5\). Ce\(_2\)SiO\(_5\) is formed as Ce\(_2\)O\(_3\) is reduced during solidification as shown in the magnified image of Figure 5(b). Then Ce\(_2\)SiO\(_5\) must be transformed from Ce\(_2\)O\(_3\) as the increasing Si concentration in the residual liquid phase which owes to the micro-segregation of solutes at the liquid–solid interface. However, it is very difficult for the decomposition of Ce\(_2\)O\(_3\) because the extremely fast cooling rate during the continuous casting process. Therefore, Ce\(_2\)SiO\(_5\) is not found in the industrial samples. What is more, the formed inclusions are only Ce\(_2\)O\(_3\) and Ce\(_2\)O\(_2\)S at 1873 K which is completely consistent with the results in the laboratory scale experiments.

The types and amounts of inclusions formed during the solidification of 253MA steel was also calculated by FactSage and the results are drawn in Figure 6. It can be seen that only Ce\(_2\)O\(_3\) and Ce\(_2\)O\(_2\)S are formed in the FactSage results where Ce\(_2\)O\(_2\)S precipitates at a lower temperature 1848 K comparing with 1873 K in the present model. However, Ce\(_2\)SiO\(_5\) and CeN are not present in the FactSage results since the solutes segregation is not considered in FactSage when
the normal equilibrium solidification model is selected. The elements activities were further calculated to understand the lower formation temperature of Ce₂O₂S in FactSage. The stable pure substances at standard conditions are adopted by FactSage as the activities standard state when 1 mass% infinite dilute solution is chosen in the present work. The activities of solutes in molten steel calculated by the two different standard states can be linked by the following equation.

\[
a_{i(w)}^{H} = \frac{a_{i}^{R}}{M_{A}^{\gamma_{i}^{0}}} \gamma_{i}^{0}
\]

where \(a_{i(w)}^{H}\) is the activity at the standard state of 1 mass% solution; \(a_{i}^{R}\) is the activity when pure substance is standard state; \(M_{i}\) is the relative atomic mass of solutes; \(M_{A}\) is the relative atomic mass of solvents, that is Fe in this work; \(\gamma_{i}^{0}\) is the activity coefficient when stable pure substance is standard state in the Henrian solution. The available activity coefficients are listed in Table 5 [39] and the activities transformed from FactSage state to 1 mass% solution comparing with that calculated by this model are present in Table 6.

As listed in Table 6, the solutes activities calculated from different standard state are basically at the same level except P and N elements. The remarkable differences of P and N activities can

\[
\begin{array}{cccccc}
\text{C} & \text{Si} & \text{Mn} & \text{Ce} & \text{O} \\
\hline
A & e^{0.57} & -11763.2 & 0 & -7103.2 & -15,280 \\
B & 0 & 0 & 0 & 3.5 \\
\text{Standard state} & \text{S} & \text{S} & \text{L} & \text{L} & \text{G} \\
\end{array}
\]

Note: \(ln\gamma^{0} = A/T + B\), \(e\): natural constant, S: pure solid, L: pure liquid, G: gas.

Table 5. Optimized Henrian activity coefficients \(ln\gamma^{0}\).
owe to the missing $\gamma^0_i$ values of P and N. It can be seen that the sulfur activity calculated by FactSage is smaller than that calculated by this model because $\gamma^0_i$ of S is not available. It is the direct explanation why the formation temperature of Ce$_2$O$_2$S is lower in the FactSage results.

Besides the industrial trials and lab scale experiments, the types of inclusions reported in the steel containing rare earth elements from literature were compared with the model prediction and the results are present in Table 7. The types of generated inclusions in various grades of steels reported in others work are almost the same as the results calculated by this model.

All the above comparisons send the message that the accomplished coupled thermodynamic in this work is precise and it is competent to exactly assess the precipitation behaviors of inclusions during solidification process of various grades of steels containing rare earth elements.

### 4. Model application

Aluminum was alloyed in the heat-resistant steel imitating the calcium treatment way to solve the nozzle clogging of 253MA steel. Since the formed inclusions resulting in nozzle clogging are mainly oxides, the inclusions transformation at different initial oxygen contents was studied. And the types of inclusions formed before and after aluminum addition are shown in Figure 7. It can be seen that the stable inclusion at high oxygen content is Ce$_2$Si$_2$O$_7$ in steel without aluminum. By contrast, the inclusions eventually transform to liquid phase as oxygen content increases to 0.018% after 0.01mass% aluminum was added in 253MA steel.

In addition, the stable areas of inclusions (predominance area diagram of inclusions or phase diagram of inclusions) in heat-resistant steel at 1873 K are summarized in Figure 8. The stable
regions of liquid inclusions are surrounded by the dash line. There is not liquid inclusions formed when the oxygen content is low (0.005% in this study). And the stable areas of liquid inclusions are growing as the increasing initial oxygen content. There can be no doubt that.

Figure 7. The inclusions types in heat-resistant steel at 1873 K.

Figure 8. The stability areas of inclusions at 1873 K.
stable areas of liquid phase will be helpful to solve the nozzle clogging issue of steels alloyed by rare earth elements.

In 2011, Kojola [6] reported that the clogging rate of 253MA steel dramatically decreased when Al, Si and Ce co-existed in the molten steel. Kojola argued that the small rare earth oxides can be dissolved after Si addition because of the negative interaction of Si to oxygen. However, no convincing proof was given. It is clear that the liquid inclusions are formed according to the prediction by the model in this work. Moreover, based on the calculated stable areas of inclusions the lab scale experiments following the procedure in Figure 3 were carried out when Si-Al alloy was chosen instead of pure Si. The FE-SEM image and EDS analysis of found inclusions were shown in Figure 9(a). The inclusions were complex phases of Ce-Al-Si-O system with the large size of 15 μm. And the complex inclusions were in the liquid region at 1873 K when be marked in the Al2O3-SiO2-Ce2O3 phase diagram.

5. Conclusions

A coupling model of inclusions generation and solutes micro-segregation during the solidification process of steels containing rare earth elements was worked out. The method for calculating the Gibbs free energy of liquid inclusions was first given. Then the reliability of mathematical model was validated by the industrial sampling, experiments in lab scale and inclusions found in literature. The inclusions calculated by FactSage software were different from this model because of the differences in the activity standard state and the solidification model. The inclusions are Ce2O3, Ce2O2S and CeN in the solidification structure of 253MA steel. These small size inclusions containing rare earth elements can be modified to the liquid inclusions after Al adding and the stable liquid regions increase as the initial oxygen content increases. Moreover, the complex liquid inclusions of Ce-Al-Si-O system were found in the preliminary experiments of lab scale. The coupling model is helpful to relieve the nozzle clogging issue of various grades of steel containing rare earth elements.
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