Research Article

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Effect of adding yttrium on precipitation behaviors of inclusions in E690 ultra high strength offshore platform steel

<https://doi.org/10.1515/htmp-2020-0089>

received January 03, 2019; accepted January 22, 2019

Abstract: The mechanism of inclusions precipitation of the E690 offshore platform steel, with and without addition of yttrium, was studied using the thermodynamic calculation method. The results show that in the E690 steel in the absence of yttrium, the MnS inclusions were precipitated in the liquid phase at the solidification front. By adding the yttrium, MnS inclusions were replaced by spindle and spherical yttrium-containing oxide and sulfide complex inclusions, and the precipitation sequence of yttrium-containing inclusions in the liquid steel was Y_2O_3 , Y_2O_2S , and YS . However, Y_2S_3 inclusions cannot be precipitated in the liquid steel under the experimental conditions. It was also found that Al_2O_3 inclusions can be formed in the liquid steel with and without addition of yttrium. The thermodynamic calculation results are in accordance with the experimental results.

Keywords: yttrium, E690 offshore platform steel, yttrium-containing inclusion, thermodynamic calculation

1 Introduction

The scientific exploration and exploitation of the ocean resources is now proceeding at a greatly accelerated rate [1]. Consequently, the offshore platform steel must possess high mechanical properties, excellent corrosion

resistance, and high heat input welding performance. The generation of nonmetallic inclusions, inevitably occurring after the contact and reaction between the active elements in steel and the refractory materials and slags during the steelmaking and casting processes, reduces the properties of steel, such as strength, toughness, and corrosion resistance [2–4]. Therefore, it is important to control the inclusions as much as possible to avoid the deterioration of steel.

Several investigations have been carried out to control the inclusions in steel, and the main control methods include the elimination and the modification of inclusions. The elimination of inclusions in steel is the use of appropriate technology in the steelmaking process to remove inclusions from the liquid steel, and the main technologies include gas stirring [5–7], electromagnetic purification [8,9], slag washing [10], and filter technique [11]. The methods of inclusions modification include calcium (Ca) treatment [12–15], magnesium (Mg) treatment [16–18], calcium–magnesium treatment [19,20], and so on. Zhang et al. [16,17] reported that Mg has very strong thermodynamic affinities with oxygen and sulfur, and magnesia inclusions present a poor agglomeration character than alumina inclusions. However, Mg treatment can easily cause liquid steel spatter. Ca treatment is commonly used to modify high melting point Al_2O_3 inclusions into fully or partially liquid calcium aluminates to diminish the clogging of the submerged entry nozzle during the continuous casting process [21]. However, either insufficient or excessive addition of calcium alloys is detrimental because incomplete or superfluous calcium can lead to the formation of solid CaO, CaS, calcium alumina, and other unfavorable inclusions deteriorating the quality of the steel [22,23].

Rare earth (RE) elements have very strong chemical activity because of their unique electronic structures, with a variable valence state of the 4f channel [24]. RE elements have a strong affinity toward O and S and react with these elements to form spindle and spherical RE_xO_y , RE_xS_y , and $RE_xO_yS_z$ inclusions, thus avoiding the anisotropy of

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mechanical properties in the final rolled products [25–27]. In recent years, extensive research has been carried out on the influence of the RE elements lanthanum and cerium on the microstructures and mechanical properties of various test steels [28–30]. Yttrium, another reactive element, not only exhibits some similarities with lanthanum and cerium but also displays its own favorable characteristics [31]. Unfortunately, to the best of the authors' knowledge, few studies have considered yttrium-modified steel, especially in terms of the inclusions modification of steels with addition of different amounts of yttrium.

In this article, the inclusion changes in E690 steel with addition of different yttrium contents were compared. In addition, the mechanism of inclusions precipitation was clarified by thermodynamic calculation.

2 Experiments

The test steels were prepared by vacuum induction melting furnace (VAIR). The pure iron with a chemical composition (wt%) of 0.002C, 0.005Si, 0.02Mn, 0.01Cr, 0.01Ni, and balance Fe was used as the raw material, in which Si, Mn, Cr, Ni, Nb, V, Ti, graphite, and yttrium ferroalloy were subsequently added. The final chemical compositions of test steels are presented in Table 1. Here, the yttrium ferroalloy is composed of 65 wt% Y and 35 wt% Fe in this study. Ingots were forged and cut into 90 mm × 90 mm × 120 mm slabs. After homogenization at 1,200°C for 30 min, 7-pass hot rolling was carried out to obtain a final thickness of 16 mm by using a rolling mill (model 350 Reversing, Shanxi Rolling Equipment Factory, China). Here, the finish rolling temperature at 810°C, which is measured by an infrared thermometer (model IR-HOH, Beijing Duhelichuang Technology Co., Ltd, China). Finally, the thick plates were air cooled to 700°C and water cooled to 430°C at a rate of 25°C s⁻¹ and then air cooled to room temperature.

To clarify the precipitation behaviors of inclusions in the test steels, 10 × 10 × 10 mm³ cubic samples were cut from the steel plates and then ground and polished

using 3.5 and 0.5 μm diamond compounds. The types of inclusions and their morphology were extensively analyzed by the scanning electron microscopy (model ProX) and energy-dispersive spectrometry (model ProX). In addition, the mechanism of inclusions precipitation was also studied using thermodynamic calculation.

3 Results and discussion

3.1 Effect of yttrium on the morphology and type of inclusions

Figure 1 shows the morphology and the type of inclusions formed in the test steels with and without addition of yttrium. In the absence of the yttrium, MnS is the dominating inclusion, as shown in Figure 1(a). In addition, Al₂O₃ inclusions can be precipitated in the steel without the addition of yttrium, and MnS inclusions adhere to the surface of the Al₂O₃ inclusions. During the rolling process, the MnS inclusions extend along the rolling direction, resulting in the Al₂O₃ inclusions embedded in the MnS inclusions. By adding the yttrium, the strip-like sulfide inclusions were replaced by yttrium-containing complex inclusions with the size lower than 10 μm, as shown in Figure 1(b–d). Compared with Mn and Fe, yttrium has a stronger affinity toward O and S and is more prone to react with these elements to form yttrium-containing oxide and sulfide. In addition, Al₂O₃ inclusions were found in the test steels with addition of yttrium. This is because of the formation of Al₂O₃ inclusions in steel before the addition of yttrium.

3.2 Thermodynamic calculation of inclusions precipitation in test steels

The formation of inclusions in steel is a complex process, and it is difficult to determine the precipitation condition

Table 1: Chemical compositions of test steels with and without addition of yttrium (wt%)

No.	C	Si	Mn	P	S	O	Al	Nb	V	Ti	Ni	Cr	Cu	Mo	Y
1	0.070	0.25	1.0	0.0080	0.0020	0.0028	0.029	0.030	0.030	0.012	0.60	0.70	0.30	0.35	0
2	0.074	0.28	1.1	0.0080	0.0020	0.0019	0.022	0.029	0.024	0.022	0.63	0.77	0.45	0.39	0.015
3	0.070	0.25	1.0	0.0077	0.0014	0.0015	0.031	0.027	0.021	0.019	0.78	0.60	0.41	0.32	0.036
4	0.077	0.3	1.1	0.0070	0.0016	0.0017	0.037	0.032	0.028	0.019	0.62	0.67	0.46	0.39	0.055

Figure 1: Morphology and type of inclusions formed in test steels. (a) No. 1 steel; (b) No. 2 steel; (c) No. 3 steel; and (d) No. 4 steel.

Table 2: Liquidus temperature and solidus temperature of test steels with and without addition of yttrium (K)

Test steel	No. 1	No. 2	No. 3	No. 4
Liquidus temperature	1,793	1,792	1,794	1,792
Solidus temperature	1,770	1,768	1,770	1,767

and the process of inclusions by means of experimental methods. Therefore, this article uses the thermodynamic calculation to study the precipitation regularity of inclusions so as to better control the precipitation of inclusions in steel.

The liquidus temperature (T_L) and the solidus temperature (T_S) of steel can be calculated by equations (1) and (2), respectively [32]. Table 2 presents the liquidus temperature and solidus temperature of test steels with and without addition of yttrium.

$$T_L = 1809 - 83 \text{ wt\%}(\text{C}) - 7.8 \text{ wt\%}(\text{Si}) - 5 \text{ wt\%}(\text{Mn}) \\ - 32 \text{ wt\%}(\text{P}) - 31.5 \text{ wt\%}(\text{S}) - 1.5 \text{ wt\%}(\text{Cr}) \\ - 2 \text{ wt\%}(\text{Mo}) - 2 \text{ wt\%}(\text{V}) - 3.6 \text{ wt\%}(\text{Al}) \\ - 18 \text{ wt\%}(\text{Ti}). \quad (1)$$

$$T_S = 1809 - 344 \text{ wt\%}(\text{C}) - 12.3 \text{ wt\%}(\text{Si}) - 6.8 \text{ wt\%}(\text{Mn}) \\ - 124.5 \text{ wt\%}(\text{P}) - 183.5 \text{ wt\%}(\text{S}) \\ - 1.4 \text{ wt\%}(\text{Cr}) - 4.1 \text{ wt\%}(\text{Al}) - 4.3 \text{ wt\%}(\text{Ni}). \quad (2)$$

3.2.1 Thermodynamic calculation of inclusions precipitation in liquid steel

In No. 1 test steel, namely, the steel without addition of yttrium, MnS, and Al_2O_3 are the dominating inclusions. By adding the yttrium, because the RE yttrium has a strong affinity towards S and O, and therefore, Y_2O_3 , $\text{Y}_2\text{O}_2\text{S}$, Y_2S_3 , and YS may form in the molten steel. The standard Gibbs free energy change for the formation of these various inclusions in the liquid steel is reported in equations (3)–(8) [33].

In the liquid steel, the reaction equation of metal element E reacts with nonmetal element F to generate E_xF_y can be expressed through equation (9).

When equation (9) reaches equilibrium, the Gibbs free energy (ΔG) is equal to zero. Therefore, the relation between the standard Gibbs free energy (ΔG^θ) and the equilibrium constant (K) can be expressed as equation (10).

$$\ln K = -\frac{\Delta G^\theta}{RT} = -C_2 - \frac{C_1}{T}, \quad (10)$$

where R is the gas constant, in $\text{J mol}^{-1} \text{K}^{-1}$; C_1 and C_2 are constants; and T is the temperature (K).

According to equation (9), the equilibrium constant can also be described by equation (11).

$$K = \frac{\alpha_{\text{E}_x\text{F}_y}}{\alpha_{\text{E}}^x \cdot \alpha_{\text{F}}^y} = \frac{1}{f_{\text{E}}^x \cdot w(\text{E})^x \cdot f_{\text{F}}^y \cdot w(\text{F})^y}, \quad (11)$$

where α_i is the activity of component i ; f_i is the activity coefficient of element i ; and $w(i)$ is the mass fraction of component i (wt%).

Substituting equation (11) into equation (10) can result in equation (12).

$$x \ln f_{\text{E}} + y \ln f_{\text{F}} + \ln(w(\text{E})^x \cdot w(\text{F})^y) = C_2 + \frac{C_1}{T} \quad (12)$$

Therefore, the equilibrium solubility product of E_xF_y in the liquid steel can be expressed as equation (13).

$$\ln(w(\text{E})^x \cdot w(\text{F})^y) = C_2 + \frac{C_1}{T} - x \ln f_{\text{E}} - y \ln f_{\text{F}} \quad (13)$$

In the E690 liquid steel, the activity coefficient is related to the temperature and interaction coefficient of various elements in the liquid steel. However, E690 offshore platform steel belongs to high-strength low alloy steels, the mass fraction of each solute element tends to 0, and the mass fraction of the solvent iron approaches 1. The second-order interaction coefficients have little effect on the activity coefficient of solute; therefore, the activity coefficients of the components E and F are calculated directly by using the Wagner model

Table 3: First-order interaction coefficients e_i^j of various elements in liquid steel

e_i^j	C	Si	Mn	P	S	O	Cr	Ni	Mo	Cu	Al	Y
O	-0.45	-0.131	-0.021	0.07	-0.133	-0.2	-0.04	0.006	0.0035	-0.013	-3.9	-16.3
S	0.112	0.063	-0.026	0.029	-0.028	-0.27	-0.011	0	0.0027	-0.0084	0.035	-0.55
Y	-0.22	—	—	—	-7.34	-90.7	—	—	—	—	—	-0.006
Al	0.091	0.0056	0.012	0.05	0.03	-6.6	0.025	0.008	—	0.008	0.045	—
Mn	-0.07	0.39	0	-0.0035	-0.048	-0.083	0.003	-0.007	0.0045	—	0.07	—

characterized by the first-order interaction coefficients [32]. The activity coefficient of each solute element in the liquid steel is calculated by equation (14).

$$\ln f_i = 2.303 \sum_{j=1}^n e_i^j w[j], \quad (14)$$

where e_i^j is the first-order interaction parameter between i and j and $w[j]$ is the mass percentage of element j .

Table 3 presents the first-order interaction coefficient e_i^j of various solute elements in the liquid steel. Substituting the data in Table 3 into equation (14), the activity coefficients of O, S, Y, Al, and Mn in the liquid steel are calculated and presented in Table 4.

Substituting the activity coefficients of O, S, Y, Al, and Mn into equation (13), the logarithm of the equilibrium solubility product of MnS, Al_2O_3 , Y_2O_3 , $\text{Y}_2\text{O}_2\text{S}$, Y_2S_3 , and YS can be obtained. Figures 2–7 show the logarithm of the equilibrium solubility product and the actual solubility product as a function of temperature for MnS, Al_2O_3 , Y_2O_3 , $\text{Y}_2\text{O}_2\text{S}$, Y_2S_3 , and YS.

During the cooling process of the liquid steel, the solubility of inclusions in steel is gradually reduced. When the actual solubility product of the inclusion generating elements is larger than the equilibrium solubility product, the inclusion can be formed. As shown in Figures 2 and 3, for test steels No.1 to No.4, MnS inclusions cannot be generated in the liquid steel, while Al_2O_3 inclusions can be precipitated. Therefore, for test steels with addition of yttrium, as yttrium has a strong affinity toward O and S and react with these elements, Y_2O_3 , $\text{Y}_2\text{O}_2\text{S}$, Y_2S_3 , and YS may form in the

liquid steel. Wang and Du [34] investigated the thermodynamics of deoxidation and desulfuration of yttrium in the liquid steel. Their research results show that when yttrium is added to the liquid steel, it reacts with oxygen first; when the precipitated Y_2O_3 inclusions are not removed from the liquid steel, S in the liquid steel reacts with the precipitated Y_2O_3 inclusions to generate $\text{Y}_2\text{O}_2\text{S}$ inclusions; at very late times, when the oxygen content in the liquid steel is very low, yttrium in the liquid steel will react with sulfur to generate Y_2S_3 or YS inclusions. Wang and Du [34] also reported that under the reaction equilibrium conditions, the product of the reaction between yttrium and S is mainly YS. As shown in Figures 4–7, Y_2O_3 , $\text{Y}_2\text{O}_2\text{S}$, and YS inclusions can be precipitated and Y_2S_3 inclusions cannot be formed in the liquid steel with addition of different amounts of yttrium. When the yttrium content in the liquid steel is 0.015 wt%, there are no YS inclusions in the liquid steel. This is because all the yttrium in the liquid steel reacts with O to generate Y_2O_3 inclusions, and the partial Y_2O_3 inclusions react with S to form $\text{Y}_2\text{O}_2\text{S}$ inclusions. However, when the yttrium content in the liquid steel increases up to

Table 4: The activity coefficients of O, S, Y, Al, and Mn in liquid steel

No.	O	S	Y	Al	Mn
1	0.5674	0.9702	—	1.0725	1.2421
2	0.3315	0.9458	0.6260	1.0997	1.2750
3	0.1452	0.9274	0.6887	1.0935	1.2383
4	0.0646	0.9059	0.6558	1.0994	1.2999

Figure 2: Logarithm of the solubility product as a function of temperature for MnS in the liquid steel.

Figure 3: Logarithm of the solubility product as a function of temperature for Al_2O_3 in the liquid steel.

Figure 5: Logarithm of the solubility product as a function of temperature for $\text{Y}_2\text{O}_2\text{S}$ in the liquid steel.

Figure 4: Logarithm of the solubility product as a function of temperature for Y_2O_3 in the liquid steel.

Figure 6: Logarithm of the solubility product as a function of temperature for Y_2S_3 in the liquid steel.

0.036 wt%, the residual yttrium after reacting with O in the liquid steel will react with S to precipitate YS inclusions. The calculated results are in accordance with the experimental results.

3.2.2 Thermodynamic calculation of MnS precipitation in solid-liquid dual phase zone

Because there is no MnS inclusions precipitation in the liquid steel, it is necessary to calculate the thermodynamics of MnS inclusions precipitation at the solidification front. When the liquid steel begins to crystallize into δ -ferrite, a solid-liquid dual phase zone is formed. In the solidification process of the liquid steel, the

forming elements of MnS inclusions in steel tend to be enriched in the liquid phase at the solidification front, leading to an increase in the actual solubility product [32]. Provided that the forming elements of MnS inclusions in the solid phase are nondiffused, the liquid phase is uniformly mixed, and the solid-liquid interface is in a local equilibrium state. Under these conditions, the contents of S and Mn can be used in the Scheil model, namely, equations (15) and (16).

$$w(\text{S})_{\text{L}} = w(\text{S}) / [P(K_{\text{S}} - 1) + 1] \quad (15)$$

$$w(\text{Mn})_{\text{L}} = w(\text{Mn}) \cdot (1 - P)^{(K_{\text{Mn}} - 1)}, \quad (16)$$

where $w(\text{S})_{\text{L}}$ and $w(\text{Mn})_{\text{L}}$ indicate the mass fractions of S and Mn in the liquid phase at the solidification front,

Figure 7: Logarithm of the solubility product as a function of temperature for YS in the liquid steel.

respectively; $w(S)$ and $w(Mn)$ are the mass fractions of S and Mn in the liquid phase when the liquid steel begins to solidify, respectively, in wt%; K_S and K_{Mn} are the equilibrium distribution coefficients of S and Mn, respectively. Zhang et al. [35] reported that the equilibrium distribution coefficients of S and Mn are 0.035 and 0.785, respectively; P is the solid phase fraction, and its relationship with temperature can be expressed in equation (17).

$$P = \frac{(T_m - T_S) \cdot (T_L - T_f)}{(T_L - T_S) \cdot (T_m - T_f)}, \quad (17)$$

where T_m is the melting point of pure iron, and its value is 1,809 K; T_f is the temperature at the solidification front (K); and T_S and T_L are the solidus temperature and liquidus temperature (K), respectively.

According to equations (15) and (16), the actual solubility product in the liquid phase at the solidification front can be calculated. Zhang et al. [35] and Ueshima et al. [36] reported that the equilibrium solubility product for MnS inclusions in the liquid phase at the solidification front can be calculated by equation (18).

$$\ln [w(Mn) \cdot w(S)] = -19873.92/T + 10.93 - \ln f_{Mn} - \ln f_S \quad (18)$$

Figure 8 shows the logarithm of the equilibrium solubility product and the actual solubility product as a function of temperature for MnS inclusions in the liquid phase at the solidification front.

The contents of S and Mn in the solid phase at the solidification front can be used in the Scheil model and expressed through equations (19) and (20) [37].

Figure 8: Logarithm of the solubility product as a function of temperature for MnS in the liquid phase at the solidification front.

$$w(S)_S = K_S \cdot w(S) / [P(K_S - 1) + 1] \quad (19)$$

$$w(Mn)_S = K_{Mn} \cdot w(Mn) \cdot (1 - P)^{(K_{Mn}-1)}, \quad (20)$$

where $w(S)_S$ and $w(Mn)_S$ indicate the mass fractions of S and Mn in the solid phase at the solidification front, respectively.

According to equations (19) and (20), the actual solubility product in the solid phase at the solidification front can be calculated. In addition, Zhang et al. [35] and Ueshima et al. [36] reported that the equilibrium solubility product for MnS inclusions in the solid phase at the solidification front can be calculated by equation (21).

$$\ln [w(Mn) \cdot w(S)] = -21274.24/T + 6.97 \quad (21)$$

Figure 9 shows the logarithm of the equilibrium solubility product and the actual solubility product as a

Figure 9: Logarithm of the solubility product as a function of temperature for MnS in the solid phase at the solidification front.

Figure 10: Logarithm of the solubility product as a function of temperature for MnS in the solid steel.

function of the temperature for MnS inclusions in the solid phase at the solidification front.

As shown in Figures 8 and 9, when the test steels with addition of yttrium, no separate MnS inclusions are formed in the solid–liquid dual phase zone. This is because yttrium has a strong affinity toward O and S and reacts with O and S to form Y_2O_3 , Y_2O_2S , and YS inclusions. For test steels without addition of yttrium, MnS inclusions can be precipitated in the liquid phase at the solidification front. While the equilibrium solubility product was greater than the actual solubility product, and no MnS inclusions can be precipitated in the solid phase at the solidification front. The calculated results are in accordance with those reported by Zhang et al. [35], who indicated that MnS inclusions precipitated at the end of solidification, rather than in the liquid steel.

3.2.3 Thermodynamic calculation of MnS precipitation in solid steel

It can be seen from the iron–carbon phase diagram that when the liquid steel solidifies completely, the liquid phase and ferrite transform into austenite almost at the same time. Because the solubility of MnS inclusions in the austenite phase is very small, the solid phase can be considered to be in accordance with Henry's laws (1 wt% standard state). The equilibrium solubility product can be calculated through equation (21). Figure 10 shows the logarithm of the equilibrium solubility product and the actual solubility product as a function of temperature for MnS inclusions in solid steel.

As shown in Figure 10, it was found that the actual solubility product is always larger than the equilibrium

solubility product. This means that MnS inclusions can be precipitated in solid steel. However, MnS inclusions precipitation is a chemical reaction controlled by S and Mn diffusion in the solid steel because the diffusion rate of S and Mn in the solid steel is very slow. Therefore, the precipitation of MnS inclusions in solid steel is mainly controlled by dynamic conditions.

4 Conclusions

- (1) The MnS inclusions were precipitated in the liquid phase at the solidification front in E690 steel in the absence of yttrium and were replaced by yttrium-containing oxide and sulfide complex inclusions on addition of yttrium.
- (2) By adding the yttrium, Y_2O_3 , Y_2O_2S , and YS inclusions were precipitated in the liquid steel, and the precipitation sequence was Y_2O_3 , Y_2O_2S , and YS. While Y_2S_3 inclusions cannot be formed in the liquid steel.
- (3) In E690 steels with and without addition of yttrium, Al_2O_3 inclusions can be formed in the liquid steel.

Acknowledgments: The authors gratefully acknowledge the support by the National Natural Science Foundation of China (NSFC, No. 51874116, 51664021 and 51734003).

Conflict of interest: The authors declare no conflict of interest.

References

- [1] Bhandari, J., F. Khan, R. Abbassi, V. Garaniya, and R. Ojeda. Modelling of pitting corrosion in marine and offshore steel structures – A technical review. *Journal of Loss Prevention in the Process Industries*, Vol. 37, 2015, pp. 39–62.
- [2] Garrison Jr, W. M., and A. L. Wojcieszynski. A discussion of the effect of inclusion volume fraction on the toughness of steel. *Materials Science and Engineering: A*, Vol. 464, 2007, pp. 321–329.
- [3] Chiba, A., I. Muto, Y. Sugawara, and N. Hara. A microelectrochemical system for in situ high-resolution optical microscopy: morphological characteristics of pitting at MnS inclusion in stainless steel. *Journal of the Electrochemical Society*, Vol. 159, 2012, pp. C341–C350.
- [4] Chiba, A., S. Shibukawa, I. Muto, T. Doi, K. Kawano, Y. Sugawara, et al. Microelectrochemical aspects of interstitial carbon in type 304 stainless steel: improving pitting

- resistance at MnS inclusion. *Journal of The Electrochemical Society*, Vol. 162, 2015, pp. C270–C278.
- [5] Zhang, L. F., and S. T. Taniguchi. Fundamentals of inclusion removal from liquid steel by bubble flotation. *International Materials Reviews*, Vol. 45, 2000, pp. 59–82.
 - [6] Rogler, J. P., L. J. Heaslip, and M. Mehrvar. Inclusion removal in a tundish by gas bubbling. *Canadian Metallurgical Quarterly*, Vol. 43, 2013, pp. 407–415.
 - [7] Geng, D. Q., J. X. Zheng, K. Wang, P. Wang, R. Q. Liang, H. T. Liu, et al. Simulation on decarburization and inclusion removal process in the Ruhrstahl–Heraeus (RH) process with ladle bottom blowing. *Metallurgical and Materials Transactions B*, Vol. 46, 2015, pp. 1484–1493.
 - [8] Trindade, L. B., J. E. A. Nadalon, A. C. F. Vilela, M. T. M. B. Vilhena, and R. B. Soares. Numerical modeling of inclusion removal in electromagnetic stirred steel billets. *Steel Research International*, Vol. 78, 2007, pp. 708–713.
 - [9] Zhang, L. F., S. Q. Wang, A. P. Dong, J. W. Gao, and L. N. W. Damoah. Application of electromagnetic (EM) separation technology to metal refining processes: a review. *Metallurgical and Materials Transactions B*, Vol. 45, 2014, pp. 2153–2185.
 - [10] Du, G., J. Li, and Z. B. Wang. Effect of initial large-sized inclusion content on inclusion removal during electroslag remelting of H13 die steel. *Ironmaking & Steelmaking*, Vol. 45, 2018, pp. 919–923.
 - [11] Liu, X. T., Y. H. Zhou, B. L. Shang, and W. M. Jiang. Flow behaviour and filtration of steel melt in continuous casting tundish. *Ironmaking & Steelmaking*, Vol. 19, 1992, pp. 221–225.
 - [12] Zhang, L. F., Y. Liu, Y. Zhang, W. Yang, and W. Chen. Transient evolution of nonmetallic inclusions during calcium treatment of molten steel. *Metallurgical and Materials Transactions B*, Vol. 49, 2018, pp. 1841–1859.
 - [13] Verma, N., P. C. Pistorius, R. J. Fruehan, M. Potter, M. Lind, and S. Story. Transient inclusion evolution during modification of alumina inclusions by calcium in liquid steel: Part I. Background, experimental techniques and analysis methods. *Metallurgical and Materials Transactions B*, Vol. 42, 2011, pp. 711–719.
 - [14] Verma, N., P. C. Pistorius, R. J. Fruehan, M. Potter, M. Lind, and S. R. Story. Transient inclusion evolution during modification of alumina inclusions by calcium in liquid steel: Part II. Results and discussion. *Metallurgical and Materials Transactions B*, Vol. 42, 2011, pp. 720–729.
 - [15] Xu, J. F., F. X. Huang, and X. H. Wang. Formation mechanism of CaS–Al₂O₃ inclusions in low sulfur Al-killed steel after calcium treatment. *Metallurgical and Materials Transactions B*, Vol. 47, 2016, pp. 1217–1227.
 - [16] Zhang, T. S., D. Y. Wang, and M. F. Jiang. Effect of magnesium on evolution of oxide and sulphide in liquid iron at 1873 K. *Journal of Iron and Steel Research, International*, Vol. 21, 2014, pp. 1073–1080.
 - [17] Zhang, T. S., D. Y. Wang, C. W. Liu, M. F. Jiang, M. Lu, B. Wang, et al. Modification of inclusions in liquid iron by Mg treatment. *Journal of Iron and Steel Research, International*, Vol. 21, 2014, pp. 99–103.
 - [18] Zhang, T. S., C. J. Liu, and M. F. Jiang. Effect of Mg on behavior and particle size of inclusions in Al–Ti deoxidized molten steels. *Metallurgical and Materials Transactions B*, Vol. 47, 2016, pp. 2253–2262.
 - [19] Shin, J. H., and J. H. Park. Modification of inclusions in molten steel by Mg–Ca transfer from top slag: experimental confirmation of the ‘refractory-slag-metal-inclusion (ReSMI)’ multiphase reaction model. *Metallurgical and Materials Transactions B*, Vol. 48, 2017, pp. 2820–2825.
 - [20] Ma, W. J., Y. P. Bao, and M. Wang. Effect of Mg and Ca treatment on behavior and particle size of inclusions in bearing steels. *ISIJ International*, Vol. 54, 2014, pp. 536–542.
 - [21] Lamut, J., J. Falkus, B. Jurjavec, and M. Knap. Influence of inclusions modification on nozzle clogging. *Archives of Metallurgy and Materials*, Vol. 57, 2012, pp. 319–324.
 - [22] Choudhary, S. K., and A. Ghosh. Thermodynamic evaluation of formation of oxide-sulfide duplex inclusions in steel. *ISIJ International*, Vol. 48, 2008, pp. 1552–1559.
 - [23] Ohta, H., and H. Suito. Deoxidation equilibria of calcium and magnesium in liquid iron. *Metallurgical and Materials Transactions B*, Vol. 28, 1997, pp. 1131–1139.
 - [24] Pan, F., J. Zhang, H. L. Chen, Y. H. Su, C. L. Kuo, Y. H. Su, et al. Effects of rare earth metals on steel microstructures. *Materials*, Vol. 9, 2016, pp. 1–19.
 - [25] Zhao, Y. Y., J. F. Wang, S. Zhou, and X. D. Wang. Effects of rare earth addition on microstructure and mechanical properties of a Fe–15Mn–1.5 Al–0.6 C TWIP steel. *Materials Science and Engineering: A*, Vol. 608, 2014, pp. 106–113.
 - [26] Ånmark, N., A. Karasev, and P. G. Jönsson. The effect of different non-metallic inclusions on the machinability of steels. *Materials*, Vol. 8, 2015, pp. 751–783.
 - [27] Torkamani, H., S. Raygan, C. G. Mateo, R. Jafar, V. Javier, P. Yahya, et al. The influence of La and Ce addition on inclusion modification in cast niobium microalloyed steels. *Metals*, Vol. 7, 2017, pp. 377–393.
 - [28] Liu, H. L., C. J. Liu, and M. F. Jiang. Effect of rare earths on impact toughness of a low-carbon steel. *Materials Design*, Vol. 33, 2012, pp. 306–312.
 - [29] Chu, R. S., Y. Fan, Z. J. Li, J. G. Liu, N. Yin, and N. Hao. Study on the control of rare earth metals and their behaviors in the industrial practical production of Q420q structural bridge steel plate. *Metals*, Vol. 8, 2018, pp. 240–247.
 - [30] Liu, H. H., P. X. Fu, H. W. Liu, C. Sun, J. Z. Gao, and D. Z. Li. Carbide evolution and tensile property of 4Cr5MoSiV1 die steel with rare earth addition. *Metals*, Vol. 7, 2017, pp. 436–443.
 - [31] Chen, L., X. C. Ma, L. M. Wang, and X. N. Ye. Effect of rare earth element yttrium addition on microstructures and properties of a 21Cr–11Ni austenitic heat-resistant stainless steel. *Materials Design*, Vol. 32, 2011, pp. 2206–2212.
 - [32] Shi, X., J. Z. Wu, H. J. Guo, J. Guo, S. C. Duan, and W. S. Yang. Precipitation behaviors of carbides and carbonitrides in DH36 high - strength ship plate steel. *Journal of Central South University (Science and Technology)*, Vol. 49, 2018, pp. 518–528 (in Chinese).
 - [33] Zhou, Y., X. W. Song, W. G. Zhao, L. G. An, and S. L. An. Preparation of yttrium oxide sulfide and its thermodynamics in iron-base solution. *Journal of Baotou University of Iron and Steel Technology*, Vol. 18, 1999, pp. 222–226 (in Chinese).

- [34] Wang, L. M., and T. Du. Thermodynamics of deoxidation, desulfurization and deoxysulfurization of yttrium in liquid iron. *Iron and Steel*, Vol. 20, 1985, pp. 9–15 (in Chinese).
- [35] Zhang, X. W., L. F. Zhang, W. Yang, Y. C. Dong, and Y. Z. Li. Thermodynamics and dynamics of MnS inclusions precipitation during solidification process in heavy rail steels. *Iron and Steel*, Vol. 51, 2016, pp. 30–39 (in Chinese).
- [36] Ueshima, Y., K. Isobe, and S. Mizoguchi. Analysis of the rate of crystallization and precipitation of MnS in the resulphurized free-cutting steel. *Tetsu-to-Hagane*, Vol. 74, 1988, pp. 465–472.
- [37] Clyne, T. W., and W. Kurz. Solute redistribution during solidification with rapid solid state diffusion. *Metallurgical and Materials Transactions A*, Vol. 12, 1981, pp. 965–971.