Effect of Sulphur Concentration on Precipitation Behaviors of MnS-containing Inclusions in GCr15 Bearing Steels after LF Refining

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The precipitation behavior and mechanism of MnS-containing inclusions in GCr15 bearing steels were analyzed. The results show when the optical basicity of the refining slag is 0.776, the minimum sulphur concentration is 0.0020 mass% in the present samples. MgO·Al₂O₃ (MA) and CaO–MgO–Al₂O₃ (CMA) inclusions are easy to become nucleation cores for MnS precipitating. MnS-containing inclusions are main MnS, MA and CMA encapsulated with MnS, and a little amount of MnS compounded with TiN. It is the concentration of sulphur in the steel and the composition of oxide cores that influences the precipitation behavior of MnS-containing inclusions. The thickness of MnS on CMA type inclusions is about 2.5–4.5 times larger than that on MA type inclusions even if the precipitation ratio of MnS is lower. MnS can precipitate on CMA type inclusions when the mole percent of CaO in the inclusions is less than 33 mole% (0.33), and the thickness of MnS precipitation is decreased with the increase of CaO concentration. However, MnS can't precipitate on CMA inclusions when the mole percent of CaO exceeds 38 mole% (0.38) and CMA type inclusions without MnS precipitating are almost in liquid region.

KEY WORDS: GCr15 bearing steels; refining slag; sulphur concentration; MnS-containing inclusions; precipitation behaviors.

1. Introduction

Sulphur is a harmful impurity for most steel grades and exists in the steels in the form of sulphides. Sulphur manifests mainly as MnS and oxide-sulphide complex with oxide inclusions as cores. And there is also a little of CaS in the calcium treated steels. It is commonly accepted that large and shape irregular sulphide inclusions jeopardize microstructure uniformity and deteriorate mechanical as well as processing properties of the steels.^{1–3)} The precipitation behavior and influence factors of MnS-containing inclusions have been studied intensively in many steel grades. Davies *et al.*⁴⁾ reported that the fraction of oxides encapsulated by sulphides increased with reducing of the oxygen concentration in the steels. Wakon *et al.*⁵⁾ reported that the precipitation ratio of MnS on oxide inclusions was affected by the concentration of sulphur in the steel. And the growth rate of MnS was determined by the diffusion of manganese and sulphur in the liquid steel. Zheng *et al.*⁶⁾ found that not only the precipitation rate but also the thickness of MnS on the oxides increased with the increase of sulphur concentration

in the steel, and the morphology of MnS on the oxides was changed from parceling precipitation to local precipitation with the decreases of sulphur concentration from 0.0034 mass% to 0.0010 mass%.

High-carbon chromium bearing steel (GCr15) is widely used to manufacture rolling parts including balls, cylinders or barrel shapes and rings of bearings, and their metallurgical quality seriously affects the stability of mechanical equipment. Chemical composition, cleanness (inclusions) and microstructure uniformity are required to control strictly to obtain better quality for high hardness and wear resistance in bearing steels production. Many researchers had approved and verified that number, composition, morphology and size of inclusions in the steels are the main factor that influences the fatigue life of bearings.^{7–10)} Early work indicated that MnS was uneasy to develop tensile stress around inclusions for its less expansion coefficient than that of iron in bearing steels.¹¹⁾ And any detrimental effect can be mitigated by large reduction ratios since MnS presents to be plastic during hot-deformation.¹²⁾ Bhadeshia¹³⁾ reviewed the research results that sulphides acted as barriers to damage propagation by encapsulating brittle oxides such as alumina in bearing steels and sulphur in the concentration range of 0.013 mass%–0.043 mass% resulted in fatigue performance

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improvement. However, it is well known any type of inclusions in bearing steels will contribute to the initiation of cracks undergoing large contact stresses service period when the inclusions is large to some degree.¹⁴⁾ Gubenko *et al.*¹⁵⁾ pointed out that excessive local concentrations of sulphides or oxide-sulphide led to low melting-temperature eutectics which then compromises the ability to hot-deforming of the steel. On the other hand, TiN will precipitate on the surface of sulphides or oxide-sulphide during solidification of liquid steel,¹⁶⁾ which intensified the harm for the as-cast slab or finished products. Furthermore, modern bearing steels are required much higher overall cleanness and the role of sulphides in bearings steels must be reacquainted. Andersson *et al.*¹⁷⁾ pointed out that an appropriate minimum sulphur concentration in steels should be obtained for optimum service properties of the steels after low concentrations of oxides and titanium compounds are ensured in steels.

Sulphur in bearing steels is mainly removed by refining slag in ladle furnace. It was once reported that sulphur concentration must be controlled according to oxygen concentration in bearing steels.¹⁸⁾ Although there were many researches on the removal of oxide inclusions in bearing steels,^{19–23)} how much sulphur concentration should be controlled and how it effects on precipitation behaviors of sulphides are seldom reported for high quality GCr15 bearing steels. In order to decrease sulphur concentration and sulphide inclusions in the steel, desulphurization ability of refining slag is evaluated by analyzing samples sampled from industrialized production of GCr15 bearing steels during LF refining process in the present work. And the influences of sulphur concentration and the composition of oxide inclusions in the steel on the precipitation behavior of MnS-containing inclusions are also analyzed. The information about sulphur concentration and the composition of oxide inclusions related with composition, size and size distribution, quantities and morphology of MnS-containing inclusions in the sampled GCr15 bearing steels is obtained. The formation and evolution mechanism of MnS-containing inclusions are analyzed which aims at understanding the formation conditions of sulphides in the steel. The research results are expected to provide theoretical basis for better control harmful inclusions by adjusting the compositions of refining slag to decrease sulphur concentration in the steel and absorb oxides, sulphides or oxide-sulphide in practical process of LF refining.

2. Experiments

2.1. GCr15 Bearing Steels Smelting and Desulphurization Procedure

GCr15 bearing steels were sampled from Daye Special Steel Corporation Limited. The steels were smelt in an 120 t basic oxygen furnace (BOF) and refined in a 70 t ladle furnace (LF). After being treated in a 70 t Ruhrstahl-Hausen (RH) equipment, the steels were cast in a continuous casting machine (mould size in 180 mm×210 mm). Finished products were obtained after rolling the steels. The endpoint carbon concentration in BOF was controlled about 0.10 mass%–0.45 mass%. During the process of BOF tapping, ferroaluminum was used as deoxidizer, and ferrosilicon, ferromanganese, ferrochromium and carburant were added

into the molten steel and used as alloying elements. Refining slag and lime were also added into the ladle to desulphurize and absorb inclusions formed in the molten steel. During LF refining process, aluminum granule was added into the molten steel for intensive deoxidization, and ferromanganese, ferrochromium, silicocarbid, carburant were used to adjust alloy elements to the aimed composition. High basicity refining slag and lime were added into the ladle furnace for desulphurization and absorption inclusions more exhaustively. The composition of refining slag was adjusted to meet the requirement for desulphurization at the endpoint of LF refining. Liquid steel was sampled at the endpoint of LF refining and then quenched in the water with the cooling rate about 900 K/min. Three heats of steel were desulphurized by different compositions of refining slag and sampled, which were marked as 1[#], 2[#] and 3[#] respectively to investigate the effect of sulphur concentration on precipitation behavior of MnS-containing inclusions at the endpoint of LF refining.

2.2. Chemical Composition Analysis of Slag and Steel

Concentration of carbon and sulphur in the steel samples was analyzed by infrared carbon and sulphur analyzer (Model: CS-8800). The concentration of acid soluble aluminum (Al_s), titanium (Ti), chromium (Cr), silicon (Si), calcium (Ca), magnesium (Mg) in the steel samples and Al₂O₃, SiO₂, CaO, MgO in the refining slag samples was analyzed by ICP-AES using a Single-channel Scanning Spectrometer (Model: IRIS-Advantage). Total oxygen (T.[O]) and total nitrogen (T.[N]) concentration in the steel samples were determined by oxygen and nitrogen analyzer (Model: LECO-TC500C).

2.3. Characterization of Inclusions in the Steel Samples

The morphologies of inclusions in the samples were observed by field emission scanning electron microscope (FE-SEM, Model: Nova 400 Nano) at 20.0 kV and the chemical composition of inclusions was analyzed with energy dispersive X-ray spectroscopy (EDS, Model: Le350 PentaFETx-3) equipped on FE-SEM. Thirty connected fields of view at 2 000 magnification were selected to observe for each specimen. The number, mean diameter, size distribution and area density of the inclusions were statistically analyzed by Image Pro-plus 6.0 software. In order to observe the morphologies and identify chemical compositions of the inclusions more clearly, the samples were electrolyzed in a nonaqueous solution to expose the inclusions from steel matrix.

3. Results

3.1. Composition of Refining Slag and Steel

The composition of the LF refining endpoint slag which meets the requirement for desulphurization, including the calculated optical basicity (A) and binary basicity ($R_2 = w(\text{CaO})/w(\text{SiO}_2)$) and refining temperature are shown in **Table 1**. L_s is the sulphur distribution ratio and calculated according to the concentration of sulphur both in slag $w(\text{S})$ and steel $w[\text{S}]$ by $w(\text{S})/w[\text{S}]$. The chemical composition of steels corresponding with the refining slag listed in Table 1 is shown in **Table 2**.

3.2. Composition and Morphology of Oxide Inclusions in the Samples

The composition and morphology of oxide inclusions in metallographic specimens or extracted by nonaqueous solution electrolysis from the samples are shown in **Fig. 1**, where the concentration of each element in inclusions is expressed in mole percent. Singly and complexly precipitated oxide inclusions in the samples at the end of LF refining are listed as follows: (1) Al_2O_3 inclusion (Fig. 1(a)); (2) spherical $\text{MgO}\cdot\text{Al}_2\text{O}_3$ (MA) inclusion (Fig. 1(b)); (3)

spherical $\text{CaO}\text{--}\text{MgO}\text{--}\text{Al}_2\text{O}_3$ (CMA) type inclusions (Figs. 1(c) and 1(f)); (4) a little of aluminosilicate inclusions (Fig. 1(d)); (5) silicate inclusions mixed with chromium and iron (Fig. 1(e)). The morphology of aluminosilicate and silicate inclusions in the samples is irregular, and they are often larger than $3\text{ }\mu\text{m}$ in size. The number percentage of inclusions in the samples is shown in **Table 3**.

Table 1. The composition of the endpoint refining slag, mass percent and treatment temperature, K.

Sample	Composition of refining slag/mass%					T/K	A	R_2	$\log L_s$
	$w(\text{CaO})$	$w(\text{MgO})$	$w(\text{Al}_2\text{O}_3)$	$w(\text{SiO}_2)$	$w(\text{S})$				
1 [#]	60.05	2.73	30.36	5.06	1.43	1 835	0.792	11.87	2.554
2 [#]	58.71	3.19	30.84	5.77	1.13	1 850	0.786	10.18	2.577
3 [#]	55.67	3.86	32.46	6.17	1.15	1 835	0.776	9.02	2.758

Table 2. Chemical composition of elements balanced with Fe in the steel samples at the end process of LF refining, mass%.

Sample	C	Cr	Si	Mn	Al_s	S	T.[O]	T.[N]	Ti	Mg	Ca
1 [#]	0.972	1.47	0.24	0.40	0.026	0.0040	0.0019	0.0046	0.0022	0.0002	0.0009
2 [#]	0.976	1.47	0.24	0.40	0.024	0.0030	0.0012	0.0043	0.0023	0.0003	0.0008
3 [#]	0.960	1.47	0.22	0.40	0.027	0.0020	0.0018	0.0050	0.0024	0.0003	0.0006

Table 3. The number percentage of typical inclusions sorted by type in the samples, %.

No.	MnS	MA				CMA		MnS/TiN	Others
		MA	MA/MnS	MA/TiN	MA/MnS/TiN	CMA	CMA/MnS		
1 [#]	28.05	7.32	21.95	7.32	10.97	7.32	3.66	2.44	10.97
2 [#]	22.78	16.46	17.72	6.33	11.39	6.33	2.53	2.53	13.93
3 [#]	14.10	24.36	11.54	8.98	11.54	11.54	2.56	3.85	11.53

Fig. 1. FE-SEM images and EDS analysis of oxide inclusions.

3.3. Composition and Morphology of MnS-containing Inclusions in the Samples

The composition and morphology of MnS-containing inclusions in the metallographic specimens from the samples are shown in Fig. 2, and the ones extracted by non-aqueous solution electrolysis from the samples are shown in Fig. 3. Singly and complexly precipitated MnS-containing inclusions in the samples at the end of LF refining are listed as follows: (1) MnS (Figs. 2(a) and 3(a)); (2) Al_2O_3 oriented encapsulated with MnS (Fig. 2(a)); (3) MA encapsulated with MnS (Figs. 2(b) and 3(b)); (4) MA encapsulated with MnS and TiN (Figs. 2(c) and 3(c)); (5) CMA type inclusions encapsulated with MnS (Figs. 2(d) and 3(d)); (6) a little of MnS combined with TiN (Figs. 2(e) and 3(e)); (7) a little of CaS precipitated on CMA (Fig. 2(f) which are bigger in size and should be controlled even though their ratio are relatively low. To compare the morphology difference between MA encapsulated with MnS and TiN and that of only encapsulated with TiN, MA encapsulated with TiN is shown in Fig. 3(f). The number percentage of MnS-containing inclusions in the samples is also shown in Table 3.

Fig. 3(f). The number percentage of MnS-containing inclusions in the samples is also shown in Table 3.

3.4. Number Density, Size and Size Distribution of Inclusions in the Samples

According to the statistical results from FE-SEM/EDS and Pro-Plus Image 6 software, area density (N_a), size and size distribution, mean diameter (d_{mean}) and maximum diameter (d_{max}) of inclusions observed are giving in Table 4. In sample 1[#], 2[#] and 3[#], the number density is 379 mm^{-2} , 298 mm^{-2} , and 337 mm^{-2} respectively, and the corresponding mean size is $1.07 \mu\text{m}$, $1.12 \mu\text{m}$, and $0.97 \mu\text{m}$. The size of most inclusions in the samples is smaller than $1 \mu\text{m}$ and the ratio of them is 66.57%, 61.16%, and 73.64% in sample 1[#], 2[#], and 3[#] respectively. There are only a few inclusions larger than $3 \mu\text{m}$ in the observed samples, most of which are aluminosilicate. Aluminosilicate inclusions and silicate

Fig. 2. FE-SEM images and EDS analysis of MnS-containing inclusions in metallographic specimens.

Fig. 3. FE-SEM images and EDS analysis of MnS-containing inclusions extracted from samples in nonaqueous solution electrolysis.

Table 4. Size distribution, mean diameter and number density of inclusions.

Sample	Fraction of inclusions with different sizes/%					$d_{\text{mean}}/\mu\text{m}$	$d_{\text{max}}/\mu\text{m}$	N_a/mm^{-2}
	>5 μm	3–5 μm	1–3 μm	0.5–1 μm	<0.5 μm			
1 [#]	1.67	4.46	27.30	34.26	32.31	1.07	7.17	379
2 [#]	0.65	6.15	32.04	31.39	29.77	1.12	6.21	298
3 [#]	1.72	4.58	20.06	30.66	42.98	0.97	6.18	337

Table 5. Mean diameter and maximum diameter of MnS-containing inclusions, μm .

Sample	$d_{\text{mean}}/d_{\text{max}}$				
	MnS	MA/MnS	MA/MnS/TiN	CMA/MnS	TiN/MnS
1 [#]	0.47/1.09	0.79/1.33	0.88/1.24	1.94/2.99	0.93/1.09
2 [#]	0.43/0.89	0.61/1.02	0.71/1.12	1.75/2.49	0.78/1.01
3 [#]	0.37/0.67	0.52/0.75	0.76/1.15	1.65/2.04	0.83/0.98

inclusions mixed with chromium and iron are shown in Figs. 1(d) and 1(e), and CMA type inclusion with CaS larger than 3 μm is shown in Fig. 2(f). Compared sample 1[#] with 3[#], not only the number of inclusions but also the mean size of inclusions is larger in sample 1[#] due to the higher sulphur concentration. MnS is easier to precipitate and the precipitation amount of MnS on oxides is also increased with the increase of sulphur in the samples since the concentration of oxygen was only slightly different in the samples. In sample 2[#], the number of inclusions is the minimum and the mean size of inclusions was the largest. Table 2 indicates the concentration of oxygen in sample 2[#] is the minimum and oxide inclusions are more difficult to form. Inclusion becomes larger with the increasing of sulphur concentration in the samples and the area density of inclusions is affected by oxygen in the samples. Mean and maximum diameter (d_{mean} , d_{max}) of MnS-containing inclusions in the samples are given in Table 5.

4. Discussion

4.1. The Effect of Refining Slag Composition on Sulphur Distribution Ratio between Slag and Steel

According to our previous research results,²⁴⁾ the desulphurization ability of LF refining slag used for GCr15 bearing steel expressed by sulphur distribution ratio (L_s) was mainly affected by optical basicity Λ of the refining slag which determined by the composition of slag, acid soluble aluminum concentration in the steel, and the effect of refining temperature (T/K). Under the conditions of $1830\text{ K} \leq T \leq 1855\text{ K}$, $0.020\text{ mass}\% \leq w[\text{Al}_s] \leq 0.050\text{ mass}\%$, $0.760 \leq \Lambda \leq 0.790$, the relationship between $\log L_s$ and Λ of the refining slag, acid soluble aluminum concentration, T etc. fitted by factory experimental datum is shown in formula (1).²⁴⁾ Since acid soluble aluminum and T are basically stable under the present conditions, the desulphurization ability of refining slag was increased with the increase of Λ when Λ was lower than 0.778, but it decreased with the increase of Λ when Λ was higher than 0.778. The empirical formula can be used as a guidance for controlling sulphur

concentration reasonably in practical production. According to the present industrial production results, when Λ of the refining slag is 0.776, L_s is the maximum and the minimum sulphur concentration is 0.0020 mass%, which agrees well with the prediction formula (1).

$$\log L_s = -433.069 + \frac{17412}{T} + 0.445 \lg w[\text{Al}_s] + 1118.39\Lambda - 728.47\Lambda^2 - 0.09671w(\text{SiO}_2) - 0.04877w(\text{Al}_2\text{O}_3) \quad (1)$$

4.2. The Precipitation Behaviors of Oxide Inclusions

Seen from Fig. 1, Al_2O_3 , MA and CMA inclusions were observed in the samples after LF refining. Aluminum was used as deoxidizer for bearing steels and Al_2O_3 inclusion was the main deoxidization product in the bearing steels which may lead to submerged entry nozzle (SEN) clogging in continuous casting process. Oxide inclusions were main MA and a few of CMA inclusions. It is well known that MgO and CaO in the refining slag or refractories will be reduced by aluminum or carbon in the bath and dissolved magnesium and calcium appear in the liquid steel. When a trace of magnesium generates in the liquid steel, Al_2O_3 reacts immediately with the dissolved magnesium to form MA as the reactions in Table 6.^{25–27)} MA is a stable complex oxide in MgO– Al_2O_3 binary system. The phase stability diagram of MgO–MgO· Al_2O_3 – Al_2O_3 can be calculated according to the thermodynamic datum listed in Table 6 under the given oxygen concentration in the liquid steel at LF refining operation temperature. Referencing to the reported results,²⁸⁾ the activity of MA in MgO and Al_2O_3 is 0.8 and 0.47 respectively, and the activity of MgO and Al_2O_3 at saturated state is 0.99 and 1 respectively. The calculated phase stability diagram for MgO– Al_2O_3 binary system is shown in Fig. 4. The concentration of aluminum and magnesium in each steel 1[#], 2[#] and 3[#] is existed in MA formation zone which can explain the main oxide inclusions is MA and no single MgO inclusions was found in the FE-SEM/EDS observation results. CaO in the refining slag and refractories is more stable than MgO, and the dissolved magnesium in liquid steel will appear before calcium.²³⁾ The diffusion rate of magnesium is faster than calcium in the same matrix,^{29,30)} and MA inclusion is more easy to form compared with calcium aluminate (CA) inclusions.

The experimental results from Table 3 indicate that there are more MA inclusions compared with CMA inclusions after LF refining. Research results had indicated that a trace of dissolved magnesium in the liquid steel will react preferentially with Al_2O_3 inclusions to form MA inclusion.^{23,27)} The number of single MA inclusion increases with the decrease of sulphur in the present samples. The more MgO

in the slag is reduced, the more Al_2O_3 is modified to generate MA inclusions.

Ma *et al.*¹⁹⁾ reported CA was a finally stable phase even if the dissolved calcium was 2 ppm in bearing steels. Deng *et al.*²³⁾ pointed out that the detail of CA inclusions formation is $\text{MA} \rightarrow \text{CMA} \rightarrow \text{CA}$, and forming CA inclusions need plenty of time. This is the reason why single CA inclusions can't be found separately at the end of LF refining even if the dissolved calcium is 9, 8 and 6 ppm in sample 1[#], 2[#] and 3[#] respectively.

Seen from Fig. 1 and Table 5, MA inclusions are smaller in size with smooth surface. The size of CMA type inclusions is larger than that of MA inclusions, and the concentration of Al_2O_3 and MgO in CMA type inclusions is determined by the concentration of dissolved calcium reduced from slag or refractories. CaS will precipitate on the surface of CMA type inclusions when the activity of Al_2O_3 in the inclusions is as low as possible.

4.3. The Effect of Sulphur Concentration on MnS Precipitation in the Samples

Seen from Table 3, the number percentage of MnS inclu-

Fig. 4. Phase stability diagram of MgO, $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and Al_2O_3 inclusions, and contour lines calculated at 1 873 K.

Table 6. Reactions in $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel formation.

Reaction	$\log K$
$2[\text{Al}] + 3[\text{O}] = \text{Al}_2\text{O}_{3(\text{s})}$	$-11.62 + 45\,300/T^{25)}$
$[\text{Mg}] + [\text{O}] = \text{MgO}_{(\text{s})}$	$4.28 + 4\,700/T^{26)}$
$\text{MgO}_{(\text{s})} + \text{Al}_2\text{O}_{3(\text{s})} = \text{MgO} \cdot \text{Al}_2\text{O}_{3(\text{s})}$	$0.60 + 1\,083/T^{27)}$
$2[\text{Al}] + 4[\text{O}] + [\text{Mg}] = \text{MgO} \cdot \text{Al}_2\text{O}_{3(\text{s})}$	$6.736 + 51\,080/T^{25-27)}$
$2[\text{Al}] + 3[\text{O}] + \text{MgO}_{(\text{s})} = \text{MgO} \cdot \text{Al}_2\text{O}_{3(\text{s})}$	$-11.02 + 46\,384/T^{25,27)}$
$[\text{Mg}] + [\text{O}] + \text{Al}_2\text{O}_{3(\text{s})} = \text{MgO} \cdot \text{Al}_2\text{O}_{3(\text{s})}$	$4.89 + 5\,874/T^{26,27)}$

sions decreases when sulphur concentration in the samples decreases. The size of MnS also decreases with the decrease of sulphur concentration in the samples as seen from Table 5. The maximum size of MnS doesn't exceed $2\,\mu\text{m}$, which is harmless for the fatigue life of GCr15 steels. According to the activity product of Mn and S given in Eq. (2)³¹⁾ for MnS in liquid steel, the calculated results show MnS can't precipitate under the present LF refining conditions. Where, the interaction coefficients of elements in molten steel at 1 873 K is shown in Table 7,^{32,33)} and the effect of temperature on interaction parameters between elements is given in Eq. (5).³³⁾

$$[\text{Mn}] + [\text{S}] = \text{MnS}_{(\text{s})} \quad \log a_{\text{Mn}} \cdot a_{\text{S}} = -8\,626/T_L + 4.75 \dots (2)$$

$$a_i = f_i \cdot w[i] \dots (3)$$

$$\log f_i = e_i^j \cdot w[j] + \sum e_i^j \cdot w[j] \dots (4)$$

$$e_i^j = \left(\frac{2\,538}{T} - 0.355 \right) \cdot e_{i(1873\text{K})}^j \dots (5)$$

Where a_{Mn} and a_{S} are the activity of Mn and S, which is calculated by Eq. (3);³²⁾ f_i is the activity coefficients of element i , which is calculated by Eq. (4);³³⁾ e_i^j is the interaction coefficient of element j to i , which is listed in Table 7; $w[i]$ is the mass fractions of element i in liquid steel, and $w[\text{Mn}]$ and $w[\text{S}]$ are the mass fractions of Mn and S in liquid steel, respectively.

Since MnS inclusions are observed in the present samples, they can only originate during solidification of the refined liquid steel. In order to learn about the effect of S concentration on MnS precipitation, microsegregation model of Mn and S during solidification process is used in the present work based on Brody-Flemings model³⁴⁾ which is revised by Clyne *et al.*^{35,36)} The basic assumption, conditions and parameters used in the microsegregation model are the same as that recommended in the references.³⁴⁻³⁷⁾

The segregation concentration of any solute constituent can be calculated by Eqs. (6) to (8)³⁴⁻³⁷⁾ at solidification node m at any moment t . The calculation is carried out by the direct finite difference method.

$$\frac{w_{m,L}^t}{w_0} = \frac{w_{m,S}^t}{kw_0} = [1 - (1 - 2\alpha k)f_s]^{(k-1)/(1-2\alpha k)} \dots (6)$$

$$\alpha = \frac{4D_s\tau_s}{\lambda^2} \dots (7)$$

$$\tau_s = (T_L - T_s) \cdot 60 / R_C \dots (8)$$

Where S presents solid phase, L presents liquid phase; $w_{m,S}^t$ and $w_{m,L}^t$ are the mass concentration of solute constituents in solidification node m at any moment t in solid and liquid phase respectively, mass%; w_0 is the original mass

Table 7. Interaction coefficients of Mn and S in molten steel at 1 873 K.

e_i^j	C	Cr	Si	Mn	Al _s	S	O	N	Ti	Mg	Ca
Mn	-0.07	0.0036	0.39	--	--	-0.048	-0.083	-0.091	0.019	--	--
S	0.11	-0.011	0.063	-0.026	0.035	-0.028	-0.27	0.01	-0.072	--	-100.0

concentration of solute constituents, mass%; k is the equilibrium partition coefficients of solute constituents between S and L; α is a constant related to the appropriate arm spacing; f_s is the solid fraction; T_0 , T_L , T_S represent the melting point of pure iron (1 809 K), liquidus and solidus temperature of the steel respectively, K; D_s is the diffusion coefficient of solute in solid phase during solidification, $\text{cm}^2\cdot\text{s}^{-1}$; Λ is the secondary dendrite arm spacing, cm; τ_s is solidification time, s; R_C is cooling rate of liquid steel during solidification, K/min. The cooling rate of the solidification is about 900 K/min.

The modified model for calculation α in place with symbol α^* was provided by Clyne *et al.*³⁵⁾ and expressed by Eq. (9) which was expected to behave correctly over the whole range of α (as long as solute redistribution in the liquid is complete). The results reported by El-Bealy *et al.*³⁸⁾ showed that Λ can be calculated approximately by Eqs. (10) to (12) when the mass concentration of C is in the range from 0.53 mass% to 1.5 mass% in the steel.

$$\alpha^* = \alpha(1 - e^{-1/\alpha}) - \frac{e^{-1/(2\alpha)}}{2} \quad \text{..... (9)}$$

$$\lambda = A \times \tau_s^d \quad \text{..... (10)}$$

$$A = 21.52764 - 9.40 \times w[\text{C}] \quad \text{..... (11)}$$

$$d = 0.4 + 0.08 \times w[\text{C}] \quad \text{..... (12)}$$

The liquidus temperature (T_L) and solidus temperature (T_S) are calculated by Eqs. (13) and (14) in high carbon steels.³²⁾ The calculated result of T_L in sample 1[#], 2[#] and 3[#] is about 1 726 K–1 728 K and T_S is about 1 609 K–1 613 K. The temperature of LF refining is controlled about 1 830 K in practical production. The temperature at every solid fraction f_s during solidification process is calculated by Eq. (15).³²⁾

$$T_L = 1809 - \{78w[\text{C}] + 7.6w[\text{Si}] + 4.9w[\text{Mn}] + 34.4w[\text{P}] + 38w[\text{S}] + 1.3w[\text{Cr}] + 3.6w[\text{Al}]\} / \text{K} \quad \text{..... (13)}$$

$$T_S = 1809 - \{184.3w[\text{C}] + 40.8w[\text{Si}] + 8.6w[\text{Mn}] + 76.7w[\text{P}] + 76.7w[\text{S}] + 3.4w[\text{Cr}] + 7.8w[\text{Al}]\} / \text{K} \quad \text{... (14)}$$

$$T = T_0 - \frac{T_0 - T_L}{1 - f_s \cdot (T_L - T_S) / (T_0 - T_S)} \quad \text{..... (15)}$$

Fe-C-1.5 mass%Cr alloy phase diagram calculated by FactSage6.4 thermodynamic software indicated that the tested liquid steel changes to γ -Fe during solidification process. Data of equilibrium partition coefficients and diffusivity of solute elements are showed in Table 8.³⁹⁾

The actual solubility product of manganese and sulphur changing with solid fraction f_s in each sample was calculated and shown in Fig. 5. The temperature at every solid fraction f_s during solidification process and the corresponding equilibrium solubility product of manganese and sulphur are also shown in Fig. 5. As seen from Fig. 5, the actual solubility product of manganese and sulphur increases and the equilibrium solubility product decreases with the increase of sulphur concentration when the solidification process

Table 8. Diffusion coefficient and equilibrium partition of Mn and S solutes.

Element	$D_s^{\gamma} (\text{cm}^2/\text{s})$	$K^{\gamma/L}$
Mn	$0.055 \text{Exp} (-249\,366/RT)$	0.785
S	$2.4 \text{Exp} (-223\,426/RT)$	0.035

Fig. 5. Solubility product of MnS and temperature changing with solid fraction.

is proceeding. MnS precipitates more difficultly with the decrease of sulphur concentration in the samples at the same solidification conditions. MnS begins to precipitate when the solidification fraction is about 0.986, 0.989, and 0.993 for sample 1[#], 2[#] and 3[#] respectively. According to the experiment results in Table 3, the number percentage of MnS among all the inclusions is 28.05%, 22.78%, 14.10% and the average size of MnS is 0.47, 0.43, and 0.37 μm in sample 1[#], 2[#] and 3[#] respectively. The smaller the solidification fraction is, the easier MnS precipitates and grows up during solidification process. Therefore, the number percentage of MnS among all the inclusions and the average size of MnS decrease with the increase of solidification fraction. The calculated results agree well with the experiment results. The size of MnS is relatively small and no inclusions larger than 1.5 μm were found due to the fast cooling rate, and the morphology of MnS is oval or spherical. The results are the same as those reported by Huang *et al.*⁴⁰⁾ The number percentage of MnS precipitation increases and their size decreases with the increase of cooling rate, meanwhile, their morphology changes from long strip to ellipse or approximately spherical. Lowe *et al.*⁴¹⁾ reported that the non-metallic inclusions wouldn't influence the macroscopic properties of the material while their size was less than 1 μm and the distance between each other was greater than 10 μm . According to the above results, MnS inclusions are harmless when the concentration of sulphur doesn't exceed 0.0040 mass% in the steels.

4.4. The Effect of Sulphur Concentration on Precipitation Behaviors of Oxide-sulphide Complex Inclusions

Seen from Table 4, the main inclusions are oxide-sulphide complex inclusions in the samples. The kinds of

oxides and the concentration of sulphur in the samples decide the ratio of MnS precipitated on them. MnS precipitation ratio on a certain type of oxide is defined as the ratio of the number of oxide particles with MnS precipitation in all of the same kind of oxide particles. The relationship between precipitation ratio and the thickness of MnS on MA and CMA inclusions is shown in Fig. 6. Not only the precipitation ratio but also the average thickness of MnS precipitating on the surface of MA and CMA inclusions decreases with the decrease of sulphur concentration in the samples. Meanwhile, the precipitation ratio of MnS on MA inclusions is higher than that of on CMA inclusions. The average thickness of MnS precipitating on the surface of MA inclusions is 0.23 μm , 0.13 μm and 0.08 μm in sample 1[#], 2[#], and 3[#] respectively. However, The average thickness of MnS precipitating on the surface of CMA inclusions is 0.56 μm , 0.46 μm and 0.31 μm in sample 1[#], 2[#], and 3[#] respectively, about 2.5–4.5 times of that on MA inclusions, which leads to the diameter of CMA encapsulated with MnS inclusions is larger than that of MA encapsulated with MnS as shown in Figs. 2 (b) and 2(d). Figure 7 indicates that the precipitation nucleation mode of MnS on the sur-

face of MA inclusions changes from full covering to partly covering. Almost all MnS precipitates surrounding with MA inclusions in sample 1[#] and 2[#]. However, MnS precipitates partly on MA inclusions in sample 3[#] due to the decrease of sulphur concentration in the sample. Seen from Figs. 6 and 7, MnS precipitates more difficultly on the oxide-sulfides and the size decreases with the decrease of sulphur concentration in liquid steel. The experimental results are in agreement with the calculated results in Fig. 5. Comparing the analysis results in Tables 4 and 5 and Figs. 1, 2 and 3, MnS-containing inclusions are much smaller than aluminosilicate inclusions (Fig. 1(d)), and most of them are also smaller than CMA inclusions (Figs. 1(c) and 1(f)) in the tested samples. Oxide inclusions can precipitate in the liquid steel. When MnS precipitates on the surface of MA or CMA inclusions, the agglomeration or growth of MA or CMA inclusions is inhibited. The morphology of MnS-containing inclusions is more regular than oxides which will weaken defects arisen by large inclusions in the steels.

CMA type inclusions with MnS encapsulated or not were analyzed by using a SEM/EDS in each metallographic sample to learn about precipitation principle of MnS on this kind of inclusions. The composition distribution of inclusions encapsulated with MnS or not is marked in the CaO–MgO–Al₂O₃ ternary system phase diagram, which is shown in Fig. 8, and the liquid region drawn in Fig. 8 is calculated by FactSage 6.4 software at 1 835 K. Black spot represents that there is MnS precipitating and hollow spot represents not. Seen from Fig. 8, MnS can precipitate on CMA inclusions when the mole percent of CaO in the inclusions is less than 33 mole% (0.33) in sample 1[#], 2[#] and 3[#] respectively. However, MnS can't precipitate on CMA inclusions when the mole percent of CaO in the inclusions is more than 38 mole% (0.38) due to longer time for MA reacting with dissolve calcium. Meanwhile, CMA type inclusions without MnS precipitating are almost in liquid region. According to the composition of CMA inclusions listed in Fig. 8, the beginning melting temperature of CMA inclusion (a), (b), (c) in sample 1[#] is 1 963 K, 1 796 K, 1 617 K respectively, and the completely melting temperature of inclusions (a), (b), (c) is 2 201 K, 2 016 K, 1 728 K respectively calculated by the FactSage 6.4 software. Only CMA inclusions with high melt point can act as a core for MnS precipitation on them. CMA inclusions with lower melt point are difficult to become the core of the complex. According to our observation and statistics results shown in Fig. 8, the size of CMA inclusion (a), (b), (c) in sample 1[#] is 1.33 μm , 1.86 μm , 3.54 μm and the thickness of MnS on CMA inclusion (a), (b) is 0.96 μm and 0.37 μm respectively. The size of CMA type inclusions increases and the thickness of MnS on CMA inclusion decreases with the increase of mole percent of CaO along the direction of the arrow for each sample. Small size inclusions with a smaller discrepancy between the low-index planes of inclusions and metal phase require a lower interfacial energy for the transformation, where the nucleation of inclusions occurs more easily.⁴²⁾ Sulphur element in the steel can precipitate in the form of MnS or CaS. CaS was always found in the surface of CA inclusions because CaS precipitates only after low melt temperature CA inclusions forming in the steel. Deng *et al.*²³⁾ reported the detail evolution process of CA inclusions in the samples

Fig. 6. Effect of sulphur concentration on precipitation ratio and thickness of MnS on MA and CMA inclusions.

Fig. 7. Effect of sulphur concentration on the morphology of MnS precipitated on MA inclusions.

Fig. 8. Composition distribution of CMA type inclusions and CMA type inclusions encapsulated with MnS, mole%.

similar with present one is $\text{MA} \rightarrow \text{CMA} \rightarrow \text{CA}$, and CA inclusions evolve according to the following route as $\text{CA} \rightarrow 12\text{C} \cdot \text{aO} \cdot 7\text{Al}_2\text{O}_3 (12\text{C} \cdot 7\text{A}) \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 (3\text{C} \cdot \text{A})$ in LF refining process. The melting temperature of CMA inclusions is high when the mole percent of CaO in the inclusions is less than 33 mole% (0.33) due to the short time for MA reacting with dissolve calcium, no obvious of CA but CMA layer appeared on the outer surface of inclusion and CaS was very difficult to precipitate according to chemical reaction Eq. (16).⁴²⁾ However, Sulphur element can combine with Mn element in liquid steel to precipitate MnS especially on the surface of oxide inclusions during the solidification process as we had discussed. CaO in CA layer can easily react with dissolved aluminum, sulphur in liquid steel and form CaS as Eq. (16)⁴³⁾ when CA type inclusions form. CMA with CaS was shown in Fig. 2(f). This is the reason that MnS can't be observed when the mole percent of CaO in CMA type inclusions is more than 38 mole% (0.38).

$$\Delta G^\circ = -879\,760 + 298.73T^{42)} \quad \text{..... (17)}$$

The key to reducing the harm of CMA inclusions is to control the optical basicity of the slag and the reaction time of MA inclusions with dissolve Ca. If they are difficult to float into refining slag in RH short refining time, it is essential to ensure desulphurization to a certain degree to avoid forming large CMA inclusions and modify CMA inclusions by MnS precipitating on them.

4.5. The Effect of Sulphur Concentration on Precipitation Behavior of TiN-containing Inclusions

Using the same calculating method as MnS for TiN precipitation, the calculation results show that TiN neither precipitate in liquid phase nor in the solidification process of steel. As can be seen from Table 4, the number percentage of MA-TiN is 7.32%, 6.33%, and 8.98% in sample 1[#], 2[#] and 3[#] respectively, and it is 10.97%, 11.39%, 11.54% and 2.44%, 2.53%, 3.85% respectively for MA-MnS-TiN

and MnS-TiN type inclusions. We can see that the effect of sulphur concentration on the precipitation of MA-MnS-TiN and MnS-TiN is not obvious. Meanwhile, TiN mainly precipitates on the surface of smaller $\text{Al}_2\text{O}_3 \cdot \text{MgO}$. This reason can be explained that the concentration of Ti and N is slightly different in each sample and TiN precipitates more difficult than MnS.

5. Conclusion

The effect of sulphur concentration on precipitation behaviors of MnS-containing inclusions in GCr15 bearing steel refined by LF process was studied. The following conclusions are obtained.

(1) The sulphur distribution ratio is mainly controlled by the compositions of refining slag for the aiming sulphur concentration in liquid steel. The suitable optical basicity of the refining slag is 0.776 and the minimum sulphur concentration is 0.0020 mass% under the present refining conditions.

(2) The main oxide inclusions in steel after LF refining are MA and CMA type inclusions. CMA is often globular and partly surrounded by CA layer. And MnS-containing inclusions include MnS, MA-MnS, MA-MnS-TiN, CMA-MnS, MnS-TiN. MnS precipitating on the surface of MA inclusions changes from fully covering to partly covering, while MnS precipitating on the surface of CMA inclusions is always fully covering with spherical or ellipse shape.

(3) The number percentage of oxides, mean size and number density of the inclusions are also influenced by total oxygen concentration besides sulphur concentration in the tested samples. The maximum size of the inclusions, the number percentage and size of MnS, MA-MnS and CMA-MnS decrease with the decrease of sulphur concentration in the samples.

(4) MnS begins to precipitate when the solidification fraction is about 0.986, 0.989, 0.993 for sample 1[#], 2 and 3[#] respectively. Not only the precipitation ratio but also the average thickness of MnS precipitating on the surface of

MA and CMA inclusions decreases with the decrease of sulphur concentration in the samples. The average thickness of MnS precipitation on the surface of CMA inclusions is about 2.5–4.5 times larger than that on MA inclusions. MnS precipitating on MA or CMA is helpful for reducing large size oxide inclusions in the bearing steels.

(5) The precipitation behavior of MnS on CMA inclusions is influenced not only by sulphur concentration in the steel but also the composition of the inclusions. MnS can precipitate on CMA inclusions when the mole percent of CaO in the inclusions is less than 33 mole% in all of sample 1[#], 2[#] and 3[#]. However, MnS can't precipitate on CMA inclusions when the mole percent of CaO in the inclusions exceeds 38 mole% (0.38).

(6) The effect of sulphur concentration on the precipitation of MA–MnS–TiN and MnS–TiN type inclusions is not obvious. Meanwhile, TiN mainly precipitates on smaller Al₂O₃·MgO inclusions.

REFERENCES

- 1) M. Y. Zhu: Modern Metallurgy, Steel Metallurgy Volume, Metallurgical Industry Press, Beijing, (2005), (in Chinese).
- 2) J. Lehmann and M. Nadif: *Rev. Mineral. Geochem.*, **73** (2011), 493.
- 3) C. Y. Zhu, P. J. Chen, G. Q. Li, X. Y. Luo and W. Zheng: *ISIJ Int.*, **56** (2016), 1368.
- 4) I. G. Davies, M. A. Clarke and D. Dulieu: Effect of Steel Manufacturing Processes on the Quality of Bearing Steels, ASTM, West Conshohocken, PA, (1988), 375.
- 5) M. Wakoh, T. Sawai and S. Mizoguchi: *ISIJ Int.*, **36** (1996), 1014.
- 6) W. Zheng, Z. H. Wu, G. Q. Li, Z. Zhang and C. Y. Zhu: *ISIJ Int.*, **54** (2014), 1755.
- 7) T. Sakai, Y. Sato, Y. Nagano, M. Takeda and N. Oguma: *Int. J. Fatigue*, **528** (2006), 1547.
- 8) H. Lian, X. J. Zhao and Y. J. Qiu: *Bearing*, (2008), 26 (in Chinese).
- 9) L. T. Lu, W. Li and J. W. Zhang: *Acta. Metall. Sin.*, **45** (2009), 73 (in Chinese).
- 10) W. Li, T. Sakai and Q. Li: *Mater. Sci. Eng. A*, **528** (2011), 5044.
- 11) S. Baeckstrom: Proc. Soviet-Swedish Symp. on Clean Steel. Royal Swedish Academy of Engineering Sciences, Stockholm, (1971), 170.
- 12) J. J. C. Hoo: Creative Use of Bearing Steels, ASTM Special Technical Publication, Philadelphia, (1993), 252.
- 13) H. K. D. H. Bhadeshia: *Prog. Mater. Sci.*, **57** (2012), 268.
- 14) Q. Chen, E. Shao, D. Zhao, J. Guo and Z. Fan: *Wear*, **147** (1991), 285.
- 15) S. I. Gubenko and A. M. Galkin: *Metal. Sci. Heat Treat.*, **26** (1984), 732.
- 16) S. C. Park, I. H. Jung, K. S. Oh and H. G. Lee: *ISIJ Int.*, **44** (2004), 1016.
- 17) M. Andersson, P. G. Jonsson and M. M. Nzotta: *ISIJ Int.*, **39** (1999), 1040.
- 18) K. Mine and H. Yoshida: High Carbon Chromium Bearing Steels of Long Life. Japanese Patent Showa 5541910, (1980).
- 19) W. J. Ma, Y. P. Bao, M. Wang and L. H. Zhao: *ISIJ Int.*, **54** (2014), 536.
- 20) X. J. Ruan, Z. H. Jiang, W. Gong, Y. Li and J. S. Li: *Spec. Steel*, **29** (2008), 1 (in Chinese).
- 21) L. Zheng and M. H. Xu: *J. ASTM Int.*, **3** (2006), 20.
- 22) Y. Unigame, K. Hiraoka and I. Takasu: *J. ASTM Int.*, **3** (2006), 34.
- 23) Z. Y. Deng and M. Y. Zhu: *ISIJ Int.*, **53** (2013), 450.
- 24) P. J. Chen, C. Y. Zhu, Z. C. Zhang, G. Q. Li and M. X. Pan: *J. Iron Steel Res.*, **28** (2016), 30 (in Chinese).
- 25) H. Itoh, M. Hino and S. Ban-ya: *Tetsu-to-Hagané*, **83** (1997), 773.
- 26) H. Itoh, M. Hino and S. Ban-ya: *Tetsu-to-Hagané*, **83** (1997), 623.
- 27) H. Itoh, M. Hino and S. Ban-ya: *Tetsu-to-Hagané*, **84** (1998), 85.
- 28) K. Fujii, T. Nagasaka and M. Hino: *ISIJ Int.*, **40** (2000), 1059.
- 29) M. Masana: *Geochim. Cosmochim. Acta*, **45** (1981), 1573.
- 30) T. LaTourrette and G. Wasserburg: *Earth. Planet. Sci. Lett.*, **158** (1998), 91.
- 31) Y. Ueshima, K. Isobe, S. Mizoguchi, H. Maede and H. Kajioka: *Tetsu-to-Hagané*, **74** (1988), 465.
- 32) J. X. Chen: Handbook of Common Chart Data for Steelmaking Process, 2nd ed., Metallurgical Industry Press, Beijing, (2010), 510 (in Chinese).
- 33) X. H. Huang: The Principle of Ferrous Metallurgy, 4th ed., Metallurgical Industry Press, Beijing, (2005), 181 (in Chinese).
- 34) T. F. Bower, H. D. Brody and M. C. Flemings: *Trans. Metall. Soc. AIME*, **236** (1966), 624.
- 35) T. W. Clyne and W. Kurz: *Metall. Mater. Trans. A*, **12** (1981), 965.
- 36) T. W. Clyne, M. Wolf and W. Kurz: *Metall. Mater. Trans. B*, **13** (1982), 259.
- 37) M. Wolf and W. Kurz: *Metall. Trans. B*, **12** (1981), 85.
- 38) M. Elbealy and B. G. Thomas: *Metall. Mater. Trans. B*, **27** (1996), 689.
- 39) S. K. Choudhary and A. Ghosh: *ISIJ Int.*, **49** (2009), 1819.
- 40) Y. Huang, X. J. Yang, F. Wang, J. S. Li and S. F. Yang: *Ind. Heat.*, **15** (2016), 18 (in Chinese).
- 41) J. H. Lowe and A. Mitchell: Clean Steel, Superclean Steel Conf. Proc., Institute of Materials, London, (1995), 223.
- 42) G. L. Sun, B. Song, L. Z. Yang, S. F. Tao and Y. Yang: *Int. J. Min. Met. Mater.*, **21** (2014), 654.
- 43) G. Xu, Z. H. Jiang and Y. Li: *Metall. Mater. Trans. B*, **47** (2016), 2411.