Research Article

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Effect of Acid Slag Treatment on the Inclusions in GCr15 Bearing Steel

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Abstract: By laboratory slag/steel reaction equilibrium experiments, the variation of oxygen content, inclusion compositions and inclusion sizes were studied. The effect of acid slag treatment on the transition mechanisms of D-type inclusions and the precipitation of TiN inclusions in GCr15 bearing steel were explored. The obtained results showed that the dominant inclusions in steel were plastic and smaller $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-MnO}$. The melting point were lower than 1400°C treated by the acid refining slag of 35.1%CaO-15% Al_2O_3 -43.9% SiO_2 -6%MgO and there was no TiN found. The evolution of $\text{MgO}\cdot\text{Al}_2\text{O}_3$ inclusions is: $\text{MgO}\cdot\text{Al}_2\text{O}_3 \rightarrow \text{MgO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{MnO} \rightarrow \text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{MnO}$. Mg and Al from $\text{MgO}\cdot\text{Al}_2\text{O}_3$ inclusions were displaced by [Si] and [Mn] in steel liquid, and formation of plastic $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-MnO}$ inclusions finally, whose compositions distribution were uniform. Mg and Si, Mn were complementary in inclusions as to the spatial distribution.

Keywords: Acid slag; Inclusion type; GCr15 Bearing steel

1 Introduction

As one of the most commonly used high-chromium bearing steels, GCr15 has been widely used in manufacturing bearing ring, ball screw and other mechanical components [1]. There are three main factors affecting contact fatigue life of bearing steel: hardness, inclusions and hydrogen content in steel [2]. The development of bearing steel in the twentieth century was decreasing T.[O] [3], and the

work highlight to improve fatigue life of bearing steel was reducing the sizes of inclusions [4]. Meanwhile, many researchers had approved and verified that quantities, compositions, morphologies and sizes of inclusions in steel are the main factors which affect the fatigue life of bearings. In general, the quantities and sizes of inclusions in steel could be reduced by controlling the process of steelmaking [5]. Therefore, it is important to explore suitable slag compositions to control the inclusions in bearing steel.

Although there is low oxygen content in GCr15 after high basicity refining slag treatment, which achieved high cleanliness, most were D-type inclusions including $\text{MgO}\cdot\text{Al}_2\text{O}_3$, MgO and calcium-aluminate [7]. And the inclusions such as $\text{MgO}\cdot\text{Al}_2\text{O}_3$, calcium-aluminate and chrisotbalite had no plastic deformation ability under the conventional hot working temperature of steel. It can not be in good shape with the base body when rolling. The stress concentration can be caused between the steel matrix and the interfacial, which caused fatigue cracks and fatigue life reduction of the bearing steel [8]. Jiang [9] found that the inclusions with low melting point had good deformation ability, and they were found in liquid form with special shape which were easier to remove. Ders' theoretical calculation [10] showed that lowering the melting point of inclusions (softening inclusions) could not only effectively increase the plastic deformation ability, but also eliminate the stress concentration. Bernard [11] reviewed that the deformation ability of inclusions had an important relationship with its melting temperature: there were good plastic deformation when the melting temperature of the inclusion was less than 1673K.

In order to reduce the harmfulness of D-type inclusions in GCr15, it is necessary to be transformed into inclusions with low melting point and plastic deformation ability. How the acid slag modified the inclusions in bearing steel was seldom reported. The treatment effect of acid slag basicity and compositions on D-type inclusion were analyzed. The variation of oxygen content, inclusion sizes and compositions, the effect of acid slag treatment on precipitation of TiN-type inclusion in steel and the evolution mechanism of $\text{MgO}\cdot\text{Al}_2\text{O}_3$ inclusion during the treatment process were investigated.

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Table 1: Chemistry composition of raw material pieces, wt%.

C	Cr	Si	Mn	P	S	T.[O]	T.[N]	Ti	Als
1	1.47	0.21	0.31	0.0068	0.0018	0.0008	0.0046	0.0061	0.0066

Table 2: Compositions of the high basicity refining slag, %.

CaO	Al ₂ O ₃	SiO ₂	MgO	R
59.4	24.8	9.8	6	6

Table 3: The compositions of acid slags, %.

	CaO	Al ₂ O ₃	SiO ₂	MgO	R
S1	21.2	20	52.8	6	0.4
S2	32.9	20	41.1	6	0.8
S3	35.1	15	43.9	6	0.8
S4	33.3	15	41.7	10	0.8

Table 4: Inclusions types in steel of different acid slags

Sample	Type of inclusions
S1	Most: MgO-Al ₂ O ₃ -SiO ₂ -MnO, some: Al ₂ O ₃ -SiO ₂ -MnO
S2	Most: CaO-Al ₂ O ₃ -SiO ₂ -MnO, some: Al ₂ O ₃ -SiO ₂ -MnO
S3	Most: Al ₂ O ₃ -SiO ₂ -MnO, some: CaO-MgO-Al ₂ O ₃ -SiO ₂ -MnO
S4	Most: CaO-MgO-Al ₂ O ₃ -SiO ₂ -MnO, some: MgO-Al ₂ O ₃ (which is not modified)

2 Experimental procedure

Experiments were carried out in a tubular resistance furnace. The billet pieces of GCr15 bearing steel, which treated by high basicity refining slag, were used as start material. The chemical composition of GCr15 is listed in Table 1 and the compositions of the high basicity refining slag is listed in Table 2. The billet pieces were melted in Al₂O₃ crucible under argon protective atmosphere. The argon volume flow and pressure were monitored by a flow meter and a pressure gauge.

The detailed experimental process is described as follows: (1) 70g billet blocks and 10.5g acid slag were placed into the Al₂O₃ crucible to melt in the tubular resistance furnace. (2) The furnace was heated up to 1600°C gradually under argon protective atmosphere with a volume flow of 4 L·min⁻¹. (3) After melting clear, the temperature was maintained at 1600°C for one and half an hour to homogenize the chemical composition. (4) The samples was put out and placed into a copper plate, and then cooled down by water quenching. There are four types of acid slag, and the compositions of them are listed in Table 3.

To explore the transitional process, the sample with best acid slag treatment was picked for different holding time at 1600°C, such as 10min, 20min, 40min, 60min and 80min. Finally, the samples were cooled down by water quenching

The concentration of carbon(C) and sulfur(S) in the steel samples were analyzed by infrared carbon and sulfur analyzer (Model: EMIA-920V2). The concentration of chromium(Cr), silicon(Si), manganese(Mn) in the steel samples were analyzed by X-ray fluorescence spectrometer (Model: EDX8000). The concentration of total oxygen (T.[O]) and total nitrogen(T.[N]) in the steel samples were determined by infrared nitrogen and oxygen analyzer(Model: EMGA-830). The concentration of Phosphorus(P), Titanium(Ti) and acid soluble aluminum(Als) in the steel samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

The morphologies of inclusions in the samples observed by scanning electron microscope and the chemical compositions of inclusions were analyzed with energy dispersive X-ray spectroscopy (SEM-EDS, Model: MLA250). The quantities and sizes of the TiN-type inclusions in the steel samples were analyzed by automatic inclusion analysis system (Model: EVO18-INCAsteel).

3 Results and discussion

3.1 Effect of different acid slags treatment

The main inclusions in the steel samples before acid slag treatment were D-type inclusions, including MgO-Al₂O₃, TiN, MgO and CaO-MgO-Al₂O₃. The types of inclusions in different acid slags treatment steel samples are listed in Table 4. The main inclusions in S1, S2, S4 are CaO (MgO)-Al₂O₃-SiO₂-MnO-type containing Ca and Mg. Besides, there are MgO-Al₂O₃ inclusions in S4. However, the main inclusions in S3 are Al₂O₃-SiO₂-MnO not containing Ca and Mg. Al₂O₃-SiO₂-MnO inclusions had good plastic deformability and they stretched along the rolling direction into strips when rolling. It reduced the stress con-

Figure 1: Composition distribution of inclusions in Al₂O₃-SiO₂-MnO phase diagrams for S1

Figure 3: Composition distribution of inclusions in Al₂O₃-SiO₂-MnO phase diagrams for S3

Figure 2: Composition distribution of inclusions in Al₂O₃-SiO₂-MnO phase diagrams for S2

Figure 4: Composition distribution of inclusions in Al₂O₃-SiO₂-MnO phase diagrams for S4

centration and fatigue crack source between steel matrix and inclusion, which improved the fatigue life of bearing steel. The inner morphologies and compositions of the MgO-Al₂O₃-SiO₂-MnO inclusions were analyzed by metallographic observation (Figure 7). The results showed that MgO-Al₂O₃-SiO₂-MnO inclusions were dual-phase with MgO-Al₂O₃ core and SiO₂-MnO shell. If the core of the MgO-Al₂O₃-SiO₂-MnO-type inclusion is MgO-Al₂O₃ after Ca treatment, it's harm to the property of steels, because it remained the original MgO-Al₂O₃ shape when rolling [12].

The inclusions of S1, S2 and S3 were CaO and MgO, and (CaO+MgO) ≈ 5%, therefore, they could be projected to Al₂O₃-SiO₂-MnO-5%MgO phase diagram. While the inclusions of S3 should be projected to Al₂O₃-SiO₂-MnO phase diagram (see Figures 1-4).

The melting point of inclusions in S1, S2, S3 and S4 showed a downward trend after acid slag treatment, and all of them had some inclusion projection points distributing in the low melting area less than 1500°C. This kind of inclusion was liquid state in molten steel, which benefit to colliding, growing up and floating out [13]. There were

Figure 5: Variation of average diameter of inclusions and oxygen content in steel with time

10% inclusion projection points in S2 and 40% in S3 distributing in the low melting area less than 1400°C. And the distribution of the inclusion projection points in S3 were concentrated, while they were dispersed in S1, S2 and S4.

Inclusion sizes of the start material, S1, S2, S3 and S4 were summarized on the basis of the statistics of 50 inclusions, and the total oxygen is shown (Figure 5). The results showed that the sizes of the inclusions before treatment distributed in 1~10 μm, while the sizes of the inclusions after treatment distributed in 1~5 μm. The inclusion sizes in S1, S2, S3 and S4 were decreased, and the average inclusion size of S3 was the smallest, which was 2.05 μm. The total oxygen of S1 and S4 increased much, while it's almost invariant in S3. Above all, the S3 had the best treatment effect.

3.2 Transition mechanisms of inclusions in the acid slag treatment process

Transition process from $\text{MgO} \cdot \text{Al}_2\text{O}_3$ to $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{MnO}$ inclusions can be appeared by elements mapping distribution of different time (Figure 6-8). The content of Mn and Si in inclusions increased, while the content of Mg decreased in process of reaction. And the enrichment zones were obviously in the form of complement. In the first 20 minutes, the core of inclusions had high content of MgO and Al_2O_3 , while the side of inclusions had high content of SiO_2 and MnO , which had a good correspondence in special position. After 40 minutes, stratification of inclusions disappeared. It meant the inclusions transformed to $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{MnO}$ -type, which didn't contain Mg while Mn, Si and Al well-distributed.

Figure 9 shows the change of the average composition of inclusions over time. In the first 20 minutes, the content of MgO and Al_2O_3 decreased, while the content of MnO and SiO_2 increased. There was no MgO in the inclusions at the 40th minute, and the content of SiO_2 , MnO and Al_2O_3 were almost unchanged after that. And the inclusion had transformed to $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{MnO}$ -type.

Based on the above discussion, the transformation process of the $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusions in steel consisted of two stages: (1) $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusions transformed to $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{MnO}$ inclusions; (2) $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{MnO}$ inclusions transformed to $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{MnO}$ inclusions. The mechanism of inclusions transformation is showed in Figure 10, and the reaction steps are listed:

1. The dissolved manganese and silicon in molten steel ($[\text{Mn}]$ and $[\text{Si}]$) diffuses into the inclusion/steel-liquid interface, where reaction (1) happens and intermediate product $(x-1)\text{Mg} \cdot (y-1)\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{MnO}$ forms.

2. As time increases, more $[\text{Mn}]$ and $[\text{Si}]$ diffuses into this region. And reaction (2) happens in the inclusion/steel-liquid interface, where $(y-1)\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot (x-1)\text{MnO}$ forms.

3. After that, the content of MnO_2 and SiO_2 in this layer gradually increases while that of MgO decreases. The reaction product $[\text{Mg}]$ in reaction (2) will transfer from the $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{MnO}$ layer into molten steel.

The reaction can be seen by step (1) that Mg and Al in inclusions cemented out by $[\text{Si}]$ and $[\text{Mn}]$, and transformed to $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{MnO}$ -type plastic inclusions with well-distributed of Al, Si and Mn.

3.3 Effect of acid slag treatment on TiN-type inclusion precipitation

With the oxide inclusions greatly reduced in bearing steel, the harmfulness of TiN inclusions gradually revealed, which is second only to calcium aluminate. The generating condition of TiN-type inclusions could obtain by the following thermodynamic analysis [14, 15]:

Figure 6: The elemental mapping of typical inclusion in steel when the time of 10min ($\text{MgO} \cdot \text{Al}_2\text{O}_3$)

Figure 7: The elemental mapping of typical inclusion in steel when the time of 20min ($\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{MnO}$)

Figure 8: The elemental mapping of typical inclusion in steel when the time of 40min ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{MnO}$)

Figure 9: Variation of average composition of inclusions with time

Figure 10: The mechanism of inclusions transformation from $\text{MgO} \cdot \text{Al}_2\text{O}_3$ to $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{MnO}$

$$\Delta G^\theta = -291000 + 10791T, \text{ J} \cdot \text{mol}^{-1} \quad (3)$$

$$K = \frac{\alpha_{\text{TiN(s)}}}{\alpha_{[\text{Ti}]} \alpha_{[\text{N}]}} = \frac{1}{f_{\text{Ti}} [\% \text{Ti}] f_{\text{N}} [\text{N}]} \quad (4)$$

$$\lg K = -\frac{\Delta G^\theta}{2.3RT} = \frac{15220}{T} - 5.64 \quad (5)$$

Figure 11: The balance between N and Ti in steel-liquid within the range of solidification temperatures

$$-\frac{15220}{T} + 5.64 = \lg f_{\text{Ti}} + \lg f_{\text{N}} + \lg [\% \text{N}] + \lg [\% \text{Ti}] \quad (6)$$

$$-\frac{15220}{T} + 5.64 = \lg [\% \text{N}] + \lg [\% \text{Ti}] \quad (7)$$

$$\lg K_{\text{TiN}} = \lg ([\% \text{Ti}] [\% \text{N}]) = -\frac{13850}{T} + 4.01 \quad (8)$$

Where, K in Equation (4) represents the equilibrium constant of Equation (3); $\alpha_{\text{TiN(s)}}$ represents the activity of TiN in the slag; $\alpha_{[\text{Ti}]}$ represents the activity of Ti in steel; $\alpha_{[\text{N}]}$ represents the activity of N in steel; f_{Ti} represents the activity coefficient of Ti in steel; f_{N} represents the activity coefficient of N in steel; $[\% \text{Ti}]$ represents the mass fraction of Ti in steel; $[\% \text{N}]$ represents the mass fraction of N in steel. Take the logarithm of both sides of the Equation (4) and combine the Equation (5), leading to the Equation (6). The other elements in steel are little comparison with Fe, therefore it could ignore the effect of the activity coefficient of other elements on Ti and N in steel. The Equation (6) could simplify to Equation (7) and calculate the minimum required content of N and Ti to precipitate the TiN-type inclusions in the steelmaking and solidification process.

If there is 0.005%Ti in steel, the minimum required content of N is 0.448% at 1600°C; the minimum required content of N is 0.448% at 1500°C; the minimum required content of N is 0.143% at 1460°C. Therefore, it can't precipitate the TiN-type inclusions in the steelmaking process above the liquid line temperature(1450°C).

In the steelmaking and solidification process, the solubility of N and Ti in steel decreased with the temperature decreasing, Equation (8) represents. The stability interrelationship is shown in Figure 11.

To research the effect of acid slag S3 on the TiN-type inclusions, 60g piece of steel sample and 9g slags were put

Table 5: Amount and size distribution of TiN inclusion

	1~3μm	3~5μm	5~8μm	>8μm	Amount
Before treatment	21.5%	33.3%	33.3%	11.9%	75
After treatment	—	—	—	—	0

(Size of TiN = $\frac{\text{length} + \text{width}}{2}$)

Table 6: Ti content in steel before and after treatment (mass %)

%	Before treatment	After treatment
[Ti]	0.0038	<0.0005

into Al_2O_3 crucible at 1600°C, protected by Ar atmosphere. Held for 80 minutes at 1600°C, and then cooled inside the furnace. The quantities and sizes distribution of TiN-type inclusions are listed in Table 5. Most TiN inclusions are about 5μm, and some bigger than 8μm before treatment. There is no TiN inclusion found after treatment, but it can't be the direct absorption of the acid slag S3.

In the steel-slag balance experiment of alkaline slag, a layer of solid-state CaTiO_3 containing Ti were produced in the steel/slag interface, which prevent Ti diffusing to slag through steel/slag interface [16].

The SEM observations and thermodynamic calculations showed that calcium titanate is formed by the oxidation of dissolved titanium according to

There is no evidence for the direct reaction at the slag/inclusion interface

Reaction (9) is only observed when the CaO content of the slag is high enough to enter the CaTiO_3 field of crystallization in the $\text{CaO-TiO}_2\text{-SiO}_2$ phase diagram, as already described by Kishi et al. [17]. There was not such solid-state CaTiO_3 in the S3 slag/steel interface, and Ti could diffuse to S3 slag. Therefore, the content of Ti in steel decreased much (Table 6). TiN inclusions could be controlled by reducing the content of Ti in steel with acid slag S3 treatment.

With the high alkalinity slag refining, although the total oxygen is very low, there is a significant increase in the occurrence of D-type point inclusions in steel. Acid slag treatment after LF refining, not only reduce the harmfulness of D-type point inclusions to bearing steel, still has a well control to precipitation of TiN-type inclusions.

4 Conclusion

In this study, the effect of different acid slag treatment on the inclusions was investigated. The effect of acid slag on the kinetics of $\text{MgO} \cdot \text{Al}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{MnO}$ transformation was obtained and were discussed together with experiments results. Meanwhile, the inclusion transformation mechanism and TiN precipitation under acid slag refining was clarified. Conclusions are drawn as blow.

1. Slag with basicity of about 0.8 and Al_2O_3 content of 15%, MgO content of 6% is good for decreasing the melting temperature of inclusions in steel.
2. Slag composition is controlled well in acid slag treatment process, which would be beneficial to get proper composition of molten steel to promote the transformation of $\text{MgO} \cdot \text{Al}_2\text{O}_3 \rightarrow \text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{MnO} \rightarrow \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{MnO}$. Most inclusions' composition would begin to enter 1500°C liquid zone from late stage of acid slag treatment process, owing to proper composition of molten steel, which is beneficial for inclusions to continue to transform and to be eliminated by floatation until solidification of molten steel.
3. With the content of Ti decreased in acid slag treatment process, TiN precipitation decreased and the properties of bearing steel improved.

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