The Evolution and Thermodynamic Analysis of Inclusions in Gear Steel after Magnesium Treatment

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Abstract. The influence of different magnesium content on the inclusions in steel was studied under the condition of the same molten steel at 1873 K. The results show that, after the magnesium treatment, the tiny $MgO•Al_2O_3$ inclusions could become the nucleus of MnS in solidification of liquid steel, which weakens the large number of MnS precipitates in grain boundaries. The change of the oxide core in the composite sulfides with the increase of magnesium content is: Al_2O_3→$MgO•Al_2O_3$ →$MgO•Al_2O_3$+MgO→MgO+MgS.This evolution mechanism can provide certain reference for the application of magnesium treatment in production practice.

Introduction

The machinability of sulfur free-cutting gear steel depends on the size, shape and distribution of sulfide in steel. Sulphides also have a significant effect on the mechanical properties of steel. However, MnS will be tensile deformation along the rolling direction in the rolling process, which is harmful to the steel's lateral performance, resulting in anisotropy[1]. In order to eliminate or reduce the adverse effects of manganese sulfide on the mechanical properties of steel and ensure the cutting performance of steel, it is necessary to modify the manganese sulfide inclusions in steel.

Fu et al.[2]studied the type and formation mechanism of inclusions in Mg–bearing 35CrNi3MoV steel, and found that elongated MnS inclusion was replaced by small MgO•MgS and MgO•MgS•MnS complex inclusion. Zhang et al. [3] studied the effect of Mg treatment on the inclusions in steel with different sulfur content. MnS was easily precipitated on Mg oxides.

Based on the above, the modification rule of inclusions in steel was studied by thermodynamic calculation and scanning electron microscope, and the transformation process and modification of inclusions were deduced according to the sulfur-free cutting gear steel supplied by Baosteel, with adjusting the different amount of magnesium. The conclusion of the research can provide theoretical guidance for rationalizing the production process of Mg in molten steel, so as to effectively control the shape of sulfide inclusions in gear steel containing sulfur.

Test Methods

The raw materials include gear steel casting billet provided by Baosteel as well as Ni-Mg alloy (75%:25%), quartz tubes, molybdenum rods and high purity Ar gas (99.999%). Its components are shown in the following table 1:

Table 1 Chemical composition of gear steel wt.%

C	Si	Mn	P	S	Cr	Al	[O]
0.16	0.16	1.18	0.0065	0.0278	1.023	0.031	0.0019

The experiment procedures were as follows:600 g original billet steel were placed into in a magnesia crucible (ID: 53 mm, OD: 61 mm, H: 120 mm), and transferred into a pit-typy resistance furnace. Then, the sample was heated to 1873 K under high-purity argon flow (1 L/min), and the molten steel was hold for 20 min to achieve sufficient homogenization.

After the addition of the alloy, stirring was performed and the temperature was maintained for 10 minutes. Thereafter, the melt was held for 5 min, 10 min, 15 min and 20 min at 1873 K and then sampled, respectively. The samples were polished and observed under scanning electron microscope.

Results and Discussion

The final content of magnesium of the melts are listed in Table 2:

Table 2 Measurement results of magnesium and activity oxygen

No.	Mg（%）	Ni-Mg alloy（g）	Yielding rate	a(O)
1	0.0011	1.02	2.43%	24
2	0.0019	1.43	3.36%	20

From the measured values of oxygen in the table, it can be seen that the activity of oxygen decreases with the increase of magnesium content. The average yield of magnesium in the Ni-Mg alloy is 2.9%, which can provide a significant reference to magnesium addition experiment.

Microstructure and morphology evolution of inclusions

The shape and distribution of inclusions after the melting of the laboratory are shown in Figure 1:

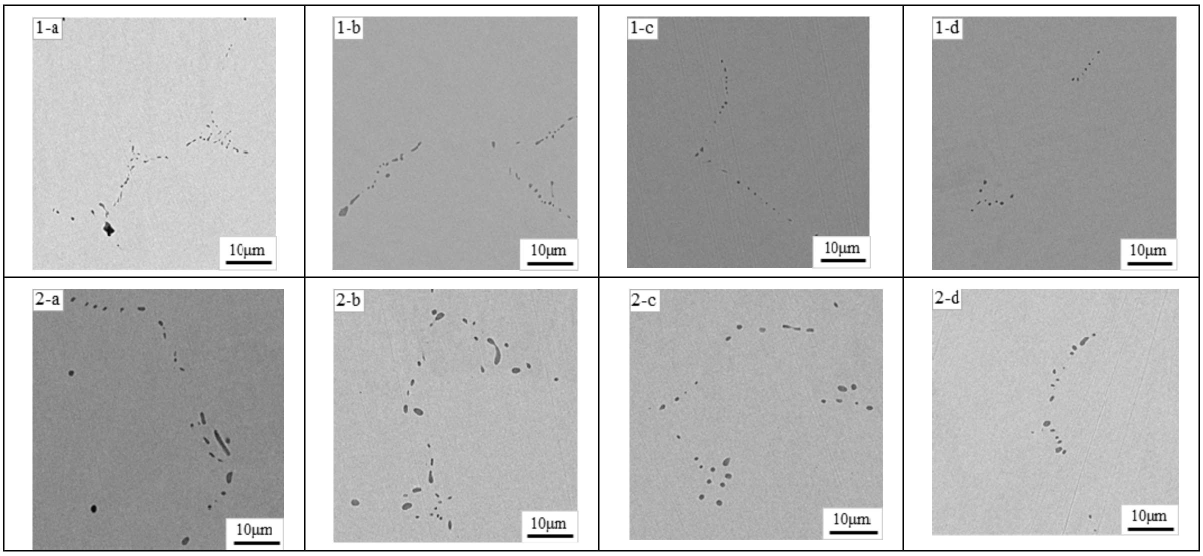

Fig.1 Variation of sulfide morphology with time

The sulfide inclusions in the sample taken at the four time points of magnesium deoxidization at 5 min, 10 min, 15 min and 20 min are shown in Fig.2 (a), (b), (c) and (d). It is found that inclusions show obvious grain boundary distribution, and many inclusions are elongated. With the increase of holding time, the number of inclusions is obviously reduced and weak the large number of MnS precipitates in grain boundaries.

Fig.2 shows the SEM micrographs of the oxide inclusions in the steel(the content of [Mg] is 19ppm) at different time after the treatment. The Mg-Al-O-oxides form the nucleus of the sulfides in the steel after Mg treatment, and the sulfide in the outer layer contains a small amount of Mg, that is, Mg-Mn-S composite sulfide, the content of [Al] in the inclusions gradually decreases with the increase of time, while the content of [Mg] increases.

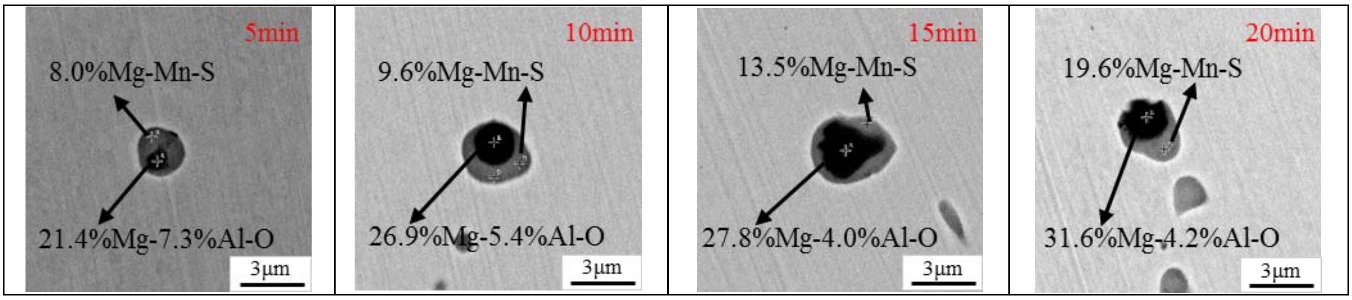

Fig.2 SEM images of inclusions with different time

The thermodynamics of oxygen and sulfur compound inclusions

To assess the evolution mechanism of inclusions,the thermodynamic calculation is necessary. Table 3 shows the Gibbs free energy of chemical reactions involved in the present work.

Table 3 Free energy data of reactions considered in the present work[4,5,6,7]

Reaction	$\Delta G/(J\cdot mol^{-1})$
$Al_2O_3(s)=2[Al]+3[O]$	867500-222.5T[10]
$MgO(s)=[Mg]+[O]$	90000+82T
$MgO\cdot Al_2O_3(s)=MgO(s)+Al_2O_3(s)$	20682+11.57T
$MgS(s)=[Mg]+[S]$	522080-201.02T
$MnS(s)=[Mn]+[S]$	167612-88.7T

Based on the thermodynamic data, the effect of sulfur and aluminum content on the MgO-MgO•Al2O3-MgS stable region is shown by the origin software at 1873K as shown in Fig 4.

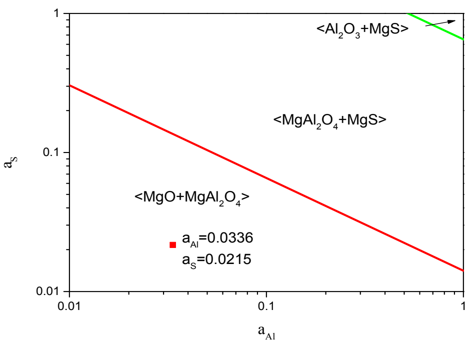

Figure 3 1873K, thermodynamic equilibrium diagram of MgO-MgS-MgAl2O4 conversion

The activity values of Al and S in the molten steel were obtained by using the experimental steel compositions given in Table 1 together with classical thermodynamic calculations. Because of the experimental steel components is much lower than the MgS-MgAl2O4-MgO equilibrium line, located in MgO and MgAl2O4 spinel temperature region,so MgS can not be formed at high temperatures. It is only possible for precipitation during the solidification process .

According to the phase diagram, with experimental steel's magnesium content marked in the figure correspondingly, drawn by Factsage thermodynamic software, it can get the following rules: The dominant zone of the inclusions in the original contrast sample is in the pure Al_2O_3 zone, while the content of Mg is 11ppm,the dominant area is in the MgAl2O4 spinel zone. As the content of Mg is further increased, MgO inclusions are formed which coexist with the MgAl2O4 spinel, and it is consistent with the observation results when the content of [Mg] is 19 ppm.

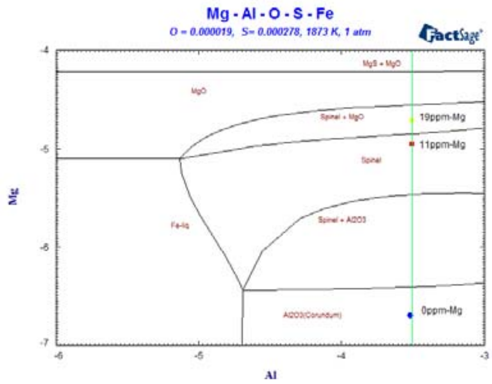

Fig. 4 stable region diagram of Fe-Mg-Al-O-S system at 1873K

Conclusions

1、By improving the effective of NiMg alloy addition method, it can be seen from the measured oxygen value that this method can effectively reduce the possibility of oxygen produced by splashing when NiMg alloy is added.the yield of Ni-Mg alloy was 2.9% according to the magnesium content after magnesium treatment.

2、The amount of inclusions in the steels decreased with the addition of Mg, and the formation of fine $MgO•Al_2O_3$ as the nucleation center of MnS in the steel weakened the precipitation of MnS at grain boundaries. The [Mg] in the composite sulfide surrounded by the O-oxide core mainly comes from the diffusion of Mg from the oxide core into the outer MnS.

3、With the increase of magnesium content, the inclusions are transformed according to the composition：$Al_2O_3 \rightarrow MgO•Al_2O_3 \rightarrow MgO•Al_2O_3+MgO \rightarrow MgO+MgS$. The observation results of the laboratory are consistent with the Factsage calculation results.

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