Evolution of Al_2O_3 inclusions by cerium treatment in low carbon high manganese steel

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ABSTRACT

The influence of cerium (Ce) treatment on the morphologies, size and distributions of Al_2O_3 inclusions in low carbon high manganese steel was investigated by OM, SEM-EDS and theoretical calculation. The results showed that Ce can modify the morphologies and types of Al_2O_3 inclusions. After Ce treatment, the irregular Al_2O_3 inclusions were replaced by smaller and dispersive spherical cerium oxysulfides. The effects of treatment time and Ce content on the evolution of Al_2O_3 inclusions were examined. It indicated that Al_2O_3 inclusions were wrapped by rare earth inclusions to form a ring like shape Ce-enriched band around the inclusions. Model was established to elucidate the evolution mechanism of Al_2O_3 inclusions. Evolution kinetics of inclusions was discussed qualitatively to analyze the velocity controlled step. It was found that diffusion of Ce^{3+} and Al^{3+} in solid inclusion core and the formed intermediate layer would be the limited step during the evolution process.

1. Introduction

Low carbon high manganese steels combined with the advantages of the superior low-temperature toughness and high strength are widely used as constructural materials[1-3]. Moreover, a series of high-quality low carbon high manganese steels have been developed to meet the expanding demand in market in the past few decades.

The strengths and toughness are influenced by many factors, such as inclusions, heat treatment, surface quality, microstructure and grain size[4]. The brittle cracks are prone to initiate from non-metallic inclusions; therefore, the inclusions are considered as the most significant factor to reduce the service life of the steels.

The compositions, shapes and size of inclusions are the main negative influencing factors on the strengths and toughness properties of the steels. Hard, large and angular inclusions could not be deformed accompanied with the steel matrix and they could easily be the stress concentration source at steel/inclusion interface during hot rolling, so they should be avoided in steels[5-8].

At present, aluminum is used for all killed carbon and alloyed steels[9]. The formed Al_2O_3 inclusions with acute-angled shape and large size are very harmful to the final quality of the steels, because they cause the defects of metal during its deformation[10]. In recent years, it has been reported that the addition of rare earth elements can improve the mechanical performance[11-15]. Most scholars mainly focused on the formation process and the control mechanism of inclusions in stainless steels, weathering steels and spring steels. However, the influence of rare earth on the low carbon high manganese steels, especially on the evolution process of Al_2O_3 inclusions, is rarely involved. Meanwhile, little was documented about the thermodynamics and kinetics of inclusions evolution and modification.

Based on the previous researches, the influence of rare earth elements on Al_2O_3 inclusions in low carbon high manganese steels is studied. The morphology, composition, and sizes of inclusions were comprehensively investigated. Moreover, the evolution mechanism of Al_2O_3 inclusions was illustrated in details.

2. Experimental

2.1. *Experimental procedure and sampling*

The experimental steels were melted in a high frequency vacuum induction furnace and then cast into ingot. The ingots were cut into small blocks by wire cutting for refining experiments. The refining experiments were carried out in a controlled atmosphere heating furnace, as shown in Fig. 1. Each sample was placed into a high purity corundum crucible and heated to 1873 K. The pure Ce element was added into the molten steel, and the experimental program is shown in Table 1. Then, the molten steel was immediately stirred for 15 s using the quartz tube. Finally, the samples were taken from the melt after Ce treatment at 0, 60, 180, 300, 480 and 600 s respectively and rapidly quenched by water.
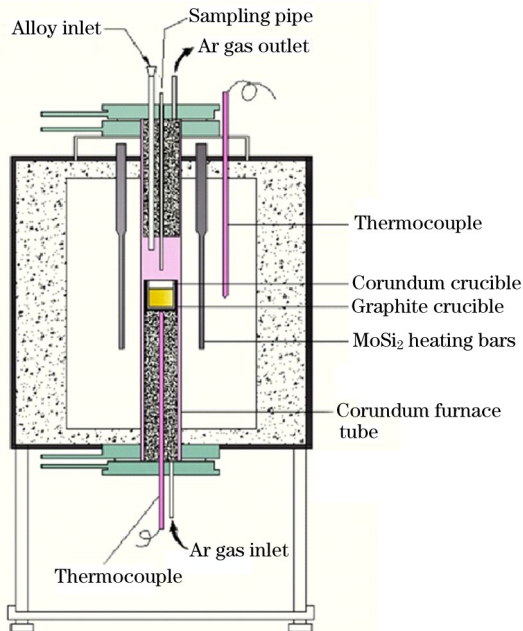

Fig. 1. Schematic diagram of controlled atmosphere heating furnace.

Table 1
Experimental program

Heat	Mass of bearing steel specimen/g	Ce content (theoretical addition)/wt. %	Total addition of Ce/g
1	463	0	0
2	445	0.02	0.089
3	457	0.03	0.137
4	466	0.05	0.233
5	453	0.07	0.317

2.2. *Analysis of samples*

All samples were prepared for chemical analysis, and the content of solid solution Ce was measured by low temperature electrolysis combining inductive

coupling plasma (ICP). Total oxygen contents were measured by fusion and the infrared absorption method. The morphology, size and chemical compositions of the inclusions were analyzed by SEM-EDS.

3. Results and Discussion

3.1. *Chemical compositions of steels*

The chemical compositions of each heat are shown in Table 2. The serial number of Table 2 are corresponding to the ones of Table 1. It can be seen that the final Ce contents in each heat are less than the theoretical ones, because a part of Ce is unavoidably lost in the metallurgical process.

Table 2
Chemical compositions of each heat (wt.%)

Sample	TO	C	Si	Mn	P	S	Al$_s$	Ce
1	0.0064	0.085	0.31	1.32	0.009	0.0085	0.011	0
2	0.0053	0.085	0.31	1.32	0.009	0.0071	0.011	0.012
3	0.0043	0.085	0.31	1.32	0.009	0.0065	0.011	0.018
4	0.0032	0.085	0.31	1.32	0.009	0.0057	0.011	0.026
5	0.0026	0.085	0.31	1.32	0.009	0.0049	0.011	0.034

3.2. *Thermodynamic calculation on Gibbs free energy of rare earth inclusions*

The thermodynamic calculations, which are based on the theory of minimum Gibbs free energy, were carried out to determine the evolution mechanism of the inclusions. Since oxygen, manganese, silicon and aluminum concentrations are very low, the melt could be assumed as an ideal solution so dilute solution of mass percent standard state was used. The Gibbs free energy data of chemical reactions and the corresponding interaction coefficient used in the present calculation are listed in Tables 3 and 4[16,17].

Based on the data involved, the Gibbs free energy of $Ce_2O_3(s)$, $Ce_2O_2S(s)$, $CeS(s)$, $Ce_2S_3(s)$, and

Table 3
Gibbs free energies of reactions used in present work

Reaction	$\Delta G^{\theta}/(J \cdot mol^{-1})$
$2[Ce]+3[O]=Ce_2O_3(s)$	$-1827424+643.8T$
$2[Ce]+2[O]+[S]=Ce_2O_2S(s)$	$-1352700+331T$
$[Ce]+[S]=CeS(s)$	$-394428+121T$
$2[Ce]+3[S]=Ce_2S_3(s)$	$-1073900+326T$
$[Ce]+2[O]=CeO_2(s)$	$-853600+250T$

Table 4
Interaction coefficients used in thermodynamic calculations at 1873 K

e_i^j	C	Si	Mn	P	S	Al	O	Ce
Ce	-0.077	—	0.13	—	-10.32	-2.58	-106	0.0069
O	-0.421	-0.066	-0.021	0.07	-0.133	-1.17	-0.20	-64
S	0.111	0.075	-0.026	0.035	-0.046	0.041	-0.27	-9.1

Note: i=Ce, O, S; j=C, Si, Mn, P, S, Al, O, Ce.