

NON-METALLIC INCLUSIONS IN CARBON STEEL CONTAINING RARE EARTH METALS

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ABSTRACT

The effect of rare earth metals (RE) on composition of carbon steel and the quantity, size and morphologies of inclusions were experimentally determined. Optical scanning electron microscopy and X-ray diffraction analysis as well as empirical calculations resulted that the RE affected the chemical composition of carbon steel and inclusions. The sulphur content did not vary. The inclusion quantity was increased. The RE modified inclusions, especially sulphides into small-smooth size under $4\mu\text{m}$. The steels containing from 0.01% to 0.02%RE have developed globular oxysulphide inclusions of Ib type; where as steels containing from 0.04% to 0.043% RE contain angular sulphide inclusions of IIIb type. When the RE content in steel was over 0.062%RE harmful cluster sulphide inclusions of IV type was formed.

Thus it was concluded that the RE beneficial affected the formation and modification of non-metallic inclusions in carbon steel.

KEYWORDS: Rare earth metals, inclusion, carbon steels

1. INTRODUCTION

The carbon steels, specially cast steels, contain significant amount of inclusions as well as stringer and ribbon manganese sulphides and macro-cluster aluminates⁽¹⁻⁷⁾. They are detrimental to steels, because they decrease mechanical, machinability and workability of steels⁽⁸⁻¹³⁾. A study on RE addition to carbon steel is necessary⁽¹⁴⁻¹⁷⁾. The RE are known to dissolve ribbon manganese inclusions of MnS and macro-cluster aluminates to refine small globular sulphide inclusions of Ib type⁽¹⁸⁻²²⁾. These inclusions were distributed uniformly in inner crystal grains of steel when the RE residual contents and ratio RE/S were convenient⁽²³⁻³⁰⁾. The heterogeneous angular sulphide inclusions of IIIb type were formed when amount of RE residual and ratio Al+Si/RE were optimal. These inclusions are less harmful than type II inclusion. When amount of residual RE is well over the threshold of cluster of globular sulphides of IV type. These inclusions were more harmful than I type sulphide inclusions during machining and deforming⁽³¹⁻⁴⁰⁾. The inclusions were

often smaller than 4 μ m and were undeformed⁽³⁷⁻⁴⁰⁾. The researchers were discussing more about the influence of RE additions on the desulphurization ability but little about the RE/S ratio regarding inclusion formation.

The present work carried out two series of experiments on the effect of RE on chemical composition of steel and inclusion, on inclusion's quantity, size and morphology.

2. EXPERIMENTAL

Two series of experiments with 8 samples each were carried out in the laboratory. The RE additions into low-carbon and high-carbon steels were varied from 0.5 to 2.0 kg/t. The RE additions were in the form of FeSiRE which composition as following: 25%RE (10%Ce and 7-8%La), 25%Si, 3%Ca, 5%Al and Fe remaining. The starting steels compositions are shown in table 1.

Table 1. Chemical compositions of RE free samples

steels	chemical content (wt.%)							
	C	Mn	Si	P	S	Al _t	O _t	N ₂
low-carbon	0.29	0.33	0.12	0.015	0.021	0.12	0.00726	0.0094
high-carbon	0.58	0.18	0.11	0.015	0.024	0.07	0.0205	0.0062

Experiments were carried out in an induction furnace of type GV-22 with a maximum electric power of 22kW. The carbon steels were melted in Al₂O₃ crucibles (99%Al₂O₃ in the form of ingot. The melting process was as following: the steels were heated to a temperature of 1600°C to 1620°C measured with a PtRhPt16 thermocouple, then it was deoxidized by aluminium wire. After one minute, the sample was taken and symbolized "o" (it means free RE). The REs were added into melts with varying amounts of 0.5, 1.0, 2.0 kg/t for each steel.

All samples were cast into copper moulds. These samples were treated and machined for analysis and measurement. The chemical compositions of steels were analyzed quantitatively. The oxygen, nitrogen and oxide phases were analyzed in LECO-TC436 machine. The microstructure analysis was carried out microoptical microscope (Neophot II). Selected samples from each series were examined with a SEM (JEOL-35CF and EDX by LINK 860/II). The type of inclusions were determined in the X-ray diffractometer (DX5000).

3. RESULTS AND DISCUSSIONS

3.1. Cleanliness of steels

The results of chemical composition of steels were shown in table 2.

The table 2 shows that residual content of RE in steel ranges from 0.007% to 0.094% (from 0.005% to 0.061%Ce). This result corresponds with point A of figure 1⁽⁴¹⁾.

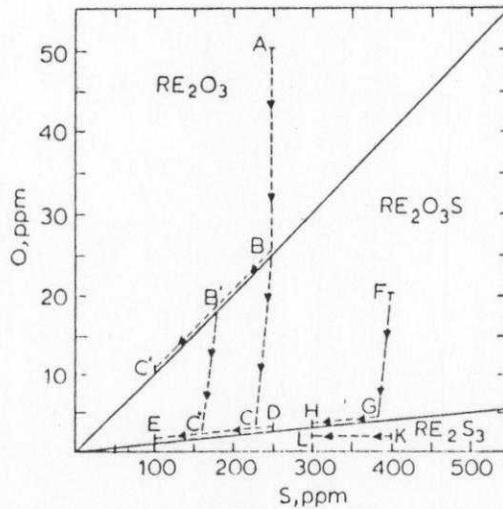


Figure 1. Schematic of reaction paths for sequential and coupled deoxidation-desulphurization reactions⁽⁴¹⁾

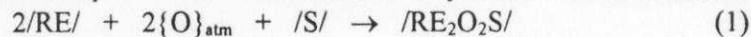
Table 2. Chemical composition of steel samples

sample No	(wt.%)										
	C	Mn	Si	P	S	Al _t	O ₂	Ce	La	RE	N ₂
A ₁	0.032	0.05	0.04	0.015	0.021	0.019	0.00806	0.005	0.002	0.007	0.00620
A ₂	0.120	0.30	0.32	0.015	0.021	0.010	0.00843	0.021	0.020	0.041	0.01475
A ₃	0.030	0.16	0.43	0.016	0.020	0.070	0.01920	0.028	0.035	0.063	0.00649
D ₁	0.590	0.28	0.17	0.015	0.024	0.070	0.01310	0.012	0.008	0.020	0.00704
D ₂	0.660	0.46	0.37	0.016	0.024	0.075	0.01260	0.025	0.014	0.039	0.01190
D ₃	0.620	0.41	0.64	0.016	0.024	0.078	0.00980	0.061	0.033	0.094	0.01110

The table 2 also shows that when RE addition was increased from 0.05 kg/t to 2.0 kg/t the low-carbon steels has varied sulphur content, but high-carbon steels show no change in sulphur content. These can be explained from modification side of sulphide inclusions i.e., means sulphide shape control. In the sample A₃ of sulphur content was reduced with RE addition to 2 kg/t. The RE addition also decreased oxygen contents in high-carbon steels and in contrast the oxygen content in low-carbon steels were increased. The RE dissolves in high-carbon steels more than in low-carbon steels as shows table 2.

The reciprocal effects of RE, O, S depend on ratios of RE/S which can be seen in figure 2.

The figure 2 shows that the RE additions into high-carbon steel have reduced oxygen content. Where as low-carbon steels increased oxygen contents. In fact, the RE additions affected the deoxidation of steels. The oxygen from atmosphere and around steel tapping current reacted with RE in steel from point E with back direction to point F. The reactions occurred as follows:



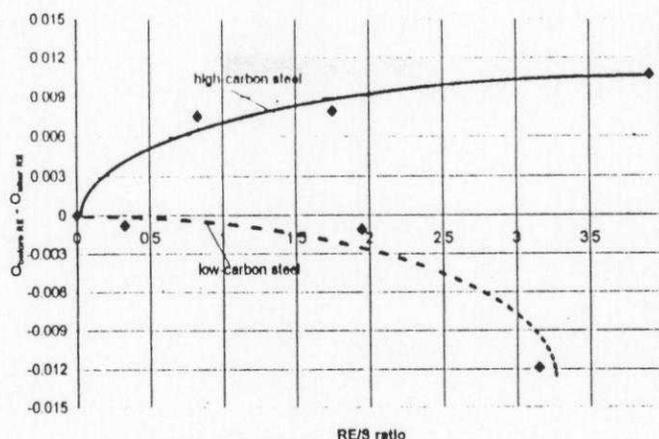


Figure 2. The relationship between $\Delta O(O_{\text{before RE}} - O_{\text{after RE}})$ and RE/S ratio in steels. This oxygen was transferred into steels, resulting in an increase of oxygen contents in low-carbon steel. The reoxidation of steel was an important problem⁽⁴²⁾.

3.2 The chemical composition of inclusions

The results of chemical compositions of inclusions were shown in table 3.

Table 3. Chemical composition of inclusions in steels

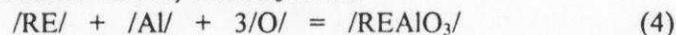
sample number	area	number	area	area/number	chemical content (wt.%)						
					No	-	μm^2	cm^{-2}	%	μm^2	Al
A ₀	271	1798	10170	0.0675	6.6	15	2	2	43	37	0
A ₁	244	5184	10988	0.2334	21.2	42	38	3	0	12	5
A ₂	258	1743	3417	0.0231	6.8	13	1	2	27	5	52
A ₃	261	1483	8398	0.0477	5.7	9	0	3	13	1	74
D ₀	273	2463	6830	0.0616	9.0	20	17	3	47	14	0
D ₁	255	1941	8203	0.0624	7.6	17	14	3	36	20	10
D ₂	262	1495	7374	0.0421	5.7	9	2	2	30	21	36
D ₃	255	2342	19139	0.1758	9.2	3	0	3	17	1	76

The table 3 shows that before additions of RE, aluminates and manganese sulphides were present in the steel. The addition of RE into steel reduced the sulphide quantity, especially in sample A₁ any sulphide wasn't observed. In fact, manganese sulphide also were not appeared. This can be explained through following reactions:

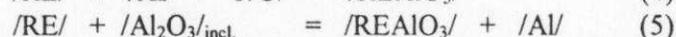
When RE content reached to 0.008% ($\text{Al} + \text{Si} / \text{RE} > 1$) $\text{REAl}_{11}\text{O}_{18}$ forms^(15,43-47):



When RE content was about 0.02%, REAlO_3 forms⁽⁴³⁻⁴⁷⁾:



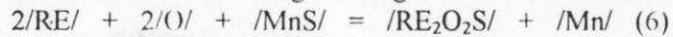
and



The quantitative examinations by SEM, EDX and X-ray resulted that the residual RE content from 0.02% to 0.07% formed oxysulphide cores ($\text{RE}_2\text{O}_2\text{S}$). The peels were surrounded by cores with stoichiometric sulphides (RE_xS_y). There was another case where REAlO_2S formed.

These results accorded with previous works^(15,17,48,49, 50). When RE contents in steel in high (over 0.07%) RES^(15,44) appeared and simple RE oxide was not observed. This result agrees with recently published works^(43,44,50).

When the RE addition is raised to 2.0 kg/t MnS gets dissolved as following:



Thus RE reacted to form mainly oxysulphides and heterogeneous oxysulphides along paths BC, B'C' and FG in figure 1. The RE affected the removal of cluster aluminates and ribbon manganese sulphides according to reactions (4), (5) and (6).

3.3. Quantity and size of inclusions in steel containing RE

Inclusion quantity and size distribution are shown in figure 3, where the relationship of RE addition to the inclusion number and size in two low-carbon and high-carbon steels were shown in sample A₂, there was the lowest number of total inclusion when RE was added in the ture of 1 kg/t. There was total of 3417 inclusions per cm²(shows figure3). While total oxide inclusions are very low, e.g., 676 inclusions per cm² (shows figure 4).

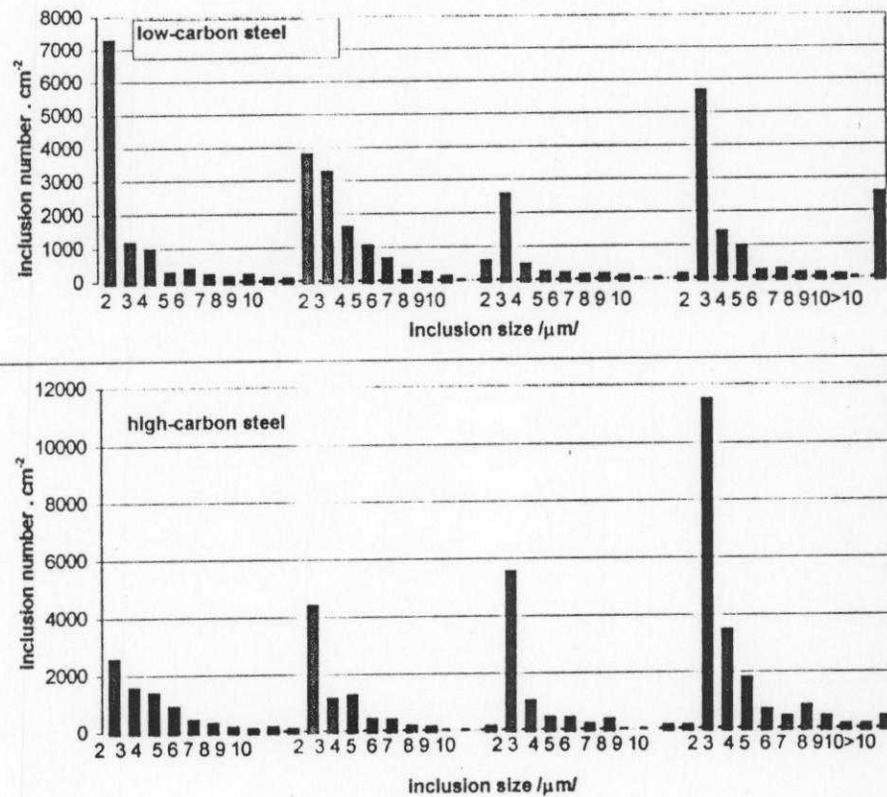


Figure 3. Effect of RE addition on inclusion number and inclusion size in carbon steel

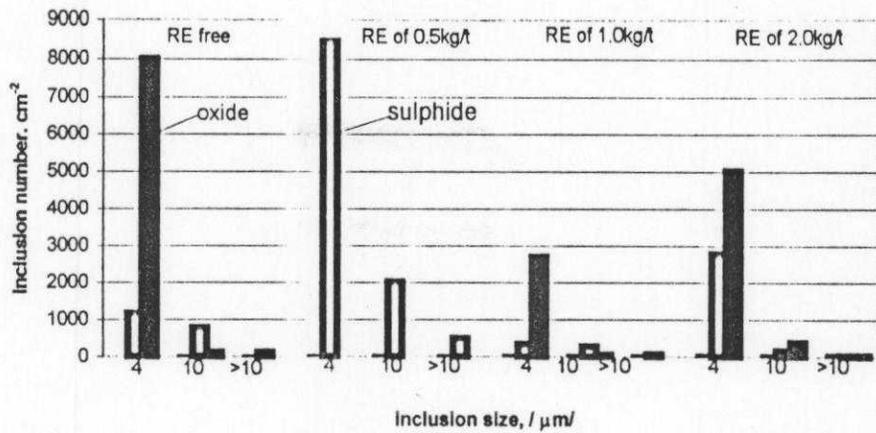


Figure 4. Oxide and sulphide numbers in low-carbon steel containing RE(series A)
 The total inclusion number was the lowest in sample D₂, when RE added in the ture of 1.0 kg/t (figure 3). The total oxide number was obtained to be 1041 inclusions per cm² (shows figure5).

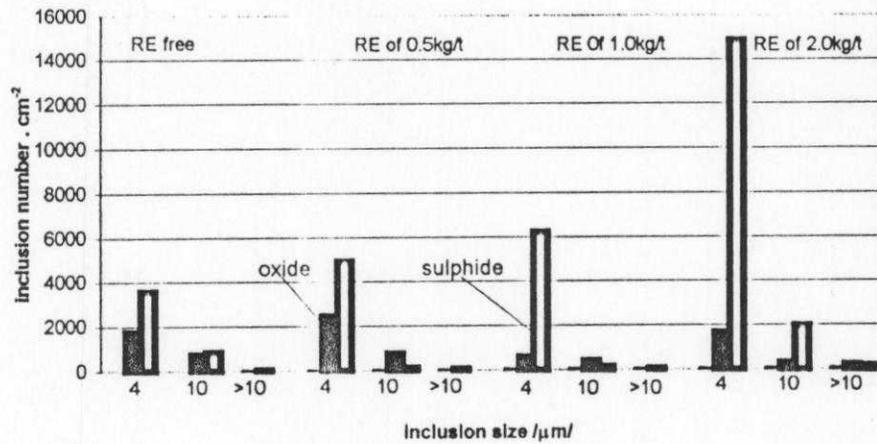


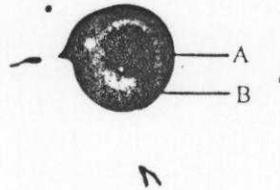
Figure 5. Oxide and sulphide numbers in high-carbon steel containing RE (series D)
 The general observation in most samples containing RE is the numbers of inclusion have increased compared with the RE free samples. This problem can be explained as follows: the added RE into steel reacted with oxides and sulphides presenting in steel and refined them into more small & smooth inclusions. These inclusions distributed uniformed in the sample. These inclusions were refined to size under 4 μm, so that they can not be harmful to steel during deformation and machining. In fact, there were about 86 to 96% inclusion refinement to 1-4 μm size range and not inclusion over 10 μm. The samples of serie D shows that the added RE to 1.0 kg/t can remain in this stee, where as 1 0.042%RE results the smallest inclusion sizes.

The RE affects surface tension of inclusions, especially surpresses and restricts surface activity of MnS. The RE oxides and sulphides are thermodynamically stabile. The value of surface tension of RE inclusion was very high, and therefore have not grown in size. It is an important character of inclusion modification.

3.4. Morphology of inclusions in steel containing RE

The results about studies of inclusion morphologies were shown in figures 6, 7, 8 and 9.

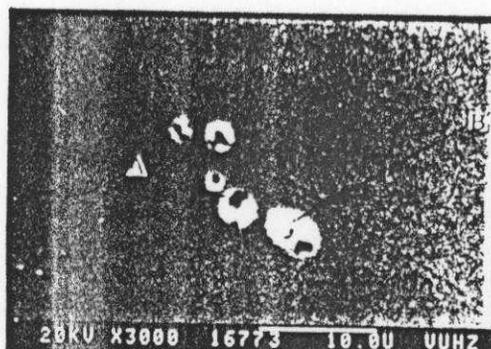
The figures shows that RE free steels only presented cluster aluminates , silicates and manganese sulphides (shows figure 6.).



A	Al	Si	Ca	S	Mn	La	Ce	O (wt%)
10.8	23.7	0.6	0.9	13.8	0.3	0	79.9	

Figure 6. Optical micrograph of an inclusion in low-carbon steel before RE adding in sample A₀, x500

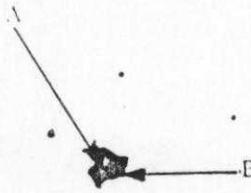
The low-carbon steel containing RE (0.5 kg/t) were observed to have globular sulphides of Ib type. The complex oxysulphides containing Al, Si, RE also appeared (shows figure 7.). Thus the residual RE contents in steel from 0.01% to 0.02% formed globular oxysulphides of Ib type. This



	Al	Ca	S	Mn	Mg	La	Ce	O (wt%)
A	8	1	21	1	1	22	31	15
B	19	-	12	1	1	18	26	23

Figure 7. The typical inclusion of Ib type in low-carbon steel after RE adding to 0.5 kg/t in sample A₁, x500,

result was accorded with recent work⁽⁸⁾. When RE addition raised to 1.0 kg/t and remained in steel from 0.041% to 0.044%RE, angular heterogeneous sulphides and oxysulphides of IIIb type formed. These inclusions contained RE, Al and Mn (shows figure 8.). These inclusions were less harmful during machining than inclusions of I type. When the RE additions were raised to 2.0 kg/t the remaining RE contents in steel change from 0.062%RE to 0.094%, causing the formation of typical cluster oxysulphides of IV type (shows figure 9). These kinds of inclusion are more harmful than inclusions of I type. From X-ray analysis and composition the globular inclusions of Ib type were formed to have the stoichiometrs RE₂O₂S type. The angular inclusion of IIIb type have stoichiometrs are of REAlO₂S. The cluster heterogeneous inclusions of IV type are of the following type : the cores were RE₂O₂S and the peels were RES or RE_xS_y. These results are not in contrast with our previous works^(19,24,25,33,34).



	Al	Ca	Si	S	Mn	La	Ce	O (wt%)
A	51,9	0.1	0	0.1	0	1.6	3.6	41.7
B	16.1	0.2	0.8	0	0	12.5	27.8	42.6

Figure 8. The typical inclusion of IIIb type in low-carbon steel after 1.0 kg/t RE addition in sample A₂, x500

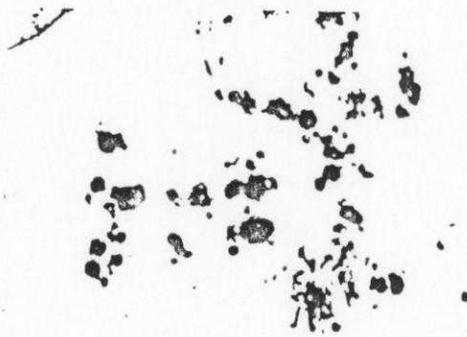


Figure 9. The typical inclusion of IV type in high-carbon steel after 2.0 kg/t RE addition in sample D₃, x500

From the results cited above excessive RE addition is not needed, otherwise it may cause harmful effects like reduction of mechanical properties and machinability of steel and cleanliness.

In the present experimental conditions, it can be emphasized that the RE additions did not reduce sulphur contents in steels. The RE sulphides formed are of high densities, and therefore could not be floated to slag and they remained in steel. The affects of RE additions were conduced from modification aspect. It was globularization, refinement and uniform distribution of inclusions. The RE additions removed macrocluster aluminates, and ribbon manganese inclusions. These characters of RE inclusions are essential.

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