

USING Ce TO MODIFY INCLUSION IN SPRING STEEL

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Abstract

The effect of rare earth metals addition on the Al_2O_3 inclusions in spring steel used in fastener of high speed railway was investigated by metallographic examination, SEM-EDS and composition analysis. To deform those harmful inclusions to improve material performance, the evolution process of Al_2O_3 inclusions was investigated through the surface and line scanning. Ce metal modifying Al_2O_3 is a stepwise reduction process based on a formation of ring shape Ce-riched band around the Al_2O_3 inclusions during reaction process. Through experiment and thermodynamic calculation, an evolution rule about Al_2O_3 inclusions change after Ce addition is obtained, i.e. $Al_2O_3 \rightarrow Ce_2O_3 \cdot Al_2O_3 \rightarrow Ce_2O_3 \cdot S$. Changing the inclusions from Al_2O_3 to rare earth inclusions could improve the resistance to pitting corrosion based on potentiodynamic anodic polarization test.

Keywords: Cerium; Inclusions; Thermodynamic calculation; Al_2O_3 ; Spring steel

1. Introduction

Al_2O_3 inclusions are often observed in Al-killed steel as the deoxidation product. Such inclusions are commonly considered to be very harmful to the quality of the final products, acting as the main sources of pitting corrosion [1] as well as the origin of micro-cracks and causing the clogging of submerged entry nozzle during continuous casting due to their high hardness and high melting temperature [2]. X.Zhang indicates that crevice can easily form around the Al_2O_3 particles when the inclusions grow up to a certain size, so that large Al_2O_3 inclusions is easy to be the origin of pitting corrosion when the environment is full of Cl⁻ [3]. The technique of rare earth metal addition into steel is sometimes used due to the beneficial effects of their use in steels. In recent years, Al_2O_3 inclusions have been widely investigated, and most of the reports mainly concentrated on calcium treatment to modify Al_2O_3 inclusions in steel [4-8], while the effect of rare earth element, such as Ce, on the modification of Al_2O_3 , is rarely involved.

A considerable amount of researches have been conducted on predicting the thermodynamic behaviors of rare earths in steelmaking during the past several decades [9-11]. S.Diao [12] determined the standard free energy of formation of $CeAlO_3$ and

$NdAlO_3$ in steel melt. G.Li and H.Suito [13] determined that the effect of Ce on the super saturation behavior of the precipitation of Al_2O_3 . A.Katsumata [14] studied large cluster inclusions by Al-Ce complex deoxidation in steel and found that deoxidation products have Al_2O_3 , $CeAlO_3$ and Ce_2O_3 and S.K. Kwon [15] also found the similar phenomenon in the formation behavior of inclusions in Ce-containing stainless steel. L.J.Wang [16] indicate the mechanism of dissolution of Al_2O_3 in the Ce_2O_3 containing slag and it could propose as three steps involved: 1) the formation of calcium aluminates $CaO \cdot Al_2O_3$ at the interface 2) the formation of $3CaO \cdot Al_2O_3 \cdot Ce_2O_3$ as the reaction progresses; and 3) the dissolution of $3CaO \cdot Al_2O_3 \cdot Ce_2O_3$ into the slag. Several researchers have reported that the rare earth oxysulfides are found more often than the sulfides or oxides [17-18], but the effect of S content is little involved in the inclusions changing process.

SH. Jeon et al [19] point out that the addition of Ce to the HDSS increases the resistance to pitting corrosion because of the formation of stable Ce oxide and a decrease of pit initiation sites. It is certainly worthwhile for industrial purposes if the pitting-corrosion resistance of spring steel can be improved through the addition of rare earth metals to the spring steel. Thus, it would be

Dedicated to the memory of Professor Dragana Živković

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useful to carry out Ce treatment to partially evolution of Al_2O_3 to reduce the possibility of pitting corrosion.

In this paper, the formation of Al_2O_3 inclusions in spring steel used in fastener of high speed railway at 1873 K is discussed in detail. The effect of Ce metal addition on a change of inclusion chemistry was discussed. In addition two thermodynamic phase stability diagram of the inclusions were calculated by FactSage6.4 software. An investigation has been made on the influence of the inclusion types on the resistance to pitting corrosion.

2. Experimental procedure

All the raw materials including the aluminum are added into a high frequency vacuum induction furnace to obtain the initial spring steel and then cast into ingot under an Ar atmosphere. Table 1 shows the chemical compositions of the experimental steel.

Table 1. Chemical composition (wt %) of the spring steel

Elements	C	Si	Mn	Cr	Ni	V	Ti
Content	0.45	1.9	0.7	0.7	0.9	0.075	0.035

2.1. Inclusion modification

The ingot was cut to appropriate block by wire cutting. In a typical run, 180g of spring steel were contained in an MgO crucible (ID of 30 mm, OD of 40 mm, and height of 85 mm) and placed in a vertical $MoSi_2$ resistance furnace. The temperature of the liquid steel was controlled in 1873K under high-purity Ar atmosphere. In order to protect Ce metal (99.9%, aladdin) from oxidation, the Ce metal was wrapped in reduced iron powder and pressed into a metal cylinder, then added the metal cylinder wrapped in pure iron chips to the molten steel and stirred the molten steel by using a long quartz tube. It has good effect on Ce homogeneity in the molten steel. The addition of Ce metal is based on the experimental program which is showed in Table 2. After 5 min for steel-inclusion reaction, the crucible was rapidly quenched by water from the furnace. All tests in our experiment have the same experimental manipulation including cooling treatment. The only difference is the content of Ce addition. Thus, we consider the different inclusions caused by Ce content in molten steel instead of cooling rate.

2.2. Analysis

To observe the inclusions in the spring steel, the metallographic sample (10mm×10mm×10mm) were

Table 2. Experimental program

No	1#	2#	3#	4#	5#	6#
Steel/g	180	180	180	180	180	180
Ce addition /%	0	0.007	0.014	0.028	0.06	0.12

obtained from treated steel center and ground to 2000 grit using SiC abrasive papers, then polished with diamond paste. The chemical compositions and morphology of inclusions were analyzed through a scanning electron microscope (SEM) and an energy dispersive spectroscope (EDS). Each sample was observed with 10 view fields under magnification 500 times (0.034 mm²), and approximately 100 inclusions were observed which depends on the cleanness of the steel sample. The chemical composition of steel samples was analyzed through ICP-AAS or ICP-MS. The oxygen activity in steel melt was measured by an electro motive force method (EMF) at 1873K.

2.3. Corrosion test

Three kinds of spring steel sampled from 1#, 2# and 6# test were used to investigate the effect of inclusion types on the resistance to pitting corrosion, and it were analyzed by a potentiodynamic anodic polarization test in the deaerated 3.56wt% NaCl solution at 298 K by applying the method defined by the ASTM G61. The test samples were welded with copper wire through solder and then embedded by the epoxy resin. The side of sample used in this test was polished with 600-grit SiC paper until previous coarse scratches were removed, then rinsed and dried. The exposed area of test samples was 1cm².

3. Result and discussion

3.1. Effect of Ce addition on spring steel chemical compositions

The chemical composition of each sample is conducted, and the results are showed in Table 3. As can be found, the alumina and magnesium contents varied in the range of 0.051~0.054% and 0.0001~0.0002%, respectively. In addition, the yield of Ce decreased with the increasing of theoretical addition. The oxygen activity, total oxygen contents and sulfur contents varied in the range of 0.000018~0.000009, 0.005%~0.0012% and 0.0042%~0.0025%, respectively. The addition of Ce decreased the oxygen activity, total oxygen contents and sulfur contents in steel melt.

Table 3. The analysis results of chemical composition (wt%)

Elements	1#	2#	3#	4#	5#	6#
Ce	0	0.006	0.011	0.017	0.034	0.056
Al	0.051	0.053	0.052	0.056	0.052	0.054
Mg	0.0002	0.0001	<0.0001	<0.0001	0.0001	0.0001
[O]	0.0018	0.0017	0.0016	0.0014	0.0011	0.0009
S	0.0042	0.0041	0.0038	0.0035	0.003	0.0025
T.O	0.005	0.0038	0.0031	0.0026	0.002	0.0012



3.2 Evolution of inclusion in spring steel after Ce treatment

3.2.1. Effect of the Ce addition on the characteristics of inclusions

The typical inclusions in 1# to 6# steel sample were observed through SEM and the chemical composition of inclusions were analyzed by EDS attached to the SEM, as shown in Fig. 1 and Table 4. From the statistical results, it was known that the inclusions in 1# steel sample were mainly composed of Al₂O₃ type after alumina deoxidation. In addition, clusters of Al₂O₃ inclusions with the angular shape were observed in the present study. The Al₂O₃ inclusions wrapped by rare earth inclusions were observed in the 2# and 3# sample. With the increasing of Ce content in steel melt, inclusions in 1# steel were completely modified to rare earth oxysulfides in 4# steel sample ([Ce%]>0.017). When Ce content further increases, the inclusions in 5# and 6# sample were still rare earth oxysulfides. In addition, the shape of the inclusions became globular or spheroid.

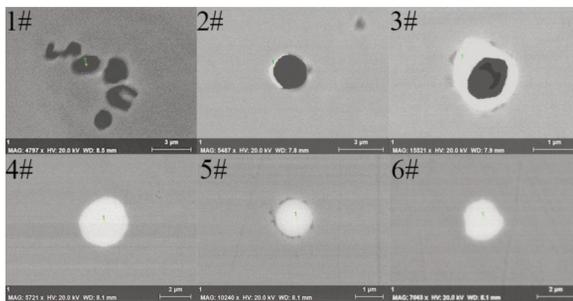


Figure 1. SEM images of typical inclusions in 1# to 6# steel sample

The inclusion size distribution and average size are shown in Fig. 2. The large inclusion distribution and inclusion average size decreased with the increasing content of Ce in the present results. It indicates that the addition content of Ce plays an important role in the size distribution of inclusions.

From these findings it could be concluded that there would be an optimal addition content of Ce in which inclusions were refined. Therefore, the appropriate addition of Ce could contribute to producing the fine and dispersive rare earth inclusions.

3.2.2 Effect of Ce addition on the evolution of Al₂O₃ inclusions

There are three main roles of rare earths in steels, which are modification of inclusions, deep deoxidation and desulphurization, alloying. As described above, modification of inclusions, such as MgO·Al₂O₃ and Al₂O₃, can be achieved through

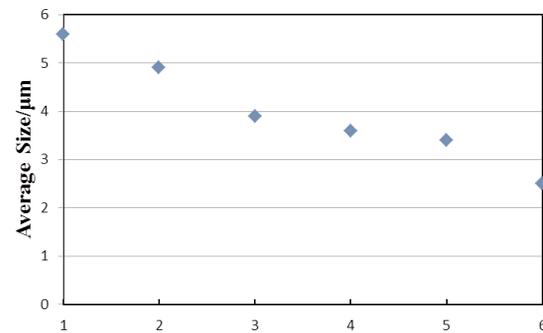
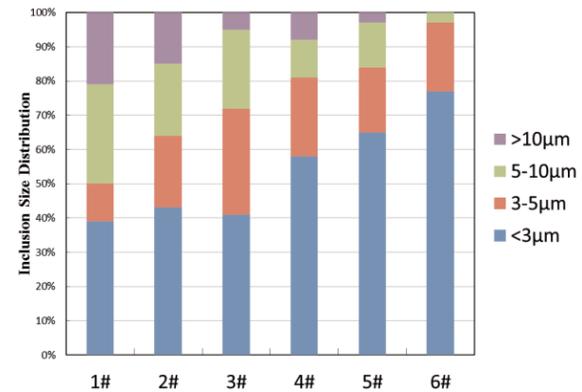


Figure 2. Changes of inclusion size distribution and average size

Table 4. EDS analysis of typical inclusions in 1# to 6# steel sample

wt%	Al	Ce	O	S	Fe (matrix)	
1#	54.41 ± 3.21		45.59 ± 4.21			Al ₂ O ₃
2#A	34.82 ± 1.81	17.26 ± 1.14	33.23 ± 2.33	3.45 ± 0.33	11.24 ± 0.89	Al ₁₁ O ₁₈ Ce + Ce ₂ O ₂ S
2#B	51.24 ± 3.89	5.46 ± 0.41	40.85 ± 4.42		2.45 ± 0.15	Al ₂ O ₃
3#	10.34 ± 1.02	53.62 ± 4.31	20.78 ± 3.14		15.26 ± 1.24	AlCeO ₃
4#		82.21 ± 6.25	17.79 ± 2.31			Ce ₂ O ₃
5#		75.99 ± 4.32	10.53 ± 1.21	3.46 ± 0.31	10.02 ± 1.16	Ce ₂ O ₂ S
6#		86.98 ± 4.16	5.19 ± 0.89	7.83 ± 0.85		Ce ₂ O ₂ S



adding the Ce metal to the steel melt. Ce plays an important role on the shape control and the modification of inclusions in spring steels.

Fig. 3 shows the SEM-Mappings of the Ce_2O_3 - Al_2O_3 or Ce_2O_3 - S - Al_2O_3 system inclusions. Fig. 3(a) and Fig. 3(b) are the typical inclusions in test 2 and test 3 after Ce treatment, respectively. When the Ce alloy added into the steel melt at 1873K, Ce compounds correlating with O began to aggregate and react with Al_2O_3 inclusions. It was determined that shared features of Ce_2O_3 - Al_2O_3 system inclusions were high Al content in the inner part while the high Ce content in the outer surface. And almost no S distributed in the inclusions. Moreover, the concentration of Ce was much higher in the outer surface of inclusion while much less in the inner part forming a ring shape Ce-riched band around the inclusion in the SEM-mapping image, as shown in Fig. 3(a). The Al_2O_3 inclusions were wrapped by the inclusions containing Ce content. However, there

were some differences between SEM-mappings of inclusions in Fig. 3(a) and that of inclusions in Fig. 3(b). It was found that common features of Ce inclusions were high Ce content in the whole inclusions except for a very small region in the inner part. Concentration of Al in the inner part of inclusions in Fig. 3(b) was lower than that in the inclusions in Fig. 3(a). And a high S content region was found in the outer surface. Particularly, Ce concentration zone and Al concentration zone seemed to be incompatible and complementary in the SEM-Mapping images, which was more obvious in Fig. 3(a).

Therefore, it is believed that rare earths inclusions can transfer from high melting temperature Al_2O_3 inclusions, which also has been proved by SEM line scanning results.

SEM line scanning results of inclusion in test 2 was shown in Fig. 4. As can be seen in Fig. 4, the inclusions core was mainly composed of Al_2O_3

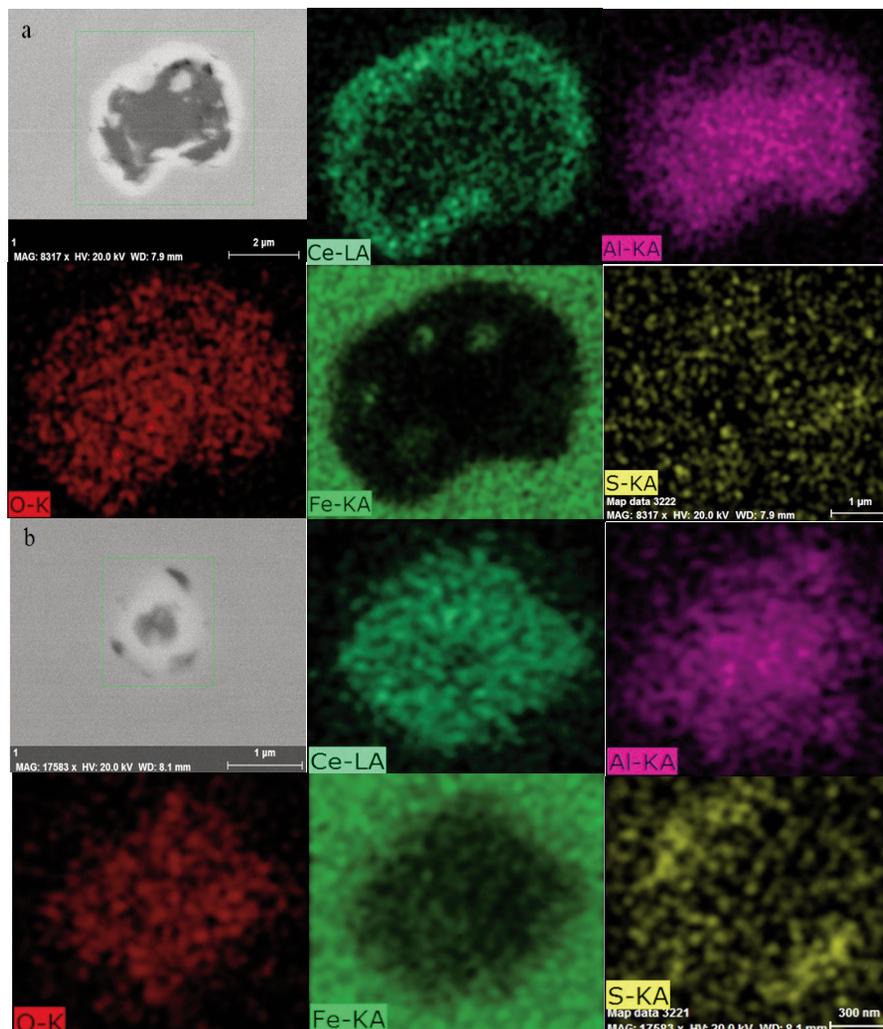


Figure 3. SEM-mappings of transferring inclusions

content that changed along width direction and Ce had a high content at the edge of inclusion. Nevertheless, S content was low and changed little along the width direction. It is concluded that the inclusion is being changed from $Al_2O_3 \rightarrow Ce_2O_3-Al_2O_3 \rightarrow Ce_2O_2S$.

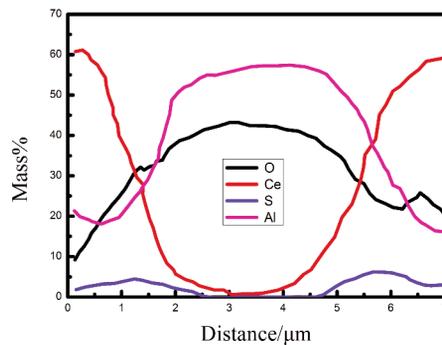
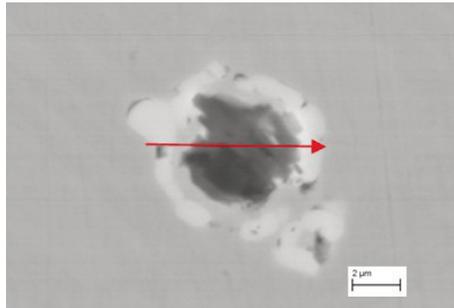


Figure 4. SEM line scanning of transferring inclusions

Based on the above SEM-mapping and line scanning results of inclusions, it was summarized that the high melting temperature and solid Al_2O_3 inclusions wrapping by rare earths inclusions layer was the common feature of all $Ce_2O_3-Al_2O_3$ or $Ce_2O_2S-Al_2O_3$ system inclusions. At last, the shape of inclusions evolved from irregular into spherical rare earths inclusions with the increase of [Ce] content.

3.3. Thermodynamic calculation on evolution of inclusions

The stability diagrams of Ce-O and Ce-S were calculated by using FactSage6.4 software (Databases:FToxid, FactPS, FTmisc, Phase Diagram module) based on the spring steel chemical composition at 1873 K. The results were shown in Fig. 5.

In Fig. 5(a), the inclusions could change in the order of “ $Al_2O_3 \rightarrow Al_{11}O_{18}Ce \rightarrow AlCeO_3 \rightarrow Ce_2O_2S$ or $Ce_2O_2S+Ce_2O_3$ ” by increasing the content of Ce at oxygen content from about 0 to 0.02 %. The Ce_2O_2S is the most stable inclusion phase by increasing the content of Ce at oxygen content less than 0.004 % in spring steel. In Fig. 5(b), the inclusions could change in the order of “ $Al_2O_3 \rightarrow Al_{11}O_{18}Ce \rightarrow AlCeO_3 \rightarrow Ce_2O_2S$ ” by increasing the content of Ce at S content

from about 0.002 % to 0.01 %. The Ce_2O_3 inclusion could generate by increasing the content of Ce at S content less than 20 ppm in spring steel. Ce_2S_3 and Ce_3S_4 inclusions could form by increasing the content of Ce at S content more than 0.01 % in spring steel.

Fig.5(a) and Fig.5(b) shows the data points corresponding to the experimental [Ce]-[O] and [Ce]-[S] contents in steel samples (5 min), respectively. It can be obtained from Fig. 1-5 and Table 3-4 that the inclusion variation is $Al_2O_3 \rightarrow Al_{11}O_{18}Ce \rightarrow AlCeO_3 \rightarrow Ce_2O_2S$ in present spring steel at 1873K and Ce_2O_2S represent the stable inclusion phase in present molten spring steel, which a similar evolution process between thermodynamic calculation and experiment results. Therefore, Ce metal modifying Al_2O_3 is a stepwise reduction process.

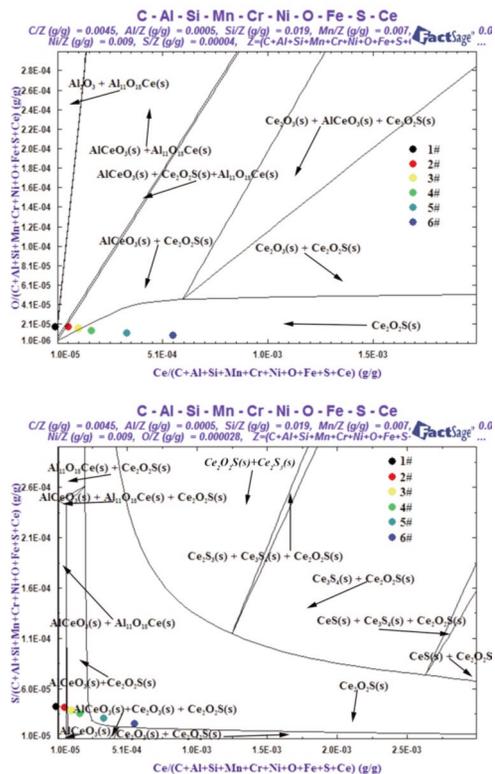


Figure 5. Phase Diagram of Ce-O and Ce-S in molten spring steel

3.4. Illustration on evolution of inclusions after Ce treatment in spring steel

Through the above results of experimental data and thermodynamic calculations, the evolution process of inclusions had been known. To further understand the evolution process of inclusions, it is necessary to illustrate the process about inclusions transformation. The change process of inclusions was clearly described by Fig. 6 and illustrated as following:



(1) Al_2O_3 inclusions and clusters were quickly formed in steel melt in a few minutes after Al deoxidization adding to steel melt, as shown in Fig. 6 (a).

(2) The formed Al_2O_3 was not stable when Ce was added into steel melt. With the process of reaction, [Al] would be reduced from Al_2O_3 inclusions by chemical reaction Eq. (1) and (2). As a result, the Al_2O_3 inclusions would be transferred into $\text{Al}_{11}\text{O}_8\text{Ce}$ and AlCeO_3 inclusions as presented in Fig. 6(b). However, Fig. 6(b) is shown the intermediate state of inclusion modification process. The inclusion modification process is fitted to the unreacted core shrinking model. Thus, the new formation phase is distributed in surface of inclusion, which would make the inclusion heterogeneous.



(3) With the increasing of Ce addition, the AlCeO_3 would be transferred into $\text{Ce}_2\text{O}_2\text{S}$ by chemical reaction Eq. (3). As shown in Fig. 6(c), all of Al_2O_3 inclusions in steel melt were completely modified to rare earth inclusions. And the distribution of rare earth inclusions was uniform in size and spherical in morphology. The content of [S] in steel melt was decreased with Ce additions.

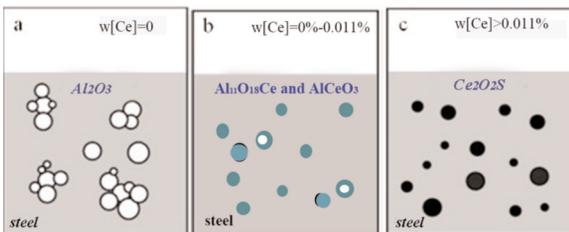
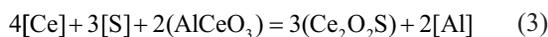


Figure 6. Schematic diagram of evolution process of inclusions

3.5 Effect of inclusion type on the resistance to pitting corrosion

In general, the pitting potential (E_p) is defined as the breakdown potential destroying a passive film. As the E_p of an alloy increases, the resistance to pitting corrosion of the alloy increases [20]. Those three steel samples used in potentiodynamic anodic polarization test represent the spring steel contained Al_2O_3 , Al_2O_3 wrapped by rare earth inclusions and rare earth inclusions, respectively. Fig. 7 shows the result of potentiodynamic anodic polarization test for 1#, 2# and 6# steel samples. Table 5 shows the variation of resistance to pitting corrosion with the increasing Ce content. With the inclusions modified from Al_2O_3 to rare earth inclusions, the breakdown potential shows

the trend of increasing. It shows that the pitting potential (E_p) of the 6# steel is the most stable, which indicate $\text{Ce}_2\text{O}_2\text{S}$ is helpful to improve the resistance to pitting corrosion of spring steel. Adding a small amount of Ce metal which would partly modified Al_2O_3 could also improve the resistance to pitting corrosion in spring steel. Fig. 8 shows SEM images of the pitting sites on the samples after the potentiostatic measurements. Fig. 8(a) shown the serious pitting corrosion occurred around the Al_2O_3 inclusion with a diameter more than $20\mu\text{m}$ which is much larger than the diameter of Al_2O_3 inclusion in test 1. As shown in Fig. 8(b) $\text{Ce}_2\text{O}_2\text{S}$ inclusions appeared to have superior resistance to pitting corrosion in test 4.

Both of the Al_2O_3 and $\text{Ce}_2\text{O}_2\text{S}$ inclusions have stable chemical property and almost insoluble during corrosion test. But large Al_2O_3 inclusions are easy to be the origin of pitting corrosion when the environment is full of Cl^- . Fig. 2 indicates that the large inclusion distribution and inclusion average size decreased with the increasing content of Ce in the present results. Small size $\text{Ce}_2\text{O}_2\text{S}$ inclusion has a low contract area with steel matrix, which would have a better pitting resistance. Therefore, the addition of Ce alloy to the spring steel led to a modification of large Al_2O_3 changing to small $\text{Ce}_2\text{O}_2\text{S}$, which could improve the resistance to pitting corrosion.

Table 5. Chemical composition (wt %) of the spring steel

Sample	1#	2#	4#	6#
Pitting potential	-568	-513	-496	-485

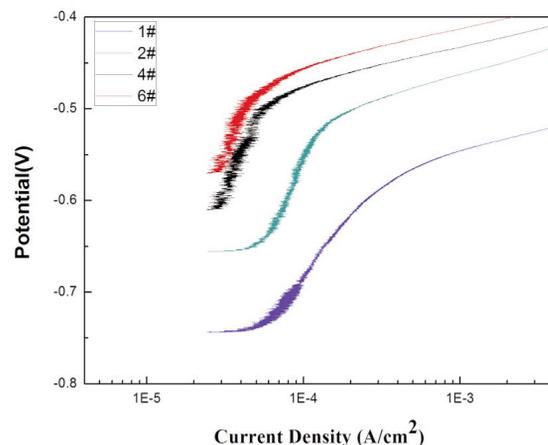


Figure 7. Schematic diagram of evolution process of inclusions

For the purpose of improving the corrosion resistance and avoiding micro-cracks in spring steel, it would be useful if the harmful Al_2O_3 inclusions could be wrapped or transformed by the rare earths. In that case, the rare earths inclusions can effectively

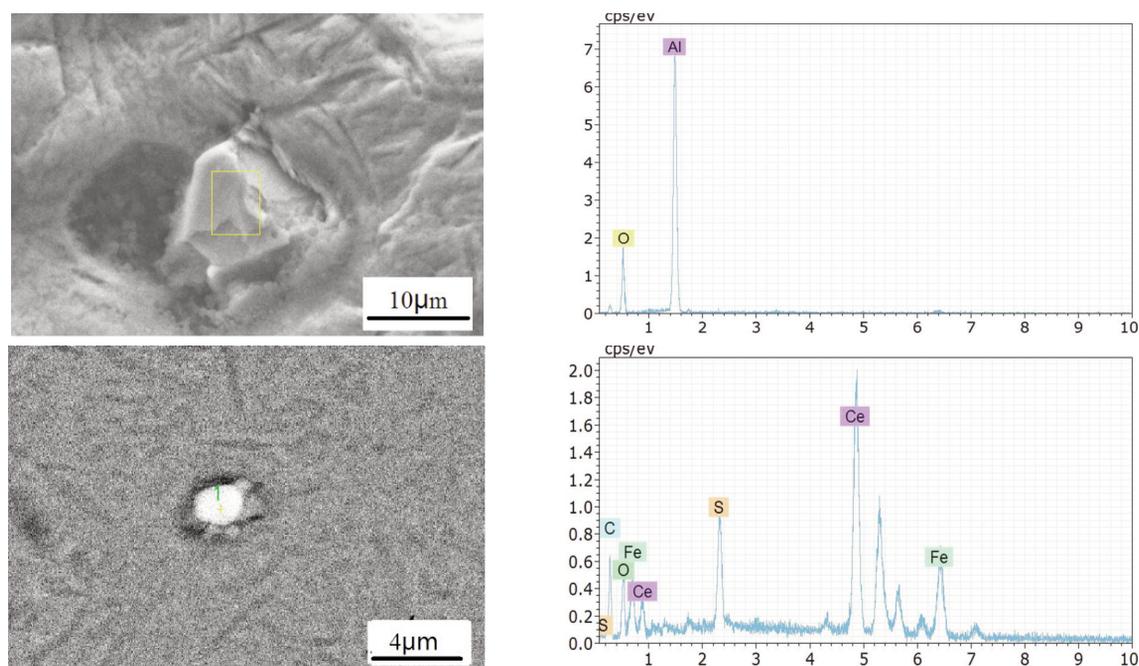


Figure 8. Schematic diagram of evolution process of inclusions

suppress formation of cracks and voids in steel matrix around the inclusions since the coefficient of thermal expansion of rare earths inclusions is close to the steel matrix [21] to avoid the additional force around the inclusions during hot rolling.

4. Conclusions

The evolution process of inclusions in spring steel used in fastener of high speed railway was investigated. According to the experimental results, the following conclusions were obtained.

(1) Inclusions existing in Al-killed spring steel are mainly Al_2O_3 inclusions and clusters of Al_2O_3 inclusions in the present study.

(2) With the increasing of Ce content in steel melt, Al_2O_3 inclusions were wrapped by rare earth inclusions to form a ring shape Ce-riched band around the inclusion. All of inclusions in steel melt would completely modify to rare earth inclusions, when Ce content is over 0.017%.

(3) The stability diagram of Ce-O and Ce-S at 1873K are obtained by using FactSage6.4. It shows that the inclusion variation is $\text{Al}_2\text{O}_3 \rightarrow \text{Al}_{11}\text{O}_{18}\text{Ce} \rightarrow \text{AlCeO}_3 \rightarrow \text{Ce}_2\text{O}_2\text{S}$ in present spring steel.

(4) The SEM-Mapping and line scanning results show that Al_2O_3 inclusions could be transferred to rare earths inclusions. The inclusion is being changed from $\text{Al}_2\text{O}_3 \rightarrow \text{Ce}_2\text{O}_3\text{-Al}_2\text{O}_3 \rightarrow \text{Ce}_2\text{O}_2\text{S}$.

(5) The modification of Al_2O_3 changing to $\text{Ce}_2\text{O}_2\text{S}$ in spring steel could improve the resistance to pitting corrosion.

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