Evolution Mechanisms of $\text{MgO}\cdot\text{Al}_2\text{O}_3$ Inclusions by Cerium in Spring Steel Used in Fasteners of High-speed Railway

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(Received on October 31, 2014; accepted on February 18, 2015)

The effect of rare earth metal addition on the non-metallic inclusions in spring steel used in fastener of high speed railway was investigated by metallographic examination; SEM-EDS and component analysis, aiming at deform those harmful inclusions to improve service life of spring steel. $\text{MgO}\cdot\text{Al}_2\text{O}_3$ inclusions were found in present experimental steel, which is also confirmed by the stability diagram of $\text{MgO}/\text{MgO}\cdot\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ from thermodynamic consideration. After Ce addition, the evolution process of $\text{Al}_2\text{O}_3\cdot\text{MgO}$ inclusions was determined through the surface and line scanning. The effects of time and Ce content on the evolution of $\text{Al}_2\text{O}_3\cdot\text{MgO}$ inclusions were examined. It was indicated that $\text{Al}_2\text{O}_3\cdot\text{MgO}$ inclusions were wrapped by rare earth inclusions to form a ring like shape Ce-riched band around the inclusion, which would be useful to improve fatigue and corrosion resistance of spring steel. It was found that diffusion of Ce^{3+} , Al^{3+} and Mg^{2+} in inclusions core and intermediate layer would be the limited step during evolutions of inclusions.

KEY WORDS: cerium; inclusions; $\text{MgO}\cdot\text{Al}_2\text{O}_3$ spinel; thermodynamic calculation; spring steel.

1. Introduction

With the development of high-speed railway, the demand for higher performance steel is steadily increasing. In recent years, the speed of railway has been improving, which is from 250 km/h to 350 km/h. Thus the more stringent requirements are proposed for the steel material used in high-speed railway, especially, the spring steel applied in fastener, which is used to fix the rail. The spring steel is bearing complex stress in the work. The fatigue failure is the main factors affecting the service life of spring steel used in fastener of high speed railway.^{1,2)} There are many factors affecting the fatigue life including inclusions, heat treatment, surface quality, corrosion resistance, and micro-structure and grain size *etc.*³⁾ Yet the inclusion is one of most important factor in reducing the service life of spring steel. To meet the demand of spring steel used in fastener of high speed railway, the inclusions of molten steel should be improved, such as Al_2O_3 and $\text{Al}_2\text{O}_3\cdot\text{MgO}$ spinel.⁴⁻⁷⁾

$\text{Al}_2\text{O}_3\cdot\text{MgO}$ spinel inclusions are often observed in Al-killed steel as the reaction product of soluble aluminum with the refractory material. Such inclusions are commonly considered to be very harmful to the quality of the final products, acting as the origin of micro-cracks which eventually cause the fatigue fracture of the steel, especially hard, irregular and un-deformable $\text{Al}_2\text{O}_3\cdot\text{MgO}$. In recent

years, $\text{Al}_2\text{O}_3\cdot\text{MgO}$ spinel inclusions have been widely investigated. Most of the reports mainly concentrated in the formation and the control technology of inclusions in stainless steels,⁸⁻¹⁰⁾ while the effect of rare earth on the spring steel used in fastener of high speed railway, especially the rare earths on the deformation of $\text{Al}_2\text{O}_3\cdot\text{MgO}$ spinel inclusions, is rarely involved.¹¹⁾ So it is certainly worthwhile for industrial purposes if the fatigue life of spring steel can be improved through the addition of rare earth metals to the spring steel.

In this paper, the formation of $\text{Al}_2\text{O}_3\cdot\text{MgO}$ inclusions in spring steel used in fastener of high speed railway at 1 873 K is discussed in detail. And the evolution process from $\text{Al}_2\text{O}_3\cdot\text{MgO}$ inclusions to rare earths inclusions is analyzed basis on the SEM-EDS results.

2. Experimental Procedure

The spring steel was prepared in a high frequency induction furnace and then cast into ingot under a protecting atmosphere. **Table 1** shows the chemical compositions of the experimental steel.

The experimental work were carried out in a vertical MoSi2 furnace. The temperature was controlled by B-type thermocouple. The ingot was cut to appropriate block by wire cutting. In each turn, sample weighted 168 g was heated to the target temperature 1 873 K in an MgO crucible (inner dia. 50 mm, outer dia. 55 mm, height 115 mm) at the Ar atmosphere, and then added the different contents

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DOI: <http://dx.doi.org/10.2355/isijinternational.55.970>

of Ce metal wrapped in pure iron chips to the molten steel based on the experimental program as showed in **Table 2**. After the required reaction time, the crucible was rapidly quenched by water from the furnace.

To observe the inclusions of the spring steel, the steel samples were ground to 2 000 grit using SiC abrasive papers, polished with diamond paste. The chemical compositions and morphology of inclusions were analyzed through a scanning electron microscope (SEM) and an energy dispersive spectroscopy (EDS).

3. Result and Discussion

3.1. Chemical Compositions of Steel

The chemical composition of each heat is conducted. The result is showed in **Table 3**. It could be read that the alumina content and magnesium content was in the range of 0.28–0.31% and 0.0007–0.0010% respectively. In addition, the yield of Ce decreased with the increasing of theoretical addition. When the content of Ce metal was up to 0.1%, the yield was about 50%. When Ce metal was less than 0.01%, the yield was more than 80%.

3.2. Thermodynamic Calculation on the Stability Phase Diagram of Inclusions

In order to study the transform of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusions, thermodynamic calculation were carried out to obtain the stability diagram of $\text{MgO}/\text{MgO} \cdot \text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ in molten steel

containing [Mg] and [Al]. Even if [Mg] content is quite low level, $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusions could be easily formed in steel. The interaction coefficients used in calculation were listed in **Table 4**. The used equations are listed as follows:

Calculation of $\text{MgO}/\text{MgO} \cdot \text{Al}_2\text{O}_3$ boundary¹²⁾

$$4(\text{MgO}) + 2[\text{Al}] = \text{MgO} \cdot \text{Al}_2\text{O}_3 + 3[\text{Mg}] \quad \text{..... (1)}$$

$$\log K = -33.09 + 50\,880 / T \quad \text{..... (2)}$$

$$K = \frac{a_{[\text{Mg}]}^3 \cdot a_{\text{MgO} \cdot \text{Al}_2\text{O}_3}}{a_{[\text{Al}]}^2 \cdot a_{\text{MgO}}^4} \quad \text{..... (3)}$$

Calculation of $\text{MgO} \cdot \text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ boundary¹²⁾

$$4(\text{Al}_2\text{O}_3) + 3[\text{Mg}] = 3(\text{MgO} \cdot \text{Al}_2\text{O}_3) + 2[\text{Al}] \quad \text{..... (4)}$$

$$\log K = -34.37 + 46\,950 / T \quad \text{..... (5)}$$

$$K = \frac{a_{[\text{Al}]}^2 \cdot a_{\text{MgO} \cdot \text{Al}_2\text{O}_3}^3}{a_{\text{Al}_2\text{O}_3}^4 \cdot a_{[\text{Mg}]}^3} \quad \text{..... (6)}$$

According to Hino *et al.*,¹³⁾ the activity of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ was taken as 0.8 and that of MgO as 0.99 for $\text{MgO}/\text{MgO} \cdot \text{Al}_2\text{O}_3$ boundary at 1 873 K as a result of the very small solubility of Al_2O_3 into MgO. At the same time, the activity of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ was taken as 0.47 and that of Al_2O_3 as unity for $\text{MgO} \cdot \text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ boundary at 1 873 K because there was no solubility of MgO into Al_2O_3 .

Substituting Eqs. (1)–(6), the phase stability diagram is calculated as shown in **Fig. 1**. It can be seen that contents of dissolved [Al] and [Mg] in molten spring steel are mainly in the formation region near or on the boundary of $\text{MgO} \cdot \text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ inclusions in steel. The results are in fair agreement with the SEM images and EDS analysis showed in **Fig. 2**. It can be found that in the scope of dissolved aluminum, small change of magnesium content in the molten steel will result in the transformation of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and MgO.

3.3. Effect of the Ce Addition on the Characteristics of Inclusions

The shape of inclusions in 1# steel sample was observed through SEM and the chemical composition of inclusions were analyzed using EDS attached to the SEM, as shown in **Fig. 2**. From the statistical results, it was known that the inclusions in 1# steel sample were composed of the types of $\text{Al}_2\text{O}_3 \cdot \text{MgO}$ mainly after alumina deoxidation. The shape of those inclusions is irregular, blocky and rectangular. And there were a small amount of (Ti, Mn, Fe) sulfides and (Si, Fe, Ti) oxides in the spring steel sample. In addition, two kinds of typical Al_2O_3 –MgO–Ce oxides inclusions were observed in steel. One kind was with characteristic of high Al_2O_3 content while the other kind was with characteristic of high MgO content, as shown in **Fig. 3**.

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

Elements	C	Si	Mn	Cr	Ni	V	Ti
Content	0.40–0.52	1.8–2.1	0.6–0.8	0.6–0.8	0.8–1.2	0.05–0.10	0.02–0.05

Table 2. Experimental program.

Heats	Steel/g	Ce theoretical addition/%
1#	168	0
2#	168	0.005
3#	168	0.01
4#	168	0.02
5#	168	0.04
6#	168	0.10

Table 3. The analysis results of chemical composition.

Elements	1#	2#	3#	4#	5#	6#
Ce	0	0.0043	0.008	0.012	0.022	0.051
Al	0.029	0.028	0.030	0.029	0.031	0.029
Mg	0.0008	0.0007	0.0009	0.0007	0.0009	0.0010

Table 4. Interaction coefficient $e_i^{j\,11-14)}$ of various elements in liquid steel at 1 873 K.

j	C	Si	Mn	Cr	Ni	V	Ti	Al	O	Mg
i										
O	−0.45	−0.131	−0.021	−0.04	0.006	−0.3	−0.6	−3.9	−0.2	−
Al	0.091	0.0056	0.012	0.025	0.008	0.06	0.008	0.045	−6.6	0.13
Mg	−0.15	−0.09	−	0.05	−	−	−	−0.12	−3	−

Fig. 1. Phase stability diagram of MgO, MgO·Al₂O₃ and Al₂O₃.

Fig. 2. SEM images and EDS analysis of Al₂O₃·MgO inclusions in steel sample.

Figure 4 presented the inclusions in the 2#, 3# and 4# steel sample after adding Ce alloy to molten steel. The Al₂O₃·MgO inclusions wrapped by rare earth inclusions were observed. It was known that 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. When rare earths addition was insufficient the shape of inclusions maintained the blocky or rectangular.

With the increasing of Ce content in molten steel, inclusions in 1# steel were completely modified to rare earth inclusions in 5# and 6# steel sample ([Ce%]>0.022), such as rare earth oxides, sulfides or oxysulfides, as shown in Fig. 5. In addition, the shape of the inclusions was changed from blocky or rectangular into globular or spheroid. The size of inclusions decreased and tended to uniform with the increasing content of Ce in the present results. It indicated that the addition content of Ce played an important role in the size

Fig. 3. SEM images and EDS analysis of MgO-based inclusions in steel sample.

Fig. 4. SEM-EDS analysis of two kind's Al₂O₃–MgO–Ce oxides inclusions in steel sample.

Fig. 5. SEM images and EDS analysis of Ce inclusions in the 5# and 6# steel sample.

distribution and shape deformation of inclusions. Based on the above analysis, it could be concluded that there would be an optimal addition content of Ce in which inclusions were transferred. Therefore, the appropriate addition of Ce could contribute to produce the fine and dispersive rare earth inclusions. In other words, the preferential sites for the initiation of fatigue in the steel containing Ce element compared to other steel samples would decrease.

3.4. Evolution Process of MgO·Al₂O₃ with Time

Here, the Ce addition was fixed as 0.01 wt%, the evolu-

Fig. 6. The evolution process of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ with Ce treatment (time effect).

tion process was investigated. With the reaction time, the morphology of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusion has changed from irregular/rectangular (a) to wrapped with Ce–O–S oxides with low content of Mg inside (b), then keep as a Al–O–S–Ce inclusion with a relatively long time, sometimes the irregular shape of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ type was still maintained, as shown in Figs. 6(c), 6(d). Since the content of Ce is not very high, the diffusion of Ce will be limited the evolution process of $\text{MgO} \cdot \text{Al}_2\text{O}_3$, thus prolong the time, for example as 10 min or 15 min, we can found much amount of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ have been transformed to Ce–O–S inclusions.

3.5. Evolutions Mechanism of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ Inclusions by Ce

Figure 7 shows the SEM-Mappings of the Ce_2O_3 – $\text{MgO} \cdot \text{Al}_2\text{O}_3$ or $\text{Ce}_2\text{O}_2\text{S}$ – $\text{MgO} \cdot \text{Al}_2\text{O}_3$ system inclusions. When the Ce alloy added to the molten steel at 1 873 K, Ce compounds correlating with O or S began to aggregate and react with $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusions based on them as nuclei. It was determined that shared features of Ce_2O_3 – $\text{MgO} \cdot \text{Al}_2\text{O}_3$ or $\text{Ce}_2\text{O}_2\text{S}$ – $\text{MgO} \cdot \text{Al}_2\text{O}_3$ system inclusions were high Al and Mg content in the inner part while the high Ce content in the outer surface. Moreover, 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. 7(a). The $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusions were wrapped by the inclusions containing Ce content. However, there were some differences in SEM-mappings of inclusions in Fig. 7(a) and that of inclusions in Fig. 7(b). Nearly pure MgO inclusions were surrounded by rare earths inclusions outer layer. It was found that concentration of Mg in the inner part of inclusions in Fig. 7(b) was higher than that in the inclusions in Fig. 7(a). Particularly, Ce concentration zone and Mg concentration zone seemed to be incompatible and

complementary in the SEM-Mapping images, which was more obvious in Fig. 7(b).

Therefore, it is believed that rare earths inclusions can be transferred from high melting temperature $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and MgO-based inclusions, which also has been proved by SEM line scanning results.

SEM line scanning results of inclusions were shown in Fig. 8. As can be seen in Fig. 8, the inclusions core was mainly composed of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ content changed along width direction and Ce content had a climax at the edge of inclusion. Meanwhile, S content was high in the outer part along the width direction. It is concluded that the inclusion is being changed from $\text{MgO} \cdot \text{Al}_2\text{O}_3 \rightarrow \text{Ce}_2\text{O}_3$ – $\text{MgO} \cdot \text{Al}_2\text{O}_3$ or $\text{Ce}_2\text{O}_2\text{S}$ – $\text{MgO} \cdot \text{Al}_2\text{O}_3 \rightarrow \text{Ce}_2\text{O}_3$ or $\text{Ce}_2\text{O}_2\text{S}$.

Based on the above SEM-mapping and line scanning results of inclusions, it was summarized that the high melting temperature and solid $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusions wrapping by rare earths inclusions layer was the shared characteristic of all Ce_2O_3 – $\text{MgO} \cdot \text{Al}_2\text{O}_3$ or $\text{Ce}_2\text{O}_2\text{S}$ – $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusions. At last, the shape of inclusions evolved from irregular into spherical rare earths inclusions.

For the purpose of improving the corrosion resistance and fatigue property of spring steel, it would be useful if the harmful $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusions could be wrapped or transformed by the rare earths. In that case, the rare earths inclusions can effectively suppress formation of cracks and voids in steel matrix around the inclusions since the coefficient of thermal expansion of rare earths inclusions is similar to the steel matrix to avoid the additional force around the inclusions during hot rolling.

3.6. Illustration on Evolution of Inclusions after Adding Ce Alloy to Molten Steel

Through the above results of experimental data and thermodynamic calculations, the evolution process of inclu-

Fig. 7. SEM-mappings of transferring inclusions. (Online version in color.)

Fig. 8. SEM line scanning of transferring inclusions.

sions had been known. To further understand the evolution of inclusions, it is necessary to illustrate the process about inclusions transformation. The change process of inclusions was clearly described by Fig. 9 and illustrated as following:

- (1) $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusions were easily formed in molten steel in a few minutes, even if the Mg content was at very low level, as shown in Fig. 9(a).
- (2) After Ce addition, Ce atom diffused from bulk into $\text{MgO} \cdot \text{Al}_2\text{O}_3$ /molten steel interface and became Ce^{3+} at $\text{MgO} \cdot \text{Al}_2\text{O}_3$ /molten steel interface as Eq. (7)

- (3) The formed $\text{MgO} \cdot \text{Al}_2\text{O}_3$ was not stable when Ce

Fig. 9. Schematic diagram of evolution process of inclusions.

was added to molten steel. Ce^{3+} would react with $\text{MgO} \cdot \text{Al}_2\text{O}_3$ through reaction Eqs. (8) or (9). And a thin layer of Ce_2O_3 – $\text{MgO} \cdot \text{Al}_2\text{O}_3$ or $\text{Ce}_2\text{O}_2\text{S}$ – $\text{MgO} \cdot \text{Al}_2\text{O}_3$

outside $\text{MgO} \cdot \text{Al}_2\text{O}_3$ was formed by the way of Ce-rich ring band as shown in Fig. 9(b).

$$2x[\text{Ce}] + (y\text{Al}_2\text{O}_3 \cdot z\text{MgO}) \\ = \left(\left(y - \frac{x}{2} \right) \text{Al}_2\text{O}_3 \cdot \left(z - \frac{3x}{2} \right) \text{MgO} \cdot x\text{Ce}_2\text{O}_3 \right) \dots\dots (8) \\ + \frac{3x}{2} [\text{Mg}] + x[\text{Al}]$$

$$2x[\text{Ce}] + x[\text{S}] + (y\text{Al}_2\text{O}_3 \cdot z\text{MgO}) \\ = \left(\left(y - \frac{x}{3} \right) \text{Al}_2\text{O}_3 \cdot (z - x) \text{MgO} \cdot x\text{Ce}_2\text{O}_2\text{S} \right) \dots\dots (9) \\ + x[\text{Mg}] + \frac{2x}{3} [\text{Al}]$$

- (4) With the progress of reaction, Ce_2O_3 or $\text{Ce}_2\text{O}_2\text{S}$ layer was gradually formed at the outside. The Ce^{3+} transferred through the newly formed layer to the inner part and continued to react with the un-reacted central $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusion, and formed the intermediate Ce_2O_3 – $\text{MgO} \cdot \text{Al}_2\text{O}_3$ or $\text{Ce}_2\text{O}_2\text{S}$ – $\text{MgO} \cdot \text{Al}_2\text{O}_3$. This layer would be further transferred toward the Ce_2O_3 or $\text{Ce}_2\text{O}_2\text{S}$. Simultaneously, Mg^{2+} and Al^{3+} would diffuse from inclusion into molten steel. The outer layer of inclusions would begin to get thicker. Then reaction rate would be much slower because diffusion resistance for Ce, Mg and Al continuously increased. As a result, all of inclusions were transferred to the rare earths inclusions which contained no $\text{MgO} \cdot \text{Al}_2\text{O}_3$ content in the theory as indicated in Eqs. (10) and (11). The distribution of rare earth inclusions was uniform in size and spherical in morphology. It was helpful to improving the fatigue and corrosion resistance properties.

$$8[\text{Ce}] + 3(\text{Al}_2\text{O}_3 \cdot \text{MgO}) = 4(\text{Ce}_2\text{O}_3) + 3[\text{Mg}] + 6[\text{Al}] \dots\dots (10)$$

$$4[\text{Ce}] + 2[\text{S}] + (\text{Al}_2\text{O}_3 \cdot \text{MgO}) = 2(\text{Ce}_2\text{O}_2\text{S}) + [\text{Mg}] + 2[\text{Al}] \dots\dots (11)$$

Since the diffusion of Ce^{3+} , Mg^{2+} and Al^{3+} in molten steel was relatively easier than in solid layer the limited step of ions diffusion would be the diffusion of Ce^{3+} , Mg^{3+} and Al^{3+} in $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusions. According to the above results, it was clearly seen that the controlled step during evolution of inclusions was diffusion of Ce^{3+} , Mg^{3+} and Al^{3+} in both of un-transferred core and intermediate layer. Although the evolution kinetics of inclusions had been discussed by model establishment, much detailed work was also necessary to quantitatively discussed limited steps during evolution process of inclusions.

4. Conclusions

The evolution process of inclusions in spring steel used in fastener of high speed railway was experimentally inves-

tigated and the evolution mechanism of inclusions was proposed correspondingly. According to the experimental results, the following conclusions were obtained.

(1) Inclusions existing in spring steel are mainly $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusions in the present study. There were a small amount of (Ti, Mn, Fe) sulfides and (Si, Fe, Ti) oxides in the spring steel sample.

(2) With the increasing of Ce content in molten steel, $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusions were wrapped by rare earth inclusions to form a ring shape Ce-rich band around the inclusion. As a result, all of inclusions in molten steel were completely modified to rare earth inclusions.

(3) The stability diagram of $\text{MgO}/\text{MgO} \cdot \text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ is obtained by thermodynamic calculation. It shows that the [Mg] and [Al] content in present results mainly position in $\text{MgO} \cdot \text{Al}_2\text{O}_3$ formation zone.

(4) The evolution process of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ was observed by SEM-mapping and line scanning. The results show that $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusions could be transferred to rare earths inclusions. The inclusion is being changed from $\text{MgO} \cdot \text{Al}_2\text{O}_3 \rightarrow \text{Ce}_2\text{O}_3$ – $\text{MgO} \cdot \text{Al}_2\text{O}_3$ or $\text{Ce}_2\text{O}_2\text{S}$ – $\text{MgO} \cdot \text{Al}_2\text{O}_3 \rightarrow \text{Ce}_2\text{O}_3$ or $\text{Ce}_2\text{O}_2\text{S}$. Based on the analysis, it was clearly seen that the controlled step during evolution of inclusions might be diffusion of Ce^{3+} , Mg^{3+} and Al^{3+} in solid inclusion phase.

Acknowledgement

The authors would like to express their appreciation to National Nature Science Foundation of China (No.51104013, 51174022), a Fundamental Research Funds for the Central Universities (FRF-TP-14-109A2), Beijing Higher Education Young Elite Teacher Project (YETP0349) and China Post-doctoral Science Foundation (2014M560046).

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