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ScienceDirect
JOURNAL OF RARE EARTHS, Vol. 32, No. 8, Aug. 2014, P. 759
JOURNAL OF RARE EARTHS
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Effect of cerium on the cleanliness of spring steel used in fastener of high-speed railway

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Received 25 February 2014; revised 24 April 2014

Abstract: The effects of Ce addition on the quantity, size, distribution of inclusions and the content of oxygen, sulfur and other hazardous residual elements in spring steel used as fastener in high speed railway were investigated by metallographic examination, SEM-EDS and composition analysis. The results indicated that the contents of oxygen decreased with the addition of Ce ([Ce]<0.1%) and the content of sulfur continually decreased with increasing content of Ce ([Ce]<1.2%). However, with the further increase of Ce element addition, the content of [O] and T[O] began to increase. The content of Ce corresponding to the lowest [O] and T[O] lied in the range of 0.10%–0.13% and 0.045%–0.065%, respectively. The addition of Ce in spring steel resulted in the formation of rare earth oxides/oxysulfides and decreased the size of inclusions to less than 3 μm in globular or spheroid shape. Moreover, the residual harmful elements (As, P, Pb and Sn) were found to exist in the Ce-containing inclusions, which had proved that the Ce addition could capture the residual elements and suppress their precipitation behaviors in the grain boundary.

Keywords: cerium; inclusions; residual elements; spring steel; high-speed railway; rare earths

In China, the speed of railway has been increasing from 250 to 350 km/h now, thus, higher requirements for the steel used in high-speed railway are put forward. One typical example is the spring steel applied in fastener, which is used to fix the rails to the ground. The quality of spring steel is of great importance to the safety of high-speed railway. The spring steel is bearing complex stress load during service. So the fatigue failure maybe is the main factor affecting the service life of spring steel used in fastener of high speed railway[1,2]. As is known, many factors affect the fatigue life, including cleanliness, heat treatment, surface quality, corrosion resistance, microstructure and grain size, etc, besides the components of the spring steel[3]. To meet the demand of spring steel used in fastener of high speed railway, the cleanliness of molten steel, which contains the content of oxygen, sulfur, and the quantity of inclusions, should be improved[4]. Meanwhile, in view of the various sources of iron ore in China, hazardous residual elements (As, P, Pb and Sn) would exist in the steel, which would be enriched in steel surface during heat treatment process and deteriorated the performance of product, such as surface cracks, temper brittleness, high-temperature strengthen, etc. So an effective way to deal with these residual elements should be developed accordingly.

Ce is known to be effective as a deoxidizer in making ultra low oxygen steel since rare earth elements have strong affinity for oxygen[5]. And a small amount of Ce is sometimes used as an alloying element of stainless steel for the improvement of oxidation resistance. Several investigations[6–10] also pointed out that addition of rare earth may improve the desulfurization, reduce the content of hazardous residual elements[11], modify the inclusions and refine the microstructure, etc. So it is certainly worthwhile for the sake of industrial application to study if the cleanliness of steel can be improved through the addition of Ce to the spring steel.

Therefore, the current study was focused on deoxidation, desulphurization and restriction of hazardous residual elements by addition of Ce in spring steel.

1 Experimental

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 composition of the experimental steel.

Table 1 Chemical composition (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

Foundation item: Project supported by National Natural Science Foundation of China (51104013, 51174022), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (44), Beijing Higher Education Young Elite Teacher Project (0349)

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DOI: 10.1016/S1002-0721(14)60137-X

The ingot was cut to appropriate blocks by wire cutting. Each sample was heated to the target temperature 1873 K in an MgO crucible in the Ar atmosphere in a vertical electric resistance furnace with $MoSi_2$ heating bar and Al_2O_3 reaction tube, and initial dissolved oxygen content was measured by solid electrolyte oxygen probe. And then different contents of Ce metal wrapped in pure iron chips were added to the molten steel based on the experimental program as shown in Table 2. The molten steel was immediately stirred for 15 s with quartz tube. After holding the molten steel at 1873 K for 15 min, the dissolved oxygen content was measured again. On the basis of previous work[6], 15 min should be sufficient time to allow the Ce-containing deoxidizing product to float out; when samples were equilibrated for longer time, there was no significant difference in the results. After the required time, the crucible was rapidly quenched by water from the furnace.

Table 2 Experimental program

Heats	Steel mass/g	Ce content/wt.% (theoretical addition)
1#	743	0
2#	754	0.01
3#	751	0.05
4#	753	0.07
5#	746	0.09
6#	744	0.12
7#	747	0.2
8#	750	0.4
9#	750	0.6

To observe the inclusions in the spring steel, the steel samples were 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).

2 Results and discussion

The chemical composition analysis of each heat was conducted. The result is shown in Table 3. Compared with Table 2, it is found that the Ce contents of final samples are smaller than the theoretical ones. These parts of Ce are unavoidable losses during metallurgical process. When the content of Ce addition was up to 0.2%, the yield was 20%–30%. The contents of As, P, Pb and Sn in referenced steel were 0.0020%, 0.0060%, 0.0010% and 0.0020%.

Table 3 Analysis results of chemical composition (wt.%)

Elements	Heats								
	1#	2#	3#	4#	5#	6#	7#	8#	9#
Ce	0	0.0081	0.015	0.028	0.033	0.046	0.047	0.12	0.18

2.1 Effect of the Ce addition on the contents of O and S

The solubility of oxygen in spring steel samples equilibrated with the Ce oxides phase at 1873 K is presented in Fig. 1. The solubility is a minimum of about 4 ppm corresponding to the content of Ce lied in the range of 0.10%–0.13%. The addition of Ce decreased the solubility to minimum oxygen content and the solubility increased with further increase of the alloying element Ce. This result shows the same trend of dissolved oxygen in the steel with the addition of deoxidation elements (Al, Cr, Ti, etc.) in Fruehan's studies[12].

The dissolved oxygen is controlled mainly by equilibrium thermodynamics with the deoxidation element. The deoxidation reaction can be expressed as follows:

$$\frac{a}{b}[\mathrm{Ce}]+[\mathrm{O}]=\frac{1}{b}\mathrm{Ce}_a\mathrm{O}_{b(S)} \tag{1}$$

$$K^\theta=\frac{\alpha_{\mathrm{Ce}_a\mathrm{O}_b}^{1/b}}{\alpha_{[\mathrm{O}]}\alpha_{[\mathrm{Ce}]}^{a/b}}=\frac{\alpha_{\mathrm{Ce}_a\mathrm{O}_b}^{1/b}}{f_\mathrm{O}[\%\mathrm{O}]f_\mathrm{Ce}^{a/b}[\%\mathrm{Ce}]^{a/b}} \tag{2}$$

$$\lg[\%\mathrm{O}]=\lg\frac{1}{K^\theta}-\left(e_\mathrm{O}^\mathrm{Ce}+\frac{a}{b}e_\mathrm{Ce}^\mathrm{Ce}\right)[\%\mathrm{Ce}]-\frac{a}{b}\lg[\%\mathrm{Ce}] \tag{3}$$

where a and b are constants, K^θ denotes equilibrium constant, α activity, and e_j^i and f are interaction coefficient and activity coefficient, respectively. Assuming that Ce_2O_3 and Ce_2O_2S were formed in deoxidation process, from Eq. (3), the equilibrium curve of dissolved oxygen was plotted, as shown in Fig. 2. It was indicated that the experimental values, as shown in Fig. 1, had the same trend as the calculation values. There was a minimum content of dissolved oxygen at 0.10%–0.13% Ce.

Fig. 3 shows the effect of Ce on total oxygen in spring steel used in fastener of high speed railway at 1873 K. The $[O]_T$ decreased with the increasing content of Ce element up to the range of 0.045%–0.065%. However, the $[O]_T$ increased with the further increase of the Ce addition. Therefore, there is an optimal interval for rare earth Ce deoxidation. The appropriate addition of Ce element can contribute to improving the cleanliness of molten steel.

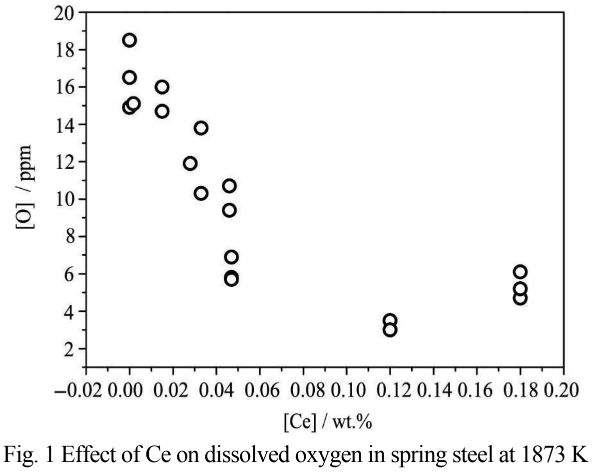

Fig. 1 Effect of Ce on dissolved oxygen in spring steel at 1873 K