FERROALLOYS FOR CLEAN STEELS PRODUCTION AND QUALITY SPECIFICATIONS

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ABSTRACT

In present work the influence of ferroalloys quality on the steel cleanness has been studied.

Experimental rail steel batches produced with using different ferroalloys grades were investigated. Total oxygen and nitrogen contents as well as the amount and composition of different oxide inclusions in steel probes sampled during the ladle treatment and casting were determined by fractional gas analysis. It was obtained that addition of ferrosilicon FeSi65 contained more than 2 wt. % Al in the melt during ladle-furnace treatment leads to oxygen decreasing from 50-60 ppm to 40-45 ppm while an addition of FeSi75 contained less 0.5 wt. % Al leads to oxygen decreasing from 50-60 ppm to 15-20 ppm. Moreover, there is high quantity of Al_2O_3 inclusions in the melt after using of the high aluminium ferrosilicon. Adding of FeSi75 allow us to achieve a low oxygen concentration in alumina in the rail steel notably about 5 ppm.

The fractional gas analysis of two ferrosilicon grades was performed. It was obtained that the ferrosilicon FeSi65 contains high oxygen amount in alumina and slag inclusions notably 0.078 and 0.033 wt. %, respectively, while the total oxygen concentration in FeSi75 is 0.016 wt. % only.

It was concluded that the regulation of some impurities and compounds in ferroalloys will make it possible to increase quality of "clean" steels with decreasing their first cost.

1 INTRODUCTION

At present the steel requirements become more exact. Steel quality is determined by not only their structure and chemical composition but also quantity and species of nitrogen and oxygen. Nonmetallic inclusions, which are present in a metal matrix in a significant amount, are known to be main cause of fatigue and tensile crack nucleation. So the size, morphology and distribution of inclusions in steel matrix are the very important parameters of "clean" steel quality. In Table 1 you can see the modern requirements for such steel grades as cord, rail, wheel, bearing, IF and others.

Exact restrictions on impurities and non-metallic inclusions in "clean" steels require an application of high purity ferroalloys. Moreover, some impurities aren't regulated in the ferroalloys. In the first place these are oxygen and nitrogen. But a transfer degree of these gases from the ferroalloys to steel melt is known to be up to 95 %. For example, the oxygen and aluminum contents in rail steel are regulated up to 20 and 40 ppm, respectively. Using the ordinary type ferrosilicon FeSi65 leads to increasing of oxygen and aluminum contents in the melt up to 20 and 100 ppm, respectively. So the steelmakers have to apply a special procedure to get the necessary contents of these elements in steel.

Railroads are the main trunk-roads in many countries. During rail operation (when a wheel rolls over a rail), a contact-fatigue load appears, which is accompanied by the formation of fatigue defects. The fraction of these defects among the other defects (welding-induced defects, operation defects, etc.) reaches 70% [1].

Table 1: The main restrictions on impurities and non-metallic inclusions in some "clean" steels

Steel grade	Impurity content, no more than	Critical inclusion size
Cord steel	[N]<40ppm, [H]<2ppm, [O]<30ppm, [Al]<10ppm, [S]<0.015%, [P]<0.015%, Σ[Cr]+[Ni]+[Cu]<0.15%, [Sn]<0.003%	Deformable < 30 μm, Nondeformable < 10 μm, in Al_2O_3 < 40 %
Valve spring steel	[N]<40ppm, [H]< 2ppm, [O]<30ppm, [Al]<40ppm, [S]<0.008%, [P]<0.015%, Σ[Cr]+[Ni]+[Cu]<0.15%, [Sn]<0.003%	Nondeformable < 20 μm min Al_2O_3
Rail and wheel steel	[H]< 2ppm, [O]<20ppm, [Al]<40ppm, [S]<0.01%, [P]<0.01%, Σ[Cr]+[Ni]+[Cu]<0.15%	Nondeformable < 20 μm min Al_2O_3
Bearing steel	[H]<2ppm, [O]<10ppm, [S]<0,01%, [P]<0.01%, [Ti] <15ppm, [Ca]<5ppm	Nondeformable < 15 μm min globular AlCa
IF steel	[C]<30ppm, [N]<40ppm, [O]<40ppm, [S]<0.01%	All inclusions < 100 μm
Electric steel	[C]<40ppm, [S]<0.001%, [H]<2ppm, [O]<15ppm, [N]<90ppm, [Al]=120ppm, [Ti]<15ppm, [Cr]<0.03%, [Ni]<0.03%, [Ca]<2ppm	All inclusions < 25-30 μm, Inhibitor phase: MnS, AlN 10-100 nm
Pipe steel	[H]<2ppm, [O]<15ppm, [N]<35ppm, [S]<0.008%, [P]<0.008%, Σ[Cr]+[Ni]+[Cu]<0.15%, [Sn]<0.003%	Deformable < 100 μm, min silicates, manganese sulfides, AlCa

The intensity of accumulation of contact-fatigue cracks depends on both the rail operation conditions (the intensity and number of wheel-rail contact pressures) and the metallurgical quality of the rail material. The authors of [2] studied the phenomenology of the processes occurring in the formation of contact fatigue defects (CFDs) and found that a complex stress tensor appears in the contact zone of a loaded rail. In the contact zone, both normal and tangential stresses are operative. Contact fatigue cracks mainly nucleate in the zones corresponding to maximum stresses [3]).

High tangential stresses operate in the bulk of the metal at a certain depth. When this zone contains large nondeformable inclusions (e.g., Al_2O_3 particles), which create an additional stress concentration, conditions for the formation of a longitudinal subsurface crack appear. When growing, this crack can change the growth direction and, eventually, form pitting or a transverse crack [2].

Inclusions with voids forming along their boundaries during hot plastic deformation are the most dangerous. These voids are formed at nondeformable corundum inclusions and spinels, since they undergo tensile stresses at the inclusion–matrix interface upon heating and have a size that is higher than a certain critical value [4].

Although the estimated critical sizes of inclusions in a rail steel are substantially different, the conclusions regarding the necessity of removal of coarse nonmetallic inclusions (larger than 15-20 μm) from this steel are beyond question [5]. According to the data obtained at the All-Russia Research Institute of Railway Transport (ARIRT) [6], aluminum oxide inclusions are most often present in the zone of CFDs. So the technology production of rail steel should provide the minimum content of nondeformable alumina inclusions in metal. This thing also concerns the cord and wheel steel production.

Thus, the regulation of some impurities and compounds in ferroalloys will make it possible to increase quality of some steel grades with decreasing their first cost.

2 EXPERIMENTAL

In this work we have studied the influence of ferroalloys quality on the rail steel cleanness. For this purpose the experimental melts with using different ferroalloys grades were carried out.

2.1 Steel melting and sampling

Two batches of rail steel were melted in the real manufacture conditions: during the 1-st batch only FeSi65 was used, during the 2-nd – only FeSi75 (low Al). Ferrosilicon FeSi75 was produced with the technology providing the content of total Al less than 0.5 wt. % in ferroalloy. Total aluminium content in FeSi65 was more than 2 wt. %. In Table 2 you can see the chemical composition of two ferrosilicon grades.

Table 2: Average chemical composition of two ferrosilicon grades.

Ferrosilicon	Chemical element			
	Si	Al	S	P
FeSi65	67.6	2.0 – 3.5	0.001	0.001
FeSi75	77.8	< 0.5	0.001	0.001

The order and procedure of ferrosilicon adding were identical for both grades. The quantities of added ferrosilicon were counted in compliance with the content of a leading element (silicon) in ferroalloy.

The probes of rail steel were sampled (dual samples) from the ladle furnace (before FeSi additional – LF1, after – LF2), RH degasser and tundish (CCM) during the ladle treatment and casting. In Table 3 you can see the chemical composition of steel samples.

Table 3: Average chemical composition of the steel melt (batches produced using FeSi65 and FeSi75).

Sample	Chemical element										
	C	Mn	Si	P	S	Cr	Ni	Cu	Al	V	Ca
batch with FeSi65											
LF1	0.74	0.79	0.15	0.014	0.023	0.03	0.04	0.01	0.0023	0.01	0.0005
LF2	0.75	0.91	0.23	0.015	0.018	0.03	0.04	0.01	0.0037	0.03	0.0009
RH	0.75	0.91	0.23	0.015	0.011	0.03	0.04	0.01	0.0039	0.03	0.0016
CCM/T	0.75	0.91	0.23	0.015	0.010	0.03	0.04	0.01	0.0040	0.03	0.0011
batch with FeSi75											
LF1	0.73	0.85	0.16	0.014	0.020	0.03	0.04	0.01	0.0036	0.01	0.0005
LF2	0.74	0.93	0.24	0.015	0.016	0.03	0.04	0.01	0.0037	0.03	0.0009
RH	0.74	0.93	0.24	0.015	0.012	0.03	0.04	0.01	0.0039	0.03	0.0007
CCM/T	0.74	0.93	0.24	0.015	0.012	0.03	0.04	0.01	0.0039	0.03	0.0006

2.2 Chemical analysis

Fractional gas analysis (FGA) of rail samples was performed on a TC-600 LECO gas analyzer using the OxSeP and OxId software packages [7]. The results of FGA allow us to determine the quantity of oxygen species in the steel samples. The samples were cut from the side of the cove of a rail head at a depth of 10-15 mm from the rolling surface. Three parallel measurements were performed and processed for each sample.

Fractional gas analysis is a modified reducing-melting procedure realized in a graphite crucible in a carrier-gas flow at a fixed linear heating rate. The analysis is based on the difference in the thermodynamic stability of oxides (nitrides) upon heating that are principal species of oxygen (nitrogen) present in a metal. Thus, we preset conditions of monotonic heating of a sample in a graphite crucible of an analyzer and obtain gas-evolution curves (evalograms) for oxygen and nitrogen in the form of CO and N_2, respectively. An evalogram is a system of maxima; each peak of the curve be related to one or other kind of inclusions and has a characteristic temperature, which corresponds to the onset and maximum of reduction (dissociation) and allows the associated compound to be identified. Principles of thermodynamic calculations of characteristic temperatures of oxide inclusions in Fe-based melts are given in [8].

Two ferrosilicon grades were also analyzed using the FGA technique to determine both total oxygen and oxygen content in various oxides forms in the ferroalloys.

3 RESULTS AND DISCUSSION

3.1 Thermodynamic calculation

Nonmetallic inclusion nucleation and steel refining are characterized through various oxidation and reduction processes coinciding with changes of the oxygen activity in liquid steel. Figure 1 presents calculated oxygen solubility in a carbon steel as a function of deoxidizers' (Al and Si) content at 1873 K in equilibrium with different reactions products, such as Al_2O_3, $3Al_2O_3{\cdot}2SiO_2$ and $Al_2O_3{\cdot}SiO_2$.

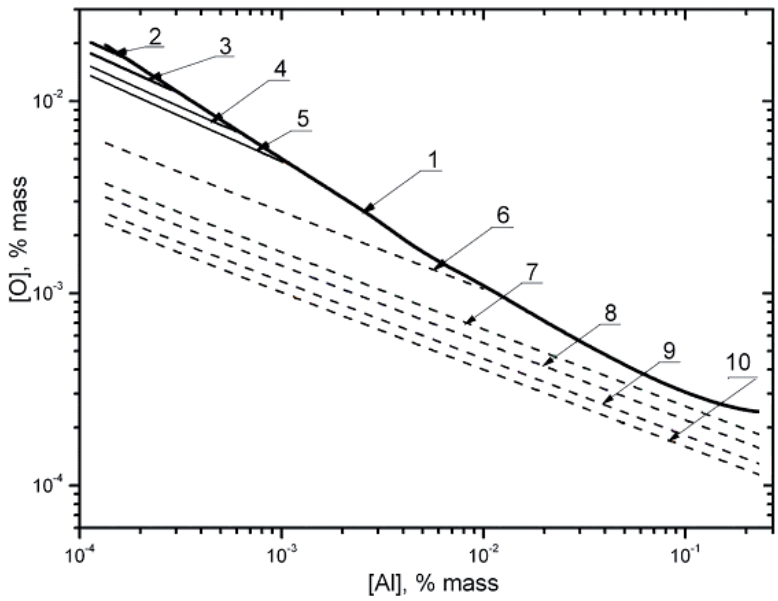

Figure 1: Deoxidation of carbon steel with ferrosilicon. Calculated oxygen solubility in a carbon steel as a function of deoxidizers' (Al and Si) content at 1873 K: Silicon content, % mass: 1 – 0; 6 – 0.01; 2, 7 – 0.10; 3, 8 – 0.20; 4, 9 – 0.40; 5, 10 – 0.6. Deoxidation product: 1 – Al_2O_3; 2-5 – $3Al_2O_3{\cdot}2SiO_2$; 6-10 – $Al_2O_3{\cdot}SiO_2$.

As you can see from Figure 1 the deoxidation of carbon steel with ferrosilicon will provide the necessary oxygen content in rail steel. However, the aluminium content in rail steel should be less than 40 ppm to get the favorable composition of oxide inclusions. It can be reached only using ferroalloys with regulated impurities content.

3.2 Influence of ferrosilicon grade on rail steel quality

Figure 2 and 3 show the FGA results for steel probes sampled from the ladle furnace (LF), RH degasser and tundish during the casting (CCM) and from finished rail (T) of two batches. This is example how the FGA results allowed us to estimate the influence of ferroalloys and deoxidizers additions during ladle treatment on the total oxygen and nitrogen contents as well as the amount and composition of different oxide inclusions in steel melt.

As you can see from the Figures 2 and 3 an addition of FeSi65 in the melt during ladle-furnace treatment (Figure 2) leads to oxygen decreasing from 50-60 ppm to 40-45 ppm whereas an addition of FeSi75 (Figure 3) leads to oxygen decreasing from 50-60 ppm to 15-20 ppm. Moreover, there is high quantity of Al_2O_3 inclusions in the melt after using of the high aluminium ferrosilicon FeSi65. Adding of FeSi75 allow us to achieve a low oxygen concentration in alumina in the steel notably about 5 ppm. Thus the using of high quality ferrosilicon results in low oxygen content and favorable oxide composition in rail steel.

3.3 Oxygen species in the ferroalloys

The results of the fractional gas analysis of two ferrosilicon grades are shown in Table 4. It was obtained that the total oxygen content in FeSi65 and FeSi75 is 0.17 and 0.016 % wt., respectively. Moreover there is a large amount of nondeformable alumina and calcium contained inclusions in the ferroalloys FeSi65. These oxides use to add in a steel melt together with ferrosilicon FeSi65 and as it was shown above part of them don't remove from the melt. So the oxides and aluminium contents in ferrosilicon are very important characteristic for rail steel producers.

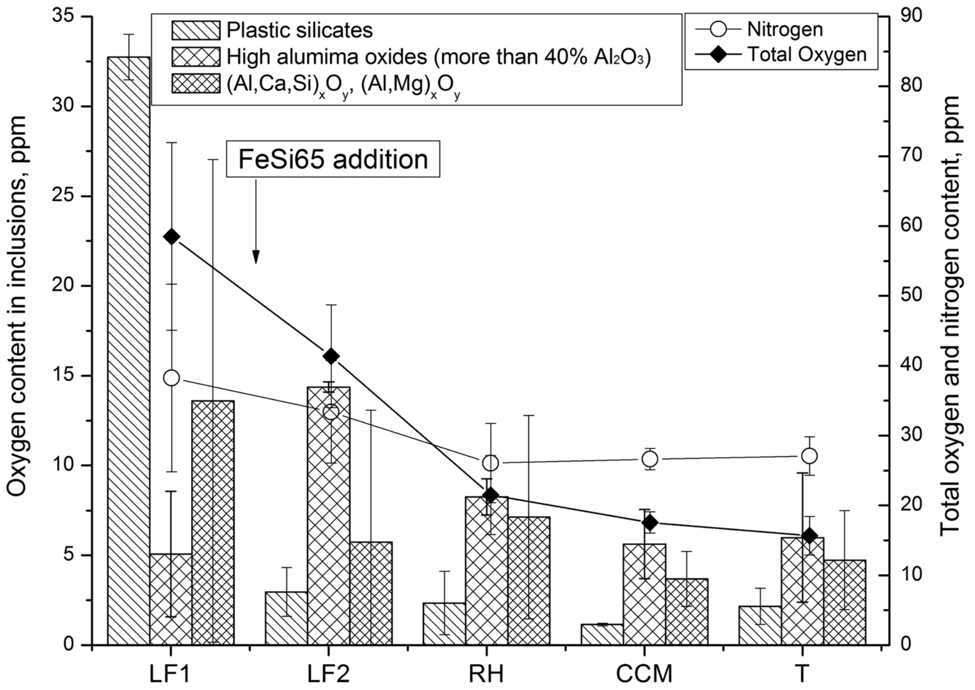

Figure 2: FGA results: oxygen content in the 3 main types of oxide inclusions in the rail steel sampled during LF and RH treatment (FeSi65 addition), casting and from rail template (average values by 5 melts).

Table 4: Oxygen content in two ferrosilicon grades.

Ferroalloy	Oxygen content, % wt.			
	Total	In silicates	In aluminates	In slag inclusions
FeSi65	0.17	0.044	0.078	0.033
FeSi75	0.016	0.01	0.001	–

Solubility of oxygen in iron-silicon melts in equilibrium with silica was measured within the range from 0.1 up to 70 % wt. Si at 1873 K in work [9]. Experimental data and thermodynamic calculation allowed authors to obtain that it is possible to achieve a low oxygen concentration in the ferrosilicon (less than 70 ppm).

As concerns other steel grades there is similar situation for application of the different ferroalloys in steel production. For example, a production technology of anisotropic electric steel should provide the concentrations of Si, Al and O in metal 3, 0.012 and 0.0015 % wt., respectively. After addition of ordinary ferrosilicon FeSi65 in the melt during ladle treatment the contents of aluminium and oxygen increase up to 0.10 and 0.01 % wt., respectively.

The limit aluminium content in high quality cord steel is known to be 10 ppm. So the application of high purity ferroalloys and special technology techniques can provide a good metallurgical quality of cord steel.

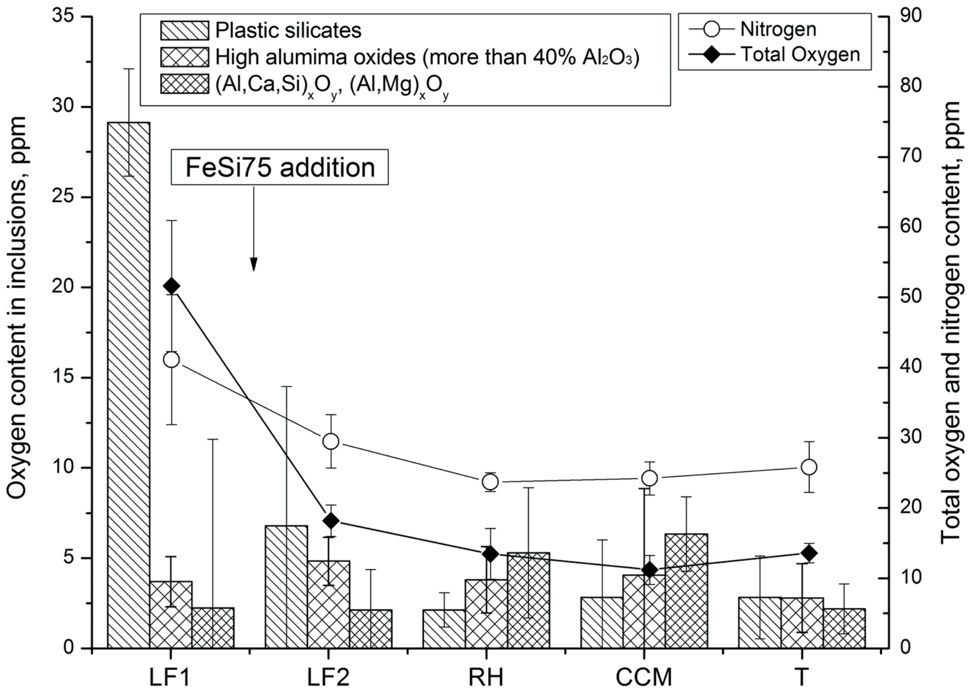

Figure 3: FGA results: oxygen content in the 3 main types of oxide inclusions in the rail steel sampled during LF and RH treatment (FeSi75 addition), casting and from rail template (average values by 3 melts).

4 CONCLUSIONS

The influence of ferroalloys purity on the steel cleanness was shown. Experimental rail steel batches produced with using different ferroalloys grades were investigated. It was obtained that addition of ferrosilicon FeSi65 contained more than 2 wt. % Al in the melt during ladle-furnace treatment leads to oxygen decreasing from 50-60 ppm to 40-45 ppm whereas an addition of FeSi75 contained less 0.5 wt. % Al leads to oxygen decreasing from 50-60 ppm to 15-20 ppm. Moreover, there is high quantity of Al_2O_3 inclusions in the melt after using of the high aluminium ferrosilicon. Adding of FeSi75 allow us to achieve a low oxygen concentration in alumina in the rail steel notably about 5 ppm. It results from the high oxygen content in alumina and slag inclusions in the ferrosilicon FeSi65 notably 0.078 and 0.033 wt. %, respectively, while the total oxygen concentration in FeSi75 is 0.016 wt. % only. Thus using the high quality ferrosilicon results in low oxygen content and favorable oxide composition in rail steel.

Thus, the regulation of some impurities and compounds in ferroalloys will make it possible to increase quality of "clean" steels with decreasing their first cost.

The revision of ongoing ferroalloys standards is necessary for the diversification and harmful impurities regulation including oxygen and nitrogen in some ferroalloys grades.

5 REFERENCES

[1] Smirnov L.A., Deryabin A.A., Dobuzhskaya A.B. et al., Proc. of Conference "Nonmetallic Inclusions in Rail Steel", UIM, Yekaterinburg, (2005), p.13.

[2] Avdzhieva T.B. and Georgiev M.N., Zavod. Lab., (2006)6, p.56.

[3] Harris U.J., Zakharov S.M., Landgren J., et al., Generalization of the World Experience of Heavy-Weight Railway Traffic: The Problems of Wheel–Rail Interaction, Intekst, Moscow, (2002).

[4] Snitko Yu.P., Grigorovich K.V. and Shur E.A., Proc. of the Jubilee Rail Commission, Novokuznetsk, (2002), p.257.

[5] Shur E.A., Trusova T.N., Grigorovich K.V. and Trushevskii S.M., Proc. of the Jubilee Rail Commission, Novokuznetsk, (2002), p.229.

[6] Reikhart V.A., Proc. of the Rail Commission 2004 "Increasing the Quality and Service Durability of Rails", Intekst, Moscow, (2005), p.29.

[7] Grigorovich K.V., Analyst and Control, 4(2000)3, pp.244-251.

[8] Krasovskii P.V., Grigorovich K.V., Metally, (2002)2, pp.10-16.

[9] Shibaev S.S., Krasovskii P.V., Grigorovitch K.V., "Solubility of oxygen in iron-silicon melts in equilibrium with silica at 1873 K", ISIJ International, 45(2005)9, pp.1243-1247