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Determination of inclusions in liquid steel after calcium treatment

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Abstract: Nozzle blocking was eliminated by calcium-treated liquid steel through changing the chemical and phase composition of alumina inclusions in aluminium-killed steel. Three different methods were applied to determine the composition of inclusions in liquid steel: total oxygen content samples, sampling spoon samples, and “lollipop” steel samples. The results show that calcium modification of liquid steel influences the inclusion composition varying from 2wt% to 14wt% depending on the method used. The composition of inclusions contains mainly Al_2O_3-CaO only, or is associated with SiO_2 or MgO depending on the initial input. The methods used in this study are indicators of the inclusion composition but can be improved to quantify the inclusion size.

Keywords: inclusion; modification; castability; deoxidation

1. Introduction

Calcium treatment is applied after steel refining to eliminate nozzle blocking by changing the chemical and phase composition of alumina inclusions in aluminium-killed steel [1-3]. This treatment is based on calcium having a considerably higher affinity for oxygen than aluminium and forming a low-melting point mixture with aluminium oxide. Successful calcium treatment relies on the following: injection of the calcium by wire feeding, use of a sufficient amount of calcium, and avoiding the reaction of calcium with dissolved sulphur rather than with alumina inclusions [1]. If the calcium content in liquid steel is not rational, however, the effect of calcium treatment is negative, the castability and fluidity of liquid steel rapidly deteriorates [3]. From a detailed analysis of the link between inclusion composition and casting behaviour, it appears that clogging is avoided if the inclusions contain more than 50wt% liquid phases in the liquid steel [1].

The aim of the present work is to evaluate the sizes and compositions of inclusions before and after calcium treatment at the Mittal Saldanha Plant. Three different methods were used: total oxygen content samples, sampling spoon samples, and “lollipop” steel samples.

Total oxygen content is used as a criterion of steel cleanliness in the steel making process. The equilibrium between aluminium and oxygen during deoxidation is represented by the following equation:

$$\lg K = \lg\left(w_{[\mathrm{Al}]}^2 . w_{[\mathrm{O}]}^3\right) = -\frac{62780}{T} + 20.54 \tag{1}$$

where K is the equilibrium constant of the reaction, $w_{[\mathrm{Al}]}$ the aluminium content in steel, $w_{[\mathrm{O}]}$ the oxygen content in steel, T the temperature.

According to Eq. (1), if $w_{[\mathrm{Al}]}$=0.03wt%-0.06wt%, the free oxygen content is 3×10^{-6}-5×10^{-6} at 1600°C. Because of the small number of large inclusions in the steel and the small sample size for total oxygen content measurement (normally 20 g), total oxygen content really represents the level of small oxide inclusions [4].

The sampling spoon shown in Fig. 1 is a steel cup with a wooden lid which has a steel handle used to manipulate the sampler. Before sampling, the wooden lid is fastened to the cup using copper wire. The cup is then submerged in the steel, below the slag layer. After a few seconds of melting, the copper wire releases the wooden lid, allowing liquid steel to enter the cup. Once the sampling spoon is removed, it is cooled and the sample is subsequently taken out. The

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sample from the spoon does not contain slag and the sampler does not filter out inclusions from the steel [5].

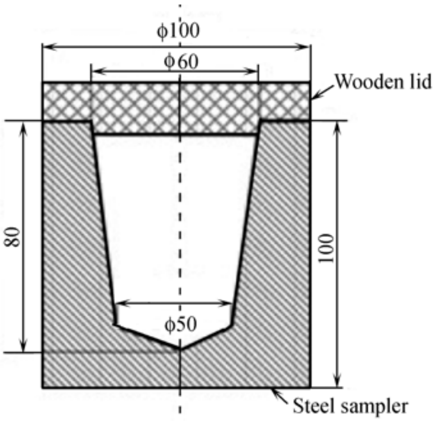

Fig. 1. Schematic drawing of the sampler used to collect liquid steel samples (unit: mm).

2. Materials and experimental procedure

Steel samples were obtained from an integrated steelworks which produced aluminium-killed low-carbon (0.05wt% C) steel. The plant used two ladle furnaces as holding vessels before continuous casting, with the holding time ranging from 45 to 401 min. The total content of FeO and MnO in the ladle slag was below 1wt% in all cases after LF refining. The ladle refractory was MgO-carbon bricks at the slagline and in the intermediate zone and alumina-spinel carbon bricks in the barrel and bottom. Calcium treatment was applied just before sending the ladle to the continuous caster, and calcium wire was used for treatment.

The samples were obtained from different heats with the steel mass ranging from 170 to 180 t. Steel temperatures after calcium treatment varied from 1591°C to 1604°C with tundish temperatures from 1561°C to 1569°C. The calcium content of the steel was from 16×10^{-6} to 34×10^{-6} in the ladle after calcium treatment, and from 16×10^{-6} to 19×10^{-6} in the tundish. The aluminium content was in the range of 0.01wt%-0.03wt%, and the sulphur content was in the range of 30×10^{-6}-50×10^{-6}. "Lollipop" steel samples were taken before and after calcium treatment in the ladle and in the tundish [1].

All the samples were cut and polished for scanning electron microscopy (SEM) using backscattered electron imaging to identify the inclusions. Inclusion compositions were analysed by energy-dispersive X-ray microanalysis (EDX), generally using 100 s of live time per inclusion. The amounts of calcium, aluminium, manganese, and sulphur were quantified. At least 20 inclusions were analysed per sample. The inclusions were classified according to the method used, and the existing states of these inclusions in the liquid steel were ascertained according to the CaO-Al_2O_3 binary, CaO-MgO-Al_2O_3, and CaO-Al_2O_3-SiO_2 ternary diagrams.

3. Results and discussion

From Figs. 2 and 3, the majority of the inclusions are alumina with a low amount of sulphur. The calcium modification of inclusions (50wt% liquid) determined by SEM-EDX analysis varies from 4wt% to 5wt% for total oxygen content samples, 2wt% to 10wt% for sampling spoon samples, and 2wt% to 14wt% for "lollipop" steel samples. This indicates a partial and full liquefaction of the oxide inclusions.

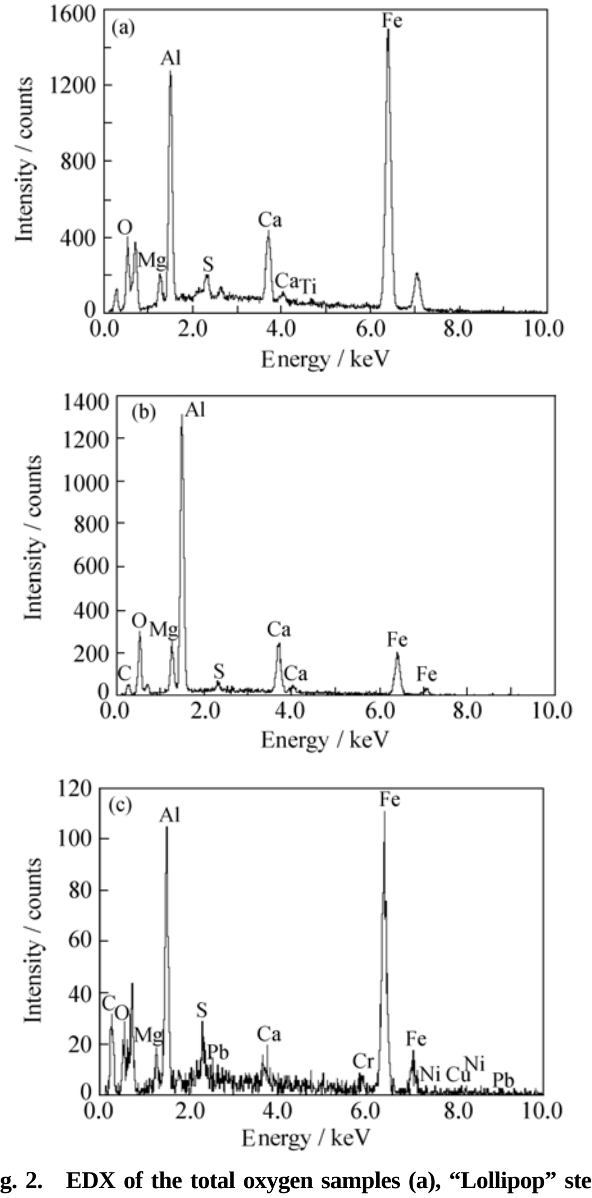

Fig. 2. EDX of the total oxygen samples (a), "Lollipop" steel samples (b), and sampling spoon samples (c) in the tundish, respectively.

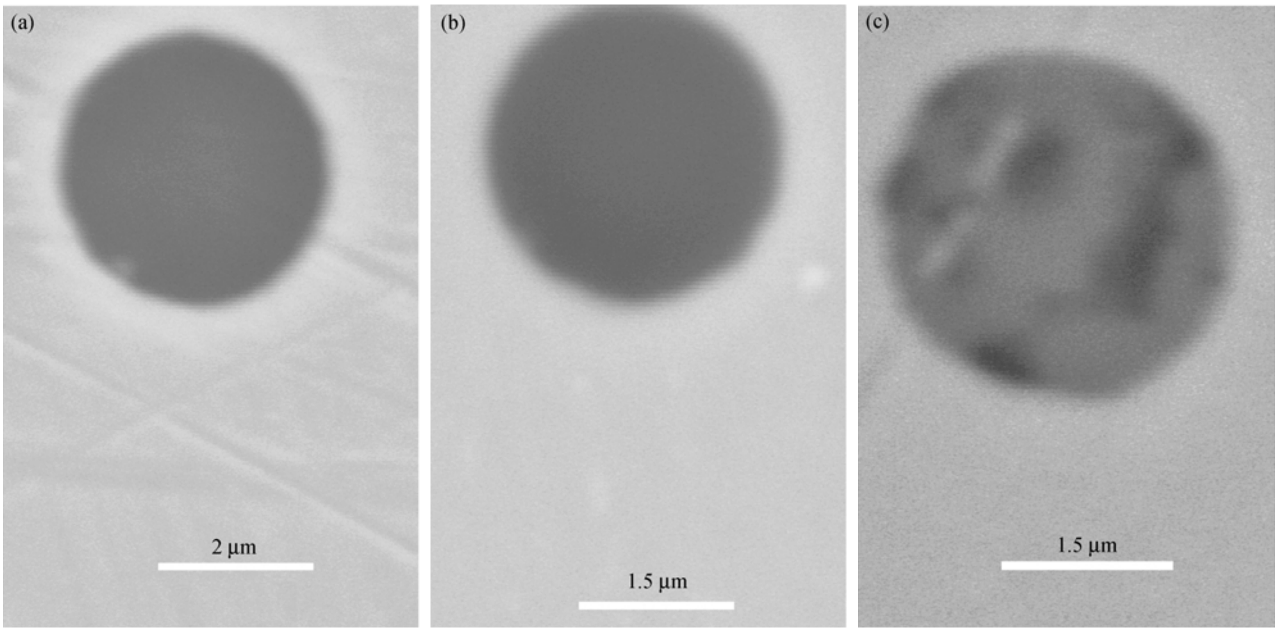

Fig. 3. Backscattered electron images of inclusions after calcium treatment: (a) total oxygen samples; (b) "Lollipop" steel samples; (c) sampling spoon samples.

The inclusions in the calcium treated steel can be classified according to their composition as: (1) Al_2O_3-CaO binary inclusions formed by the combination of alumina with calcium oxide after calcium addition; (2) Al_2O_3-SiO_2-CaO ternary inclusions formed by the combination of calcium aluminate with silicate; (3) Al_2O_3-CaO-MgO ternary inclusions formed by the combination of deoxidation product with MgO in the top slag [3].

In Fig. 4, different symbols are for the samples from different heats, where A, C, and M indicate Al_2O_3, CaO, and MgO, respectively. Calcium treatment changes the inclusion compositions considerably, which is away from MgO-Al_2O_3 spinels, and shifts to higher CaO contents and lower MgO contents [1].

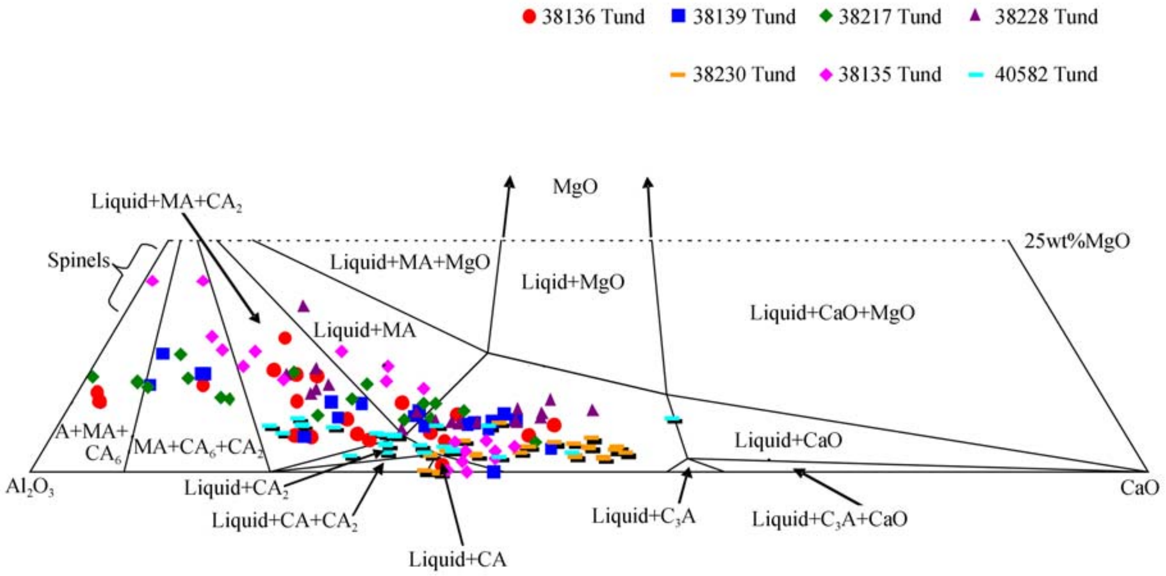

Fig. 4. Compositions independent of the method used.

Fuhr and Cicutti studied the relationship between the inclusion composition and nozzle blocking, and found that the increment of CaO could be caused by the strong interactions with the slag because of vigorous argon bubbling performed to promote steel desulphurization [6].

Fig. 5 shows that the CaS content of the inclusions increases at higher Ca/O mass ratios once the inclusions have been modified to the liquid form. Geldenhuis and Pistorius studied the minimisation of calcium additions in steel, and found that the CaS contents were generally higher than the equilibrium prediction, presumably reflecting a kinetic trend [7].

However, calcium treatment is not efficient for high sulphur steels as calcium reacts with sulphur to form solid calcium sulphide instead of liquefying the alumina [5].

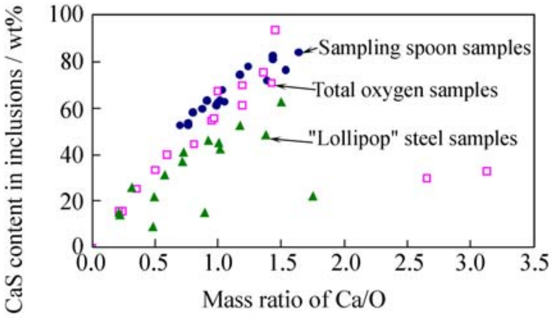

Fig. 5. Relationship between the CaS content and the Ca/O mass ratio of inclusions.

4. Conclusion

Within the investigated temperature range varying from 1560°C to 1600°C, the microinclusions observed in the ladle slag FeO are mainly composed by alumina before calcium addition. After the treatment, the microinclusions are converted into calcium aluminates with small quantities of MgO or SiO_2. Inclusions from calcium modification of liquid steel vary from 2wt% to 14wt% depending on the method used. Under soft bubbling, the compositions of microinclusions remain almost unchanged during the process, being mostly liquid at the steelmaking temperature. This ensures good castability and absence of deposits in the nozzle wall. The castability problems are mainly attributed to an insufficient modification of alumina inclusions.

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