Are Liquid Inclusions Necessary to Improve Castability ?

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1. Introduction

In Hoogovens' BOS No. 1 over one million tonnes of billets are produced annually on two continuous casting machines from 105 tonnes ladles. The start up of both machines was in 1988. Liquid steel was provided via two (out of three) converters and two stirring stations. In 1991 a ladle furnace was installed to maintain a better temperature control. In order to prevent clogging and to improve the castability, steel is treated with calcium. Calcium is injected by cored wire as CaSi or CaFe [1].

Aluminium and silicon aluminium (SiAl) killed steels are cast with slide gate and submerged entry nozzle (SEN). In resulfurized SiAl killed steel a kind of clogging occurs that is described as 'casting like pudding'. This description stems from the observation that the steel seems to get a high viscosity. The slide gate behaves very unstably and opens gradually. This eventually leads to clogging that puts an end to casting (figure 1).

Manganese silicon killed steels are cast through metering nozzles. Shrouding is performed by bellows under a nitrogen atmosphere. Castability problems sometimes occur: the steel flow between tundish and mould becomes irregular. At the same time the steel throughput decreases which eventually makes the strand stop casting.

A generally accepted view is that a calcium treatment transforms solid Al_2O_3 inclusions into liquid calcium aluminates. These liquid inclusions prevent clogging [2]. In resulfurized SiAl killed steels calcium can also react with sulfur to form CaS [3,4]. CaS is solid at steelmaking temperatures and may contribute to clogging [5].

Of the effect of calcium treatment on the inclusion population in Mn-Si killed steel little is known.

The aims of this work were (1) to investigate what kind of inclusions cause clogging in resulfurized SiAl killed steel in order to optimise the calcium practice and (2) to understand the effect calcium has in MnSi killed steels.

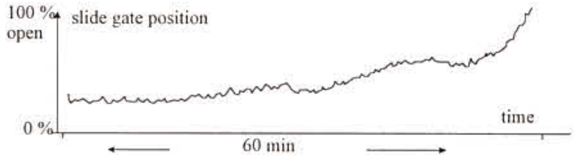


Figure 1. Casting behaviour of resulfurized SiAl killed steel investigated in this work: an unstable slide gate that opens slowly.

2. Method

The attention was focused on steel grades that showed the largest castability problems at the time of the research (1989-1992): resulfurized SiAl killed steels and high carbon MnSi killed steel (Table 1). All SiAl killed steels were calcium treated at the ladle furnace in dolomite lined ladles. The MnSi killed heats were treated at the stirring station. High carbon MnSi killed steels were calcium treated in dolomite lined ladles.
As a reference, the inclusions in medium carbon MnSi killed steel, which is not treated with calcium, are given (Table 1). Here usually no castability problems occurred if this steel grade was made without calcium treatment in an andalusite lined ladle (80% Al_2O_3, 20% SiO_2). However, in a dolomite lined ladle (60% CaO, 40% MgO) castability was bad.

Data on steelmaking practices, steel analysis and reports on castability were examined in detail. Steel samples were collected to study the inclusions as a function of lining, calcium practice and steel grade. Steel samples were taken at the secondary metallurgy station before and after calcium treatment, after sulfur addition in the case of resulfurized steel, and during casting from the tundish.

Table 1: Average steel composition of steel grades, ladle refractory and ladle treatment

	C 10^{-3} wt%	Mn 10^{-3} wt%	Si 10^{-3} wt%	Al 10^{-3} wt%	S 10^{-3} wt%	Ca ppm	Ladle refractory	Treatment	Calcium treatment
SiAl	400	800	250	35	20-45	10	dolomite	ladle furnace	yes
MnSi medium C	100	490	130	-	30	0	neutral and dolomite	stirring station	no
MnSi high C	670	610	200	-	20	20	dolomite	stirring station	yes

A fractional total oxygen analysis is made to measure the total oxygen level and to distinguish different types of oxides present in the steel. From this analysis the oxides of different stability can be distinguished because more stable oxides are reduced at higher temperatures [6].

The inclusions were studied using a Scanning Electron Microscope (SEM) and their composition was measured by Energy Disperse Spectroscopy (EDS).

Deposits were analysed from 8 SEN's using a SEM, all from resulfurized SiAl-killed heats:

- seven SEN's from charges that showed 'pudding type' clogging;
- one SEN from a sequence without clogging.

The deposits found after casting in the slide gate and SEN were studied by SEM. Occasionally X-ray Diffraction (XRD) was used to discriminate different phases.

No clogs were recovered from the Mn-Si-killed heats. It was not possible to recover a metering nozzle with adhering steel after a troublesome sequence of MnSi killed steel.

3. Results

Although common factors exist in the results of the study of the process data, steel samples and clogging material, it is possible to discuss the results for the SiAl killed steels and the MnSi killed steels separately.

3.1 Resulfurized SiAl steels

In order to investigate the influence of total oxygen level on the occurrence of clogging, several samples were analysed. Surprisingly, total oxygen level in SiAl killed steels did not show a relation to the occurrence of clogging (Table 2)

Table 2: Total oxygen in SiAl killed steels

	Resulfurized no clogging O_{tot} [ppm]	n	Resulfurized Clogging O_{tot} [ppm]	n
before CaSi	21	6	22	9
after CaSi	20	6	25	6
after S	22	6	22	9
tundish	19	8	17	10

In the SENs two kinds of deposits were found:

1 Deposits consisting of $MgO.Al_2O_3$, $CaO.y\ Al_2O_3$ (y ≈ 1.5) and CaS particles (figure 2). These deposits were found in 6 of the 7 SENs showing clogging. In the slide gate area the same deposit types were found as in the SEN.

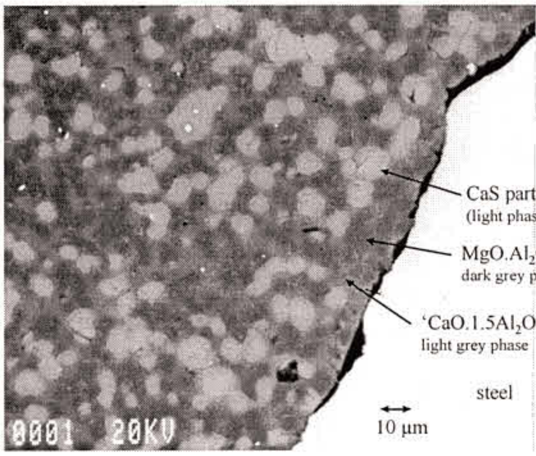
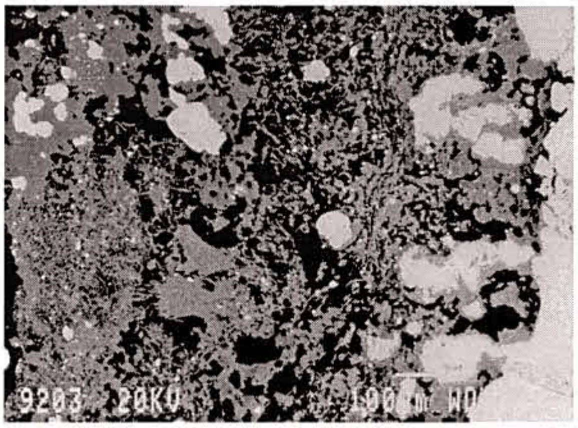


Figure 2. Deposits in resulphurized SiAl killed steel showing CaS particles

2 A deposit simlar to the previous ones, but without CaS. These were found in the SEN without clogging and in 1 of the 7 clogged SENs (figure 3).

calcium magnesium aluminates steel



100 µm

Figure 3. Deposits in SiAl killed steel without CaS

The $CaO.yAl_2O_3$ (y≈1.5) present in the deposits within the oxide phase consists of calcium aluminates ranging from $CaO.2Al_2O_3$ to $CaO.Al_2O_3$ (XRD results).

Samples taken during ladle treatment and during casting show the same kind of inclusions as the deposits: $MgO.Al_2O_3$, $CaO.yAl_2O_3$ ($1 < y < 2$) and a lot of loose CaS particles (average diameter 3µm, maximum 10 µm). Calcium aluminates surrounded by a CaS layer are rare.

Because the deposits are similar to the inclusions in liquid steel, it was concluded that the deposits leading to a pudding like casting behaviour come from inclusions in the steel. CaS is seen as the main cause for clogging because 6 out of 7 clogged SEN's contained CaS and the SEN that did not show clogging only contained $CaO.yAl_2O_3$ and $MgO.Al_2O_3$.
The Mg content in steel samples from tundish was 1.3 +/- 0.6 ppm (n=14) and no significant difference in Mg content was seen between clogged (1.3 ppm Mg) and non clogged heats (1.4 ppm Mg). Mg/Ca in the steel does nor exceed 0.17 and in the deposits Mg/Ca is approximately 0.30. So the rate at which $MgO.Al_2O_3$ particles build a deposit is twice the rate at which calcium aluminates plus CaS particles accumulate. So $MgO.Al_2O_3$ contributes more to clogging than $CaO.yAl_2O_3$, but not as severely as CaS.

If the different types of inclusions in liquid steel are ordered in clogging tendency the ranking is in descending order of harmfulness:

- CaS;
- $MgO.Al_2O_3$;
- $CaO.yAl_2O_3$ (y≈1.5).

Contrary to common opinion, the results presented here indicate that calcium aluminates need not be completely liquid at steel making temperatures to reduce clogging. A practice in which CaS is avoided at the expense of incomplete alumina modification is preferred to a practice with complete alumina modification with formation of CaS.

As a result of the investigation the steelmaking practice was improved to reduce the formation of CaS and transform Al_2O_3 to $CaO.yAl_2O_3$ (y≈1.5). The calcium level was decreased from 20 ppm to approximately 10 ppm. This could be achieved at the ladle furnace by maintaining strict alloying schedules and a low FeO + MnO content in the slag (< 1 wt%).
The level of clogging in these resulfurized steel grades has been reduced to such extent that the average sequence length was increased from 3 to 6 heats. A maximum of 12 heats in a sequence can be produced. The SEN life is now the factor limiting sequence length.

3.2 MnSi killed steels

All data were collected from steel treated at stirring stations. Soon after start up of the casting machines in 1988, it was recognised that the castability of MnSi killed steels could be increased significantly by a calcium treatment, especially those MnSi killed steels made in a dolomite lined ladles.

3.2.1 Total oxygen

In general the total oxygen level is higher in MnSi killed steel grades than in SiAl killed steel. The total oxygen value of heats is decreased during calcium treatment (Table 3).

The influence of the calcium treatment can be seen in the fractional total oxygen analysis. After a calcium treatment the inclusions become thermodynamically more stable: this can be seen from the fractional oxygen analysis where higher temperatures are required to reduce the oxides.

Table 3 Total oxygen in calcium treated high carbon MnSi killed steel

	Total oxygen [ppm]	Standard deviation	n
before CaSi	59	10	11
after CaSi	49	9	9
tundish	42	6	11

3.2.2 Inclusions in MnSi killed steel

All inclusions were very small (< 4 µm) and did not

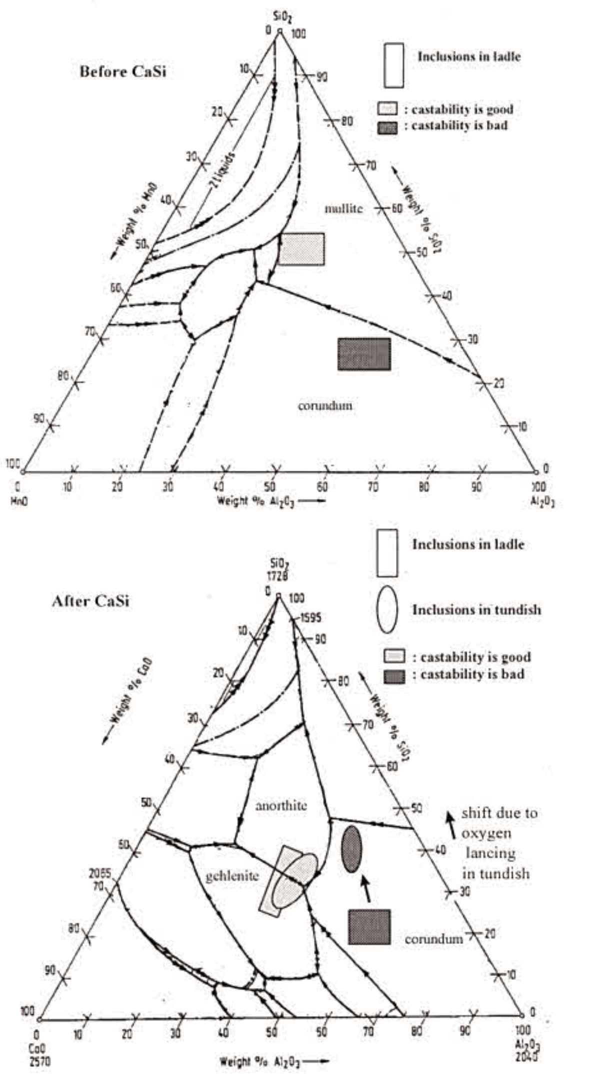


Figure 4. Inclusion composition in high carbon MnSi killed steel before and after calcium treatment. Corundum inclusions show a bad castability

cluster. Calcium treatment did not change the shape of the inclusions or their dimension. No CaS was observed.

Because of a calcium treatment the average inclusion composition shifted from mullite to calcium silicates with alumina (figure 4). The heats where the average inclusion composition is in the corundum phase (Al_2O_3 > 40%) show a bad castability. These inclusions with high Al_2O_3 are already present before calcium is added. A correct calcium treatment can make the corundum inclusions change to anorthite or gehlenite (20 wt% < Al_2O_3 < 40 wt%). Steel with inclusions from these latter phases shows a good castability.

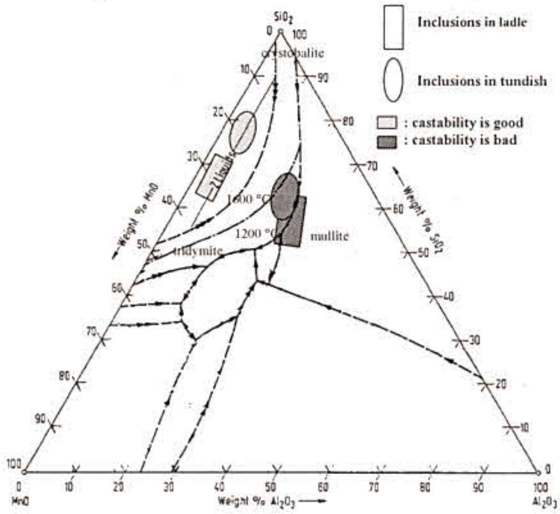


Figure 5. Composition of inclusions and the castability in medium carbon MnSi killed steel without a calcium treatment

Good castability is also seen in MnSi killed steel that is made in an andalusite lined ladle without calcium treatment.
Calculations of the inclusion composition from the steel composition show that solid manganese silicates can be present in these steels [7]. The inclusion is silicate saturated with solid crystobalite (figure 5).

The same steel quality did show severe castability problems when cast from a dolomite lined ladle. Manganese silicates with 15 – 20 wt% Al_2O_3 (tridymite/mullite) were present in the steel (figure 5).

So calcium treated MnSi killed steel can tolerate higher Al_2O_3 fractions in its inclusions before the castability deteriorates. As in resulfurized SiAl killed steel the inclusions do not have to be fully liquid to obtain a good castability.

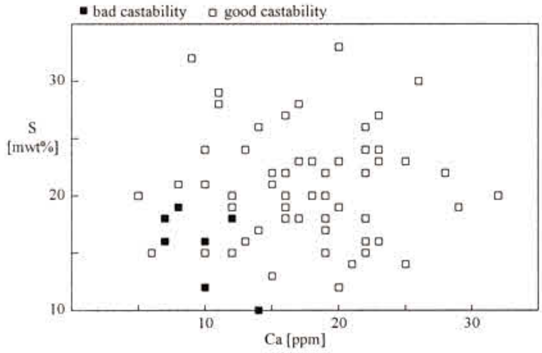


Figure 6. MnSi killed heats with castability problems have low calcium and low sulfur

Plant data show that besides calcium also sulfur improves the castability (figure 6). Because sulfur is a surface active element the interfacial tension between steel and inclusions might affect the castability.

4. Discussion

Some possibilities are discussed now in relation to the casting behaviour of resulfurized SiAl and MnSi killed steel.

4.1 Clogging in resulfurized SiAl killed steel

No inclusions are found that are liquid at steelmaking temperatures. CaS is seen as the main cause for clogging. The calcium level is kept low to reduce the amount or the size of CaS particles

Surprisingly $MgO.Al_2O_3$ is found in the steel. The appearance of $MgO.Al_2O_3$ could be linked to the ladle furnace operation. According to Ahlborg [8] a low oxygen potential in the ladle slag can lead to the formation of $MgO.Al_2O_3$ and high alumina containing calcium aluminates like $CaO.6Al_2O_3$ in steel treated at a ladle furnace.

4.2 Castability of MnSi killed steel

When the silicate inclusions contain more Al_2O_3, castability problems become more frequent. MnSi killed steel that is not treated with calcium already shows a bad castability with inclusions that contain approximately 20 wt% Al_2O_3. In calcium treated steels the critical content of Al_2O_3 in the inclusions is increased to 40 wt%.

The Al_2O_3 content in the inclusions is high (> 20 wt%) in MnSi steels made in dolomite ladles. As the dolomite lining does not contain Al_2O_3 and no aluminium is added to the steel, the slag from a previous heat is thought to be the source of the Al_2O_3 in the inclusions. The mechanism for this is not known.

The data suggest that castability is improved when inclusions do not adhere to the refractory and stay in the steel. The interfacial tension between steel and inclusions is then seen as an important parameter: the lower the better. A high sulfur content might lower the interfacial tension between steel and inclusions [9].

5. Conclusions

* To avoid clogging in resulfurized (silicon) aluminium killed steel and improve the castability of MnSi killed steel inclusions do not have to be fully liquid.

* Inclusions in resulfurized SiAl steel in order from more to less harmful to clogging are: CaS, $MgO.Al_2O$ and $CaO.yAl_2O_3$ ($1 < y < 2$).

* Calcium can improve the castability of MnSi killed steels notably if the inclusions contain more than 10 wt% Al_2O_3.

* Due to an improved calcium treatment resulfurized SiAl killed heats up to 0.060 wt% S are now cast in long sequences at BOS No.1 and the sequence length is limited by the SEN lifetime, which is 12 hours (12 heats).

Acknowledgement

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