SLAG AND IRON DROPLET FORMATION DURING DESULPHURISATION OF HOT METAL – INDUSTRIAL INVESTIGATION

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ABSTRACT

In an integrated steel plant the iron losses during desulphurisation of the hot metal in the transfer ladle may be extensive and the losses may be in the order of 2.5% of the total processed hot metal from the blast furnace. During the desulphurisation process the hot metal is treated with injection of a reagent material, normally calcium carbide or magnesium powder before the hot metal is transferred to the BOF. When desulphurisation to low sulphur content the consumption of the reaction reagent will increase and thereby as a consequence this leads to higher iron losses.

The slag formation has been investigated during normal operations of the desulphurisation station using nitrogen as a carrier gas. During the trials slag samples have been characterised with special emphasize on iron losses to the slag. One hypothesis is that the formation of titanium nitride may affect the iron losses to the slag. Earlier studies have shown that titanium nitrides may form a thin layer around the iron droplets in the slag and therefore prevent the iron droplets from going back to the iron bath.

The characterisation of slag samples have been compared with process data as well as results from long term trials of the iron losses. A trial with consecutive slag sampling during desulphurisation has been also accomplished. The paper describes the conclusions from the investigation.

INTRODUCTION

Desulphurisation agents, e.g. lime, calcium carbide and magnesium, are injected by submerged lances into the metal bath in modern hot metal treatment. Process vessels can be torpedo cars or hot metal ladles. The generated slag is skimmed off after the injection. Metallic iron will be removed together with the slag as metal droplets arrested in the slag and as carry-over during the slag skimming. The total iron losses during desulphurisation can be as large as 1.5 to 2.5% and more of the total hot metal produced by the blast furnace. This fact has an important effect of the total iron yield.

[1] and [2] have reported about the impact of titanium content in hot metal on metal losses during desulphurisation. A hypothesis is that titanium nitrides forms and attach to iron droplets and thereby capture iron droplets in the slag phase. Ender *et al.* found titanium carbonitride surrounding a hot metal granule. The predominant share of the Ti(C,N) solid solutions consisted of titanium nitride and these surface precipitations prevented the re-absorption of the granules to the hot metal bath. [2] have reported that solid Ti compunds in the slag tend to form a thick slag, difficult to skim, increasing the iron losses to the slag pot with hot metal Ti levels of 0.08-0.12 wt-%.

The main reaction during desulphurisation with calcium carbide is [3]:

$$CaC_2 + S \rightarrow CaS(s) + 2C \quad\quad\quad\quad (1)$$

At SSAB Strip Products, Luleå works, the hot metal is transported from the blast furnace with a torpedo car and is thereafter tapped from the torpedo in to the hot metal ladle. Sometimes skimming is performed before injection. The hot metal is treated with calcium carbide injection in the ladle with nitrogen as carrier gas. Calcium carbide is normally injected during a period of 10-15 minutes, depending on the sulphur level required and initial sulphur content of hot metal. The slag is skimmed off with a slag rake after injection. Hot metal sampling and temperature measurement is performed before the hot metal is transported to the BOF. The average hot metal composition consists of 4.7 wt-% carbon, 0.35 wt-% silicon and 0.1 wt-% titanium. The average hot metal temperature is 1370-1380°C.

The objective of this study was to investigate the cause for the iron losses to the slag during desulphurisation of the hot metal.

METHODOLOGY

A test campaign at SSAB Strip Products Luleå works was performed. The hot metal was sampled in the ladle prior to and after calcium carbide injection. All relevant process data during the campaign was collected. Slag samples from 33 heats were collected before slag skimming. At one specific heat the slag was sampled several times with intermediate calcium carbide injections to study the slag formation and the iron losses during injection. Totally 5 slag samples were collected from this particular heat. Calcium carbide amounts prior to each sampling can be found in Table 1.

Table 1: Injected amount of calcium carbide (kg/ton hot metal)

Sample number	A	B	C	D	E
Injected amount of calcium carbide	1.53	3.04	4.55	6.07	6.84

The chemical composition of the hot metal and slag samples from the process were analysed with X-ray fluorescence (samples prepared by fusion with LiB_4). Special investiga-

tions were performed to analyse the iron oxidation state of the slag samples with wet chemical analysis methods. Microscopy characterisation was performed with SEM, equipped with EDS. The characterisation of the samples has been compared with process data.

All slag from the desulphurisation station during the test campaign, totally 410 heats, was processed separately to weigh the magnetic and nonmagnetic fractions.

The slag compositions of the heat with intermediate injection were used for thermodynamic calculations with FactSage version 5.5 with the databases Fe(l) and Fact-slagA.

RESULTS AND DISCUSSION

The special investigation of the metal droplets in the slag samples concludes that almost 100% of the iron in the slag consisted of metallic iron. The metallic share of the slag samples, including dissolved carbon, silicon etc, was calculated to 62 weight percent in average. The remaining part consisted of 8 weight percent graphite and 30 weight percent oxides and sulphides.

From the slag analysis and injected amount of calcium carbide the slag amount has been calculated. Figure 1 shows the calculated slag amount as a function of injected calcium carbide. The slag amount is calculated from the calcium content of the slag samples and the injected amount of calcium carbide. The sampling during intermediate injection is specially marked in the figure. The slag amount is constant between 2.5-4.0 kg injected calcium carbide per ton of hot metal. Above this level the slag amount continues to increase with the amount of injected calcium carbide.
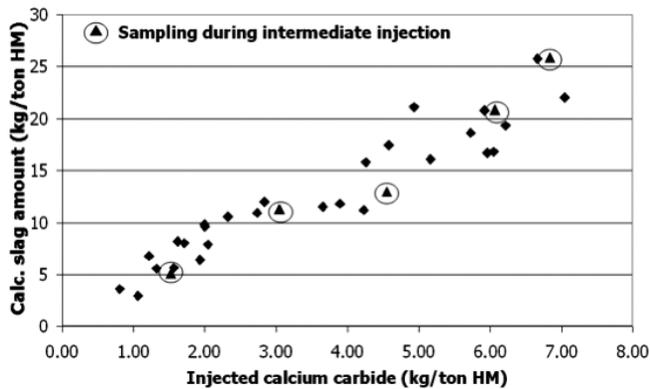

Figure 1: Calculated slag amount versus amount injected calcium carbide (kg per metric ton hot metal)

Figure 2 illustrates the calculated iron losses as a function of the slag amount. The iron losses are calculated from the iron content of the slag samples and the calculated amount of slag. The iron losses are proportional to the slag amount and amount of injected calcium carbide. The calculated iron losses from the heat with intermediate calcium carbide injection are also marked in the figure and do not differ from the other heats.
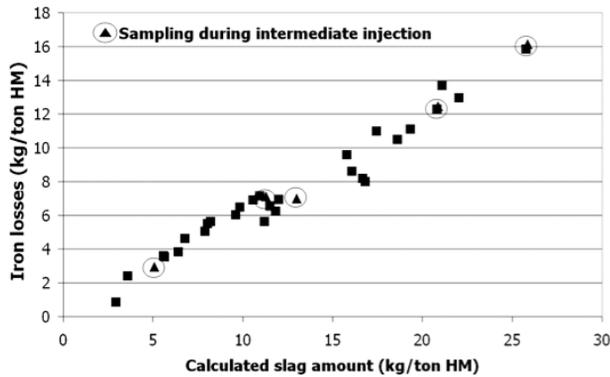
Figure 2: Iron losses to the slag versus calculated slag amount (kg per metric ton hot metal)

The calculated titanium losses increase also with the slag amount, but with a larger variance than the iron losses, c.f. Figure 3. The titanium losses are calculated from the titanium content of the slag samples and the calculated slag amount.
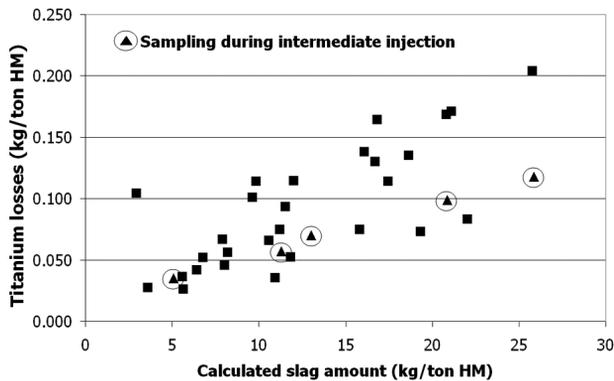

Figure 3: Titanium losses to the slag versus calculated slag amount
(kg per metric ton hot metal)

Iron in the Slag Samples

During the test campaign, totally 410 heats, 28 kg slag per ton hot metal was generated in average. The iron content of the slag after desulphurisation was in average 60%. This implies that 1.7% of hot metal after desulphurisation exists in the slag. The iron losses are higher because the slag skimming also brings some hot metal to the slag ladle.

SEM-EDS Characterisation

SEM-EDS microscope was used to study the slag formation and the iron droplets in slag samples. The slag phase surrounding the iron droplets, c.f. Figure 4, consisted mainly of calcium sulphide and calcium silicates.
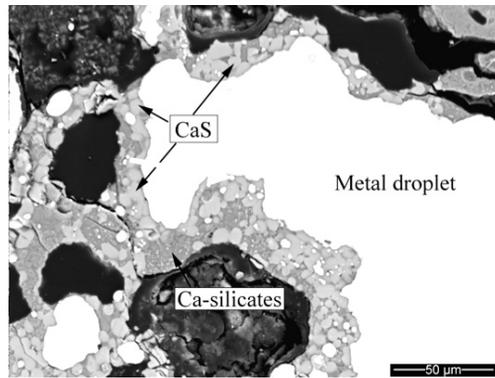
Figure 4: Slag phase composition surrounding metal droplets

Titanium compounds with a significant higher amount of nitrogen, possible TiN, were found in the slag samples, c.f. Figure 5. The appearance of these Ti-nitrides was not to the extent to fully explain for the iron losses to the slag accordingly to the hypothesis suggested by [1] and [2].
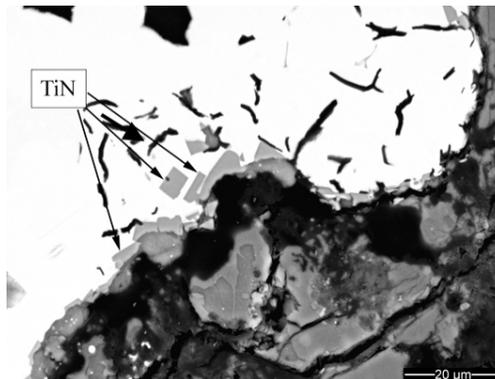

Figure 5: Titanium nitrides in droplet-slag interface

Graphite precipitations were found in the slag surrounding the iron droplets as well as in the droplets, c.f. Figure 6. The graphite appears both as lamellar grains cutting through the slag and as precipitated graphite in the metal droplets. A plausible explanation is that the graphite origins mainly from the dissolved carbon in the liquid metal and from the calcium carbide reaction with dissolved sulphur, c.f. Equation (1).

Graphite precipitates when the liquid metal solidifies and at further cooling of the metal. The metal, with a carbon content of 4.7-4.9 wt-%, starts to solidify at ~1270°C. According to the appearance of graphite, cutting through the slag grains, the slag have solidified before this precipitation. This means a solidification temperature of the slag above 1154°C.
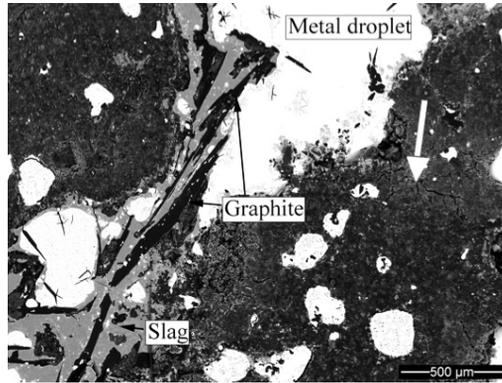
Figure 6: Graphite precipitations in slag

Factsage Calculations

The cooling course between 1600 down to 1000°C of the slag samples from the heat with intermediate carbide injection was simulated with FactSage, c.f. Figure 7. The slag compositions of the slag samples are compiled in Table 2. The cooling course was similar for all slag compositions. All slag components were solid under ~1350°C. Tri-calcium silicate, $3CaO \cdot SiO_2(s)$ were present between 1500°C down to 1280°C where a transformation to di-calcium silicate and calcium aluminates takes place. Calcium sulphide and oxide were present at all simulated temperatures.

Table 2: Slag composition (wt-%) and metal composition (wt-%) used in FactSage calculations

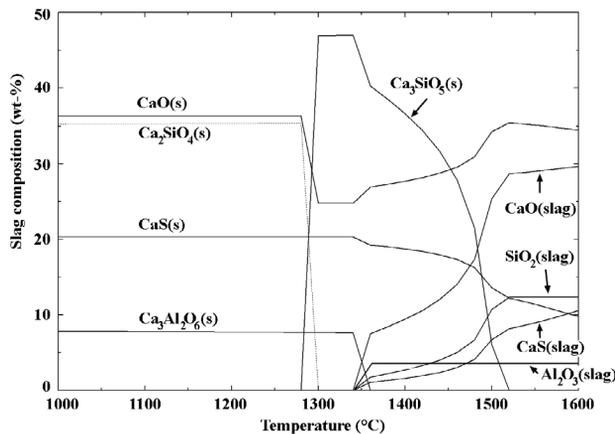|	CaO	CaS	SiO_2	MnO	P_2O_5	Al_2O_3	MgO
Slag A	64.21	20.21	11.87	0.51	0.12	2.95	0.12
Slag B	73.57	17.34	6.45	0.40	0.14	1.95	0.15
Slag C	73.74	18.94	5.00	0.20	0.10	1.88	0.14
Slag D	83.59	9.15	4.93	0.30	0.14	1.89	0.00
Slag E	83.46	9.35	4.68	0.36	0.11	1.84	0.20
Metal	Fe	C	Si	Mn	V	Ti	S
	93.97	4.88	0.35	0.32	0.34	0.14	0.001

Figure 7: Cooling course of slag components, slag composition A

During the slag sampling during the campaign the slag had a dry consistence in the form of gravel. The non-liquid slag indicates a high melting temperature.

CONCLUSIONS

This study has shown that iron losses to the slag during de-sulphurisation process are proportional to the generated slag amount. The iron losses to the slag in the examined slag samples from the test campaign were 62 wt-% in average. The titanium losses to the slag correlates also to the generated slag amount, but the agreement is not as strong.

The SEM-EDS examinations and FactSage cooling calculations have shown that the generated slag during the de-sulphurisation will solidify before the iron droplets starts to solidify. The slag will be nearly completely solidified at the de-sulphurisation process temperature of 1370-1380°C.

The SEM-EDS examinations have also shown that titanium nitrides and carbides form in the slag, surrounding the iron droplets, but not to the extent to fully explain the iron losses to the slag.

The most plausible explanation for the iron losses to the slag is the high melting temperature of the slag. The more or less solid slag arrests the liquid iron droplets. During the further cooling graphite will precipitate from the solidifying metal, penetrating the solid slag that surrounds the droplets.

To enhance the metal separation from the slag, the slag properties must be adjusted e.g. by decreasing the viscosity.

ACKNOWLEDGEMENTS

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