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A study of metal droplet distributions in slags during ladle treatment phase of secondary steelmaking

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The present paper deals with mixing between the metal and slag phase during the ladle refining process, including vacuum degassing. Dispersion of metal drops in ladle slags has been studied. The results show a larger quantity of metal droplets in ladle slag during the alloying and stirring phase than during the subsequent vacuum degassing phase. The thermodynamic and kinetic aspects of the interaction between metal drops and the slag matrix have been considered and probable reasons for the observed distribution discussed.

Introduction

The present work is part of a project financed by the Swedish organization, Jernkontoret, with the main project aiming to study the interaction between slag and metal during ladle treatment. In this work, we have determined the statistical distribution of metal droplets in ladle slags and attempt to investigate what factors affect the presence of steel droplets in slag in the alloying and stirring and vacuum degassing phases. The steelmaker's interest is always to have the minimum quantity of steel lost in the slag due to economic considerations, and it is also an important concern in the recycling of slag.

Investigations have been carried out earlier[1–4] to determine the possible mechanisms of metal droplet formation in ladle slags due to rising argon bubbles used for stirring the ladle. However, little work has been carried out to study the problem of presence of steel droplet in slags in actual industrial practice. In this work, slag samples have been collected during the alloying and stirring and vacuum degassing phases of secondary steelmaking and the distribution of metal droplets haas been statistically analysed using the Swedish standard SS111116[5].

Theoretical background

Metal droplets

Steel droplets are often found in the slag phase at various stages in steel production. Their possible mechanisms for formation have been studied previously by a number of researchers[1–4]. The commonly theorized mechanical mechanisms for steel droplet formation are based on the fact that there is usually vigorous stirring of steel ladles by gas bubbles (usually argon) introduced via porous plugs at the bottom of the ladles. These mechanisms involve entrainment of metal droplets from the steel bath into the slag due to either rupture of a metallic film around the bubble as it passes through the interface between the steel and the slag phase or due to the bubble pulling up a jet of metal behind it as it passes from the steel to the slag phase. These phenomena have been studied in experimental set-ups involving other liquids such as oils, water, mercury[1–2] etc. as well as steel and slag system based set-ups[4].

An alternate mechanism of the steel droplet formation may be reduction of surface tension between slag and steel due to the addition of deoxidants like aluminium, which are added during the deoxidation and alloying stage of the process, which has been studied in this project[8].

Droplet distribution

The distribution of droplets in the slag has been studied using the Swedish standard SS111116[5]. In this standard, optical microscopy is performed on the surfaces of samples to assess the distribution of the particles. This standard is originally intended to be used to statistically analyse non-metallic inclusions in steel. The use of the SS111116 standard in the present work was for the reverse application, i.e. steel droplets in slag. It is based on comparative pictures of inclusions using the Jernkontoret's inclusion chart[5] for assessment of non-metallic inclusions. Since almost all the steel droplets are spherical, the D type gradings applicable to undeformed inclusions in steel were used to analyse the steel droplets. The steel droplets were graded as thin (DT), medium (DM) or heavy (DH). The size ranges for the gradings have been computed using the WinPCMIC[6] which is a software to assess the inclusions using this standard and are listed in Table I. The study was performed at 200x magnification and a field of view of 1.32 mm for all the sample. For very large particles, the DP type gradings given in terms of width*height of scale divisions were used. The program uses statistical analysis as described in the standard[5] to compute quantitative parameters for the inclusions such as area %, number per mm^2 and also frequency of distributions etc.

Table I
Size designations

Designation	Size range
DT	4.7–9.3
DM	9.3–18.7
DH	18.7–37.3
DP	>37.3

Plant trials

Process description

Scana Björneborg is a company that builds tailor-made steel components for sectors such as defence, energy, marine, machinery and offshore applications. It has a scrap based steel plant in its facility at Björneborg, Sweden, for this purpose. The scrap is melted in an electric arc furnace (EAF) and tapped into a ladle. Deoxidants like aluminium and silicon are added and the steel is processed further in a ladle furnace. Graphite electrodes are used in the furnace to compensate for the heat losses and argon gas is introduced via a single porous plug in the ladle for stirring the ladle. When the steel analysis and temperature are at desired levels, the ladle is transported to a tank based vacuum degassing station where vacuum degassing with vigorous argon stirring with two porous plugs is performed to remove hydrogen, non-metallic inclusions, as well as to homogenize the steel before casting. The steel is cast in 4 to 70 tonne ingots by the uphill casting technique. Slag raking and synthetic slag additions are also performed if necessary.

Sampling procedure

The steel grades on which the plant trials were carried out all had low alloying levels so as to reduce the number of factors affecting the results. They were alloyed mainly with carbon and manganese and deoxidized with aluminium and silicon. Samplings were done at three stages in each heat. The first sampling (S1) was performed at the beginning of the alloying and stirring process after arrival from the electric arc furnace and some initial heating, the second sampling (S2) after the alloying and stirring process just prior to the vacuum degassing treatment, and the third sampling (S3) immediately after the vacuum degassing treatment. Each sampling consisted of a 12 mm thick lollipop type steel sample, a slag sample taken with a slag sampling scoop, and temperature taken with a temperature probe. Various process parameters like weight of heat, slag raking, deoxidants added etc. were also logged using the plant's computer system. A schematic figure of the sampling sequence is shown in Figure 1.

Analysis procedure

Slag analysis

Approximately half of the amount of each collected slag sample was ground and analysed with an X-ray fluorescence method. This procedure gave the oxide compositions of the various samples. The apparatus used was an ARL 9800 X-ray fluorescence analyser. The variation on the analysis results is ±0,5%.

Steel analysis

The steel samples were polished and then analysed with an ARL 3460 metals analyser spectrometer for all relevant elements except carbon and sulphur. To get the carbon and sulphur analysis, a Leco CS400 melt analyser was used. The accuracy on analysis was not less than: ±0.023wt% for carbon, ±0.005wt% for manganese, ±0.006wt% for silicon, and ±0.0022wt% for aluminium. Oxygen content was measured in the steel using a Heraeus-ElectroNite Celox®[7] oxygen probe. The accuracy of the probe was ±3% of measured value.

Limitations

The plant trials consisted of 10 heats of four different steel grades. Five of the heats (heats A, G, H, I and J) were of the same steel grade (grade 1) and many of the results are presented for these five heats to ensure that they are comparable.

Results

Slag analysis

As can be seen in Tables II and III, the slag composition varies greatly during the process. As deoxidation proceeds, the alumina content in the slag for the grade 1 steels increases. The FeO+MnO content drastically decreases between samples S1 and S2. A rise in temperature is observed in the alloying and stirring phase of the process. The temperature falls drastically during the degassing phase due to heat losses.

Steel analysis

The steel heats followed are low-alloyed steels with analysis as presented in Table III. It is observed that corresponding to the alumina content increase in the slag, the aluminium content is decreasing during the process for the grade 1 steels.

Area % and number per mm^2 vs. droplet size graphs

The graphs of area % and number per mm^2 versus droplet size for the DT and DM sized droplets show similar trends

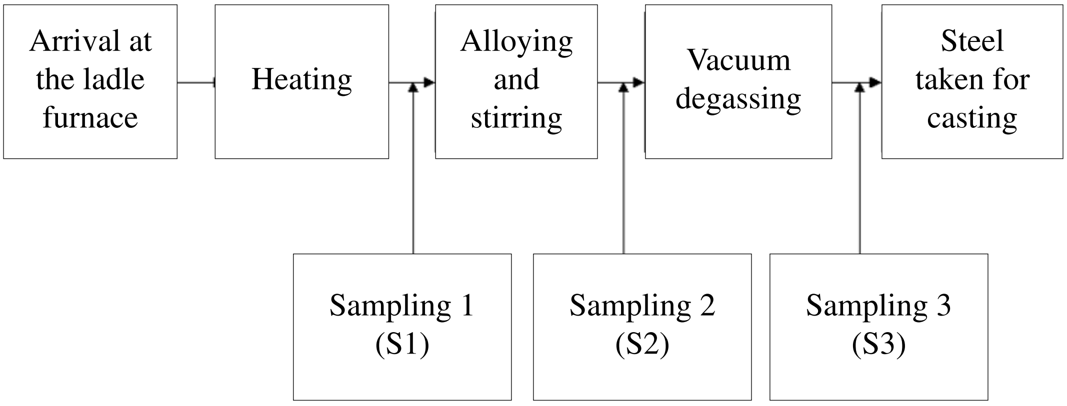

Figure 1. Schematic figure of the sampling process

Table II
Slag analysis, temperatures and calculated slag viscosities

Sample	Grade	CaO [wt%]	MgO [wt%]	SiO_2 [wt%]	Al_2O_3 [wt%]	FeO*+ [wt%]	MnO* [wt%]	FeO+MnO* [wt%]	Temperature [K]	Slag viscosity** (in 10^{-2} Pa*s)
A-S1	1	46.51	14.70	25.99	12.81	1.69	3.16	4.84	1905	7.21
A-S2	1	44.22	16.36	23.60	15.82	1.14	0.86	2.00	1929	5.03
A-S3	1	40.06	19.18	18.53	22.23	0.63	0.32	0.95	1849	5.8
B-S1	2	42.74	12.71	15.98	28.57	1.11	1.09	2.19	1911	5.3
B-S2	2	49.28	11.18	13.90	25.64	1.20	0.46	1.66	1955	3.58
B-S3	2	46.35	9.62	10.02	34.01	0.17	0.21	0.38	1842	9.6
E-S1	4	58.00	6.08	24.05	11.87	4.57	7.44	12.02	1910	10.2
E-S2	4	54.41	6.10	26.51	12.99	0.65	0.98	1.64	1932	9.2
E-S3	4	52.22	6.45	23.53	17.81	0.27	0.14	0.42	1857	12.4
F-S1	5	51.56	9.39	24.33	14.71	3.29	3.66	6.95	1891	8.92
F-S2	5	51.39	7.75	26.94	13.92	1.39	0.62	2.00	1925	8.73
F-S3	5	50.60	8.62	27.31	13.48	0.08	0.18	0.26	1838	14
G-S1	1	58.37	8.23	17.28	16.11	9.01	6.40	15.41	1903	7.32
G-S2	1	49.20	12.97	18.58	19.25	0.93	0.89	1.82	1940	4.23
G-S3	1	44.90	16.18	13.88	25.04	0.21	0.18	0.39	1843	5.86
H-S1	1	53.39	12.16	22.96	11.49	7.86	7.44	15.29	1901	8.14
H-S2	1	48.64	12.96	24.76	13.64	0.86	1.77	2.62	1932	6.19
H-S3	1	47.08	13.72	23.31	15.89	0.29	0.37	0.66	1849	9.04
I-S1	1	50.60	15.89	22.27	11.24	5.21	5.97	11.18	1905	7.06
I-S2	1	47.23	15.96	23.01	13.80	0.93	1.10	2.03	1936	5.12
I-S3	1	45.65	16.17	21.41	16.78	0.34	0.34	0.68	1856	7.26
J-S1	1	39.19	21.44	28.95	10.42	1.33	5.54	6.87	1920	6.77
J-S2	1	37.40	21.98	27.63	13.00	1.55	1.25	2.80	1942	5.12
J-S3	1	36.03	22.07	25.10	16.80	0.23	0.52	0.75	1848	7.78

\+ May include iron droplets
* Not normalized data
** Slag viscosity data calculated using ThermoSlag software based on temperature and compositon of 4 component slag system (Al_2O_3-CaO-MgO-SiO_2)[10]

Table III
Steel analysis

Heat	Grade	C (%)	Mn (%)	Si (%)	Al (%)	a(O) (ppm)
A-S1	1	0.350	0.359	0.215	0.089	3.05
A-S2	1	0.390	0.692	0.246	0.056	5.67
A-S3	1	0.440	0.687	0.262	0.019	3.9
B-S1	2	0.340	0.888	0.265	0.109	2.44
B-S2	2	0.350	0.945	0.252	0.093	4.9
B-S3	2	0.340	0.888	0.265	0.109	1.86
E-S1	4	0.370	0.446	0.225	0.124	3.6
E-S2	4	0.380	0.679	0.247	0.073	5.4
E-S3	4	0.430	0.705	0.268	0.012	5
F-S1	5	0.190	0.238	0.276	0.025	6.84
F-S2	5	0.270	0.728	0.285	0.014	9.35
F-S3	5	0.510	0.718	0.276	0.005	6.1
G-S1	1	0.210	0.183	0.234	0.152	2.31
G-S2	1	0.260	0.675	0.215	0.092	4.93
G-S3	1	0.430	0.679	0.25	0.025	3.22
H-S1	1	0.300	0.268	0.21	0.08	
H-S2	1	0.350	0.736	0.189	0.05	7.02
H-S3	1	0.440	0.762	0.182	0.015	5.48
I-S1	1	0.320	0.268	0.197	0.089	3.01
I-S2	1	0.380	0.726	0.198	0.058	
I-S3	1	0.450	0.746	0.203	0.02	5.2
J-S1	1	0.270	0.493	0.199	0.102	3.39
J-S2	1	0.290	0.648	0.235	0.068	6.15
J-S3	1	0.440	0.655	0.255	0.013	5.88

in almost all the heats observed. The S2 samples show a higher amount of steel droplets in the slag compared to the S3 samples and the S1 samples. The trend also does not seem to be affected by the changes in grade of steel observed in the present investigation. However, it must be noted that all the heats observed were low alloyed steels. The graphs of some of the heats are shown in Figures 2 and 3. The heats I and G are of the same grade of steel (grade 1) whereas the heats F and B are of different grades.

Viscosity vs. temperature graphs

In Figure 4 the viscosity of the different slag samples calculated in ThermoSlag software have been plotted against the measured temperatures for the heats of steels of grade 1. The slag viscosities have been calculated as a function of temperature and slag compositions for the quaternary slag system Al_20_3-CaO-MgO-SiO_2. It is apparent that there are large differences in slag composition at the beginning of the process (as evidenced by the differences in viscosities). However, as the process proceeds, the distributions of the viscosities as a function of temperatures tend to converge. This is as expected since the operators attempt to bring the steels, compositions to the target values.

Area % vs. temperature

In the Figures 5a and 5b the area % of droplets of size ranges DT and DM have been plotted against the measured temperatures of the heats of steels of grade 1. It is apparent that there are far more droplets in the S2 samples than in the S1 and S3. The temperatures at that stage of the heat are also correspondingly higher due to the heat input by the ladle furnace. The smaller size DT droplets are also a generally much higher quantity than the DM size droplets.

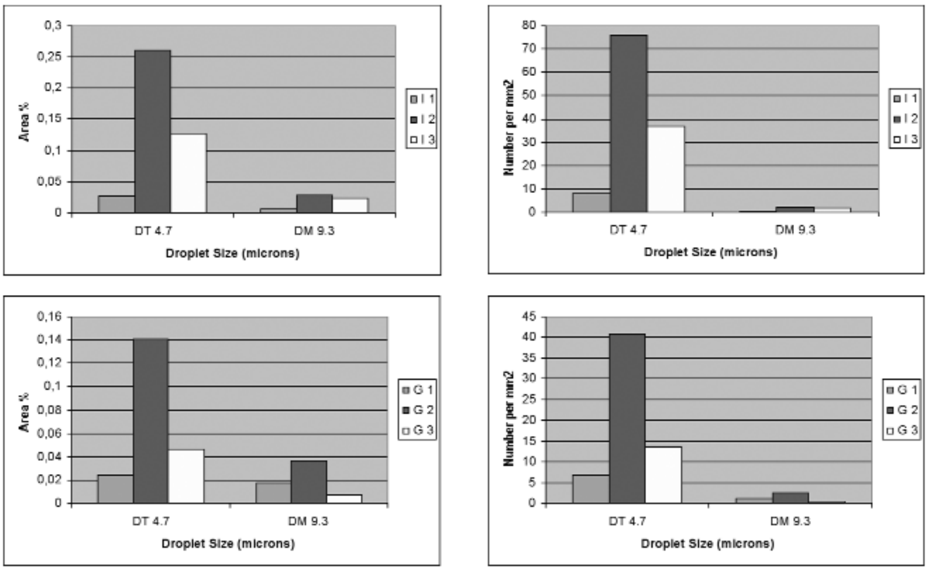

Figure 2. Area % and number/mm² of steel droplets vs. size for steel grade 1, heats G and I

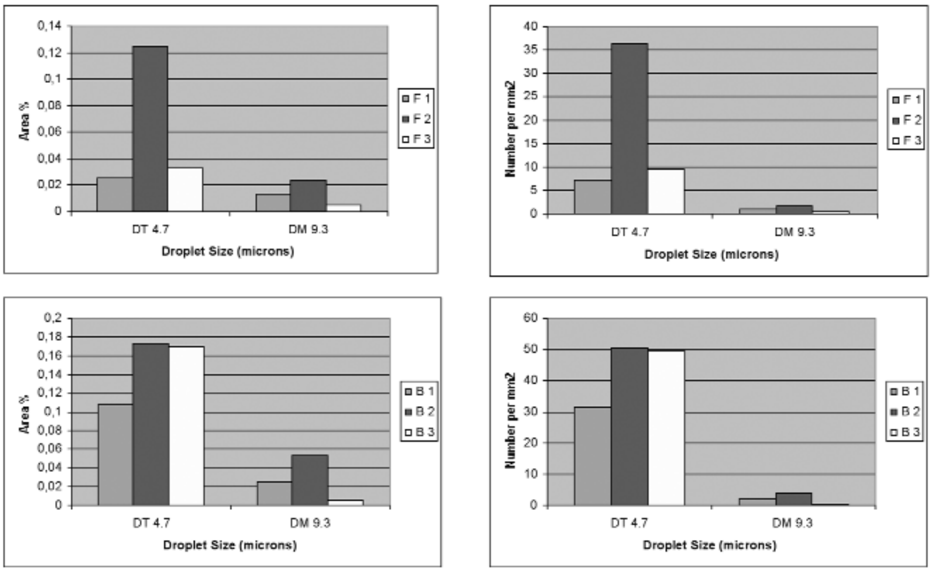

Figure 3. Area % and number/mm² of steel droplets vs. size for steel grades 2 and 5, heats B and F

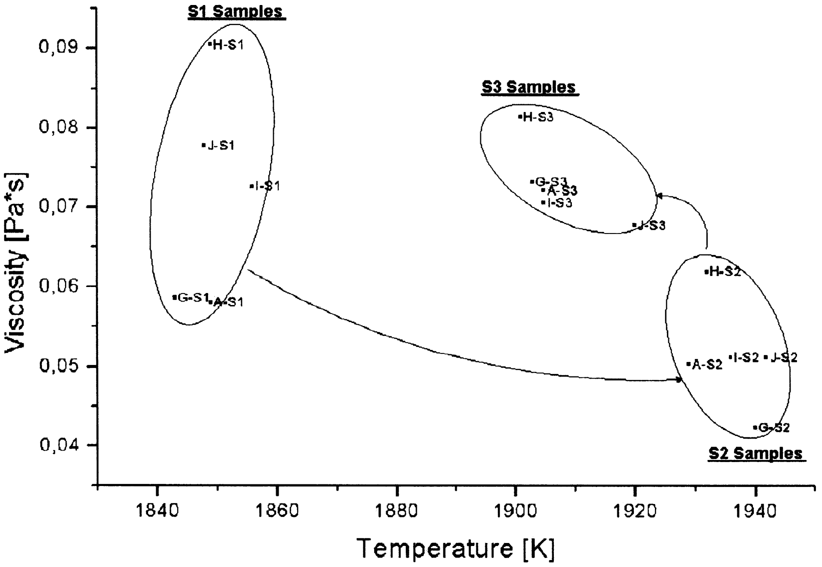

Figure 4. Slag viscosity vs. steel temperature for five heats of steel grade 1

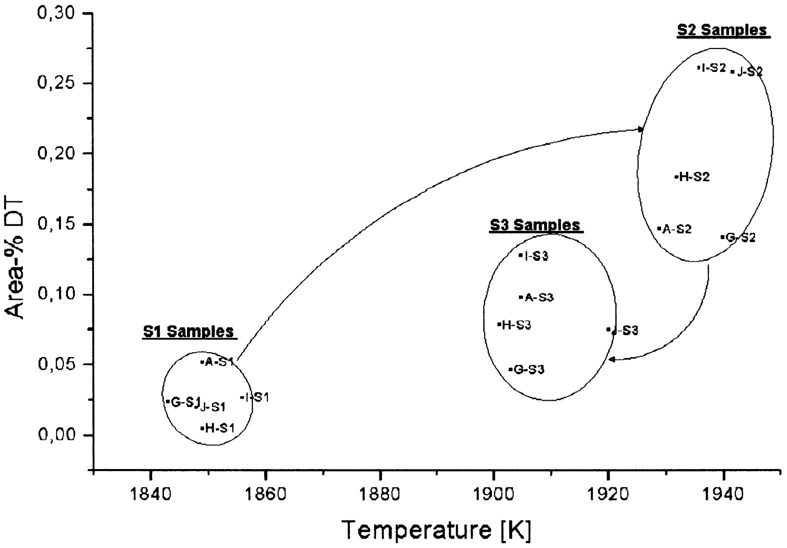

Figure 5a. Area% of DT size steel droplets vs. steel temperature for five heats of steel grade 1

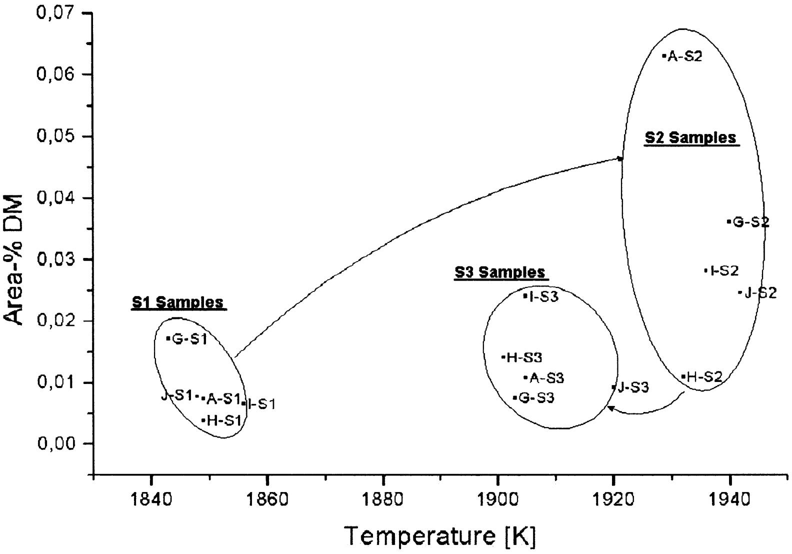

Figure 5b. Area% of DM size steel droplets vs. steel temperature for five heats of steel grade 1

Area % vs. viscosity

In the Figures 6a and 6b the area % of droplets of size ranges DT and DM have been plotted against the measured viscosities of the heats of steels of grade 1. The area% of droplets in S1 samples seems to be not very greatly dependent on the viscosity, and hence the slag composition. Maximum droplets are observed in the S2 samples where viscosity is lower and temperature is higher. These two factors should result in a greater mixing between slag and metal in the ladle.

Discussion

The S2 samples taken just after the alloying and stirring consistently show a much higher quantity of steel droplets in slag compared to the S3 samples taken after vacuum degassing and the S1 samples taken before the start of the alloying process. This profile is common for the DT sized and DM sized droplets in all of the heats analysed.

Firstly it can be caused by vigorous argon bubbling during the alloying and stirring process[1–4]. This has been investigated extensively in experimental set-ups using both liquid systems like water and oils or mercury and more recently with actual steel and slag systems[1–2]. Mechanisms based on breakdown of metal film around the argon bubble as it passes through the slag-metal interface or on pulling up of a jet of metal into the slag layer as the bubble passes through the interface, have been proposed based on observations. However, such investigation is difficult to perform in an industrial environment. Also, it must be noted that argon bubbling was done with a single porous plug in the alloying and stirring phase, while two porous plugs were used in the vacuum degassing phase.

Secondly, emulsification between slag and metal can be promoted by the slag-metal reactions involving surface active elements such as oxygen as discussed by Chung and Cramb[8]. They have observed that high reaction rates result in spontaneous emulsification between slag and steel. It is observed from the slag and steel analysis in the present work that significant slag-metal reactions are taking place during the process. Chung and Cramb have also suggested

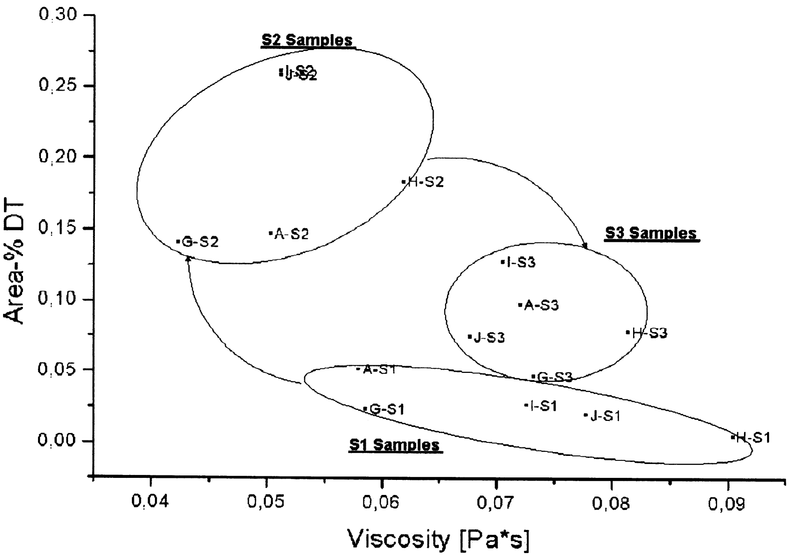

Figure 6a. Area% of DT size steel droplets vs. slag viscosity for five heats of steel grade 1

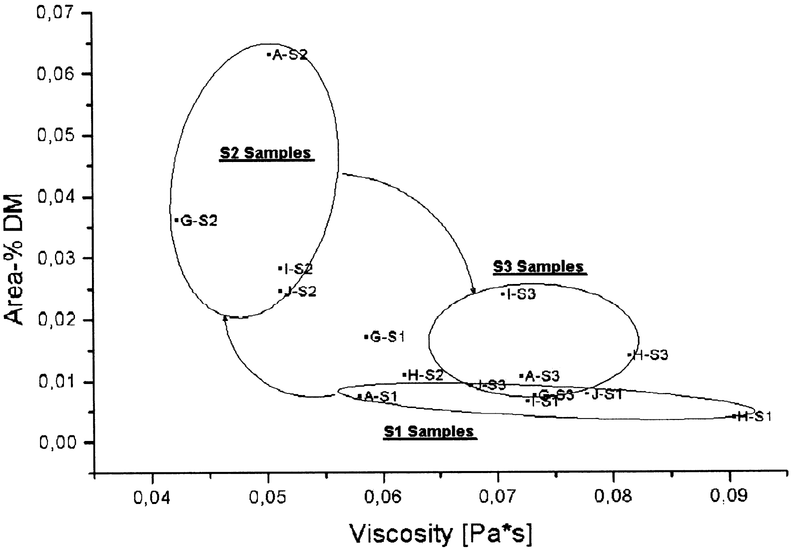

Figure 6b. Area% of DT size steel droplets vs. slag viscosity for five heats of steel grade 1

that low-viscosity slags should be more sensitive to emulsification. The present observations seem to confirm their suggestions since the low viscosity S2 slag samples show a greater quantity of metal droplets in the slag.

Investigations of Riboud and Lucas[9] have suggested that when oxygen is transferred from the slag phase to the metal-slag interface, the surface tension between the slag and metal phase is lowered to approximately zero and therefore a great amount of emulsification should take place between slag and metal. This could be an explanation of the greater number of droplets in the S2 samples, since more reoxidation takes place during the alloying and stirring phase, as may be inferred from the significant fall in FeO and MnO content between S1 and S2 samples in grade 1 steels in the present work. The overall reoxidation reactions at the interface may be represented as:

$$3FeO + 2\underline{Al} = 3Fe(l) + Al_2O_3$$

$$3MnO + 2\underline{Al} = 3\underline{Mn} + Al_2O_3$$

These above reactions are exothermic in nature and local temperature rise would result in localized lowering of viscosity and surface tension and promote emulsification. It is also possible that the metal formed in the reactions contributes to droplet formation.

It is likely that the combination of the above factors contribute to the greater presence of metal droplets in slags of the S2 samples as compared to the S1 and S3 samples.

Conclusions

In the present work, we conclude that far more metal droplets are observed in slag after the alloying and stirring than after the vacuum degassing, despite the higher gas flow rates employed during the vacuum degassing process. The lower calculated viscosities, higher temperatures, and significant slag-metal interactions may account for the results obtained. This would tend to confirm the suggestion made by Chung and Cramb[8]. This could also be attributed to the possible lower surface tension during deoxidation with aluminium and silicon as observed in the earlier work by Riboud and Lucas[9] since in the whole process followed in the present work, the maximum mass transfer of oxygen between steel and slag occurs during the alloying and stirring stage when the deoxidation and alloy additions are made and the operators attempt to bring the steel compositions to the target values. The argon bubbling and heat input, combined with the above mentioned phenomena seems to result in higher droplet formation in the ladle slag during the alloying and stirring stage.

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