Mineralogical Evaluation of Ladle Slags of VOEST-ALPINE STAHL LINZ GmbH

Dipl.-Ing. W. Posch, VOEST-ALPINE STAHL LINZ GmbH, Austria
Dr. H. Preßlinger, VOEST-ALPINE STAHL LINZ GmbH, Austria
Prof. H. Hiebler, Leoben University of Mining, Austria

Key Words: secondary metallurgy, ladle slag, phases, melting point

Abstract

A large number of steel grades are produced at VOEST-ALPINE STAHL LINZ GmbH. The ladle slag must meet different requirements according to the relevant steel grade. The mineralogical structure of ladle slag is highly dependent on its basicity. At a basicity of less than 0.8, MA-spinels occur, and at values in excess thereof, periclase or (Mg,Fe)-wustite occur, depending on the degree of slag deoxidation. At basicities between 0.6 and 1.6, calciumaluminates $C_{12}A_7$ and C_3A are predominant. Calciumsilicates C_2S and C_3S occur throughout the basicity range, CaO_{free} occurs already as of basicities of 1.2, both depending on the SiO_2 content. This enables the metallurgist to specifically adjust the ladle slag according to the steel grade requirements. The knowledge of the slag condition is essential in order to achieve certain metallurgical results, such as desulphurisation or degree of oxidic purity.

INTRODUCTION

Steel is a material on which various demands are placed today, such as specific microstructures, high cleanliness and selective analyses with narrow ranges. In order to meet these high demands, secondary steel making processes must be employed selectively. Secondary steel making may be considered a link between converter operation (= primary metallurgy) and continuous casting operation[1]. Secondary steel making means the treatment of liquid steel in the ladle[1,2].

Depending on the customer's demands on the steel quality, secondary steel making is to meet various targets[1-3]:

- Fine adjustment of the chemical composition
- Adjustment of the superheating temperature required for continuous casting
- Homogenisation of the chemical composition and temperature
- Removal of undesirable tramp elements by decarburisation and degassing
- Deoxidation and separation of deoxidation products
- Modification of sulphidic and oxidic inclusions
- Logistical buffer between the converter and the continuous casting machine

To meet these requirements, VOEST-ALPINE STAHL LINZ GmbH operates two ladle furnaces, one stirring unit and two RH plants as secondary steel making unit.

The ladle furnaces have the following functions:

- Heating by means of an electric arc (3–5°C/min)

- Stirring with inert gas for the purpose of
  - Homogenisation of the melt (temperature and chemical composition)
  - Separation of non-metallic inclusions
  - Desulphurisation with ladle slag by intensive stirring
- Deep desulphurisation by injection of calcium alloys (CaSi or CaC_2)
- Fine deoxidation
- Fine adjustment of the chemical composition
- Modification of inclusion by wire injection

With the exception of heating, the above activities are also carried out on the stirring unit.

The RH plants have the following functions:
- Oxygen correction by means of the O_2 lance for deep decarburisation
- Chemical heating by means of the O_2 lance and aluminium (aluminothermic heating)
- Deep decarburisation for the production of steels with C < 200 ppm
- Removal of nitrogen and hydrogen (degassing)
- Alloying large quantities (e.g., high-carbon steel grades and magnetic sheet steel)
- Alloying of O-affine alloying elements (e.g., Zr, B),
- Adjustment of narrowest ranges of analysis
- Improvement of cleanliness

This list reveals the great variety of tasks to be performed by secondary steel making. As a result, the ladle slags used in this process may vary greatly depending on the steel grade.

Basically, ladle slags must fulfil the following tasks[3]:
- Absorption of deoxidation products to improve the oxidic cleanliness
- Desulphurisation by slag emulsification
- Prevention of reoxidation by air contact
- Insulation to prevent temperature losses of liquid steel
- Protection of refractory lining

Apart from the chemical composition and the mineralogical structure, the melting behaviour of ladle slags is discussed in particular.

PROGRAMME OF PRODUCTION AT VOEST-ALPINE STAHL LINZ

VOEST-ALPINE STAHL LINZ GmbH is a producer of flat rolled steel, which is mainly sold to the automotive and household appliances industries. Other customers are processing industries in the field of pipes and tubes, sections, cold rolling, steel service centres as well as as mechanical engineering companies, structural steel works and apparatus engineering companies. The range of supplies and services comprises hot and cold rolled steel products, with increasing shares of strips with metallic and organic coating.

Fig. 1 gives a survey of the production programme and the production routes, roughly subdivided into four groups. These groups result from the different compositions of the ladle slags at specific steel grades. In the Linz works, the following metallurgical units are operated at present: three LD converters, two ladle furnaces, one stirring unit, two RH plants and three continuous casting machines.

ULC steel grades are heated, decarburised and precision alloyed in the RH plant. Low carbon steels (DDQ) are heated and alloyed in the ladle furnace. Higher-carbon steels (structural steel grades) are heated, alloyed and, if necessary, desulphurised in the ladle furnace. Tubular steels (heavy plate) are to be treated on both secondary steel making units; in the ladle furnace, they are subjected to caciumtreatment for the purpose of desulphurisation, and on the RH plant, nitrogen and hydrogen degassing takes place.

RESULTS AND DISCUSSION

Lime as well as Calumet of Treibacher Industrie AG (a premelted calcium aluminate with a mass content of 72% Al_2O_3, and 23% CaO and some MgO) are charged as slag forming additions. Deoxidation products as well as carry-over slag from the converter, refractory consumption, residual slag are the main components contributing to the formation of ladle slag[4]. The metallurgical success is highly dependent on the amount and composition of the ladle slag. Accordingly, different demands are placed on the ladle slag depending on the steel grade. This also points to the fact that different ladle slag volumes with different chemical compositions will occur in secondary steel making depending on the steel grade. These investigations were aimed at the chemical and mineralogical evaluation of ladle slags.

Results of Chemical Analysis

The average analyses of the ladle slags of the relevant steel group are shown in Table 1. The main components of the ladle slags are CaO - Al_2O_3 - SiO_2 - FeO - MnO - MgO. Additionally, the sulphur content is indicated. The characteristic value of ladle slag is its basicity, which is defined as the ratio of CaO and the sum of Al_2O_3 and SiO_2.

The analyses of the steel groups showed the following characteristic contents: ULC steel grades have a mass content of FeO of approx. 13%, with a mean basicity of 0.6. DDQ and structural steel differ in that structural steel shows lower contents for all slag components, except for CaO and sulphur. The higher CaO content is attributable to the higher amount of lime added, and the higher sulphur content is attributable to the desulphurisation process at structural steel grades. DDQ has a mean basicity of 1.0 and structural steel 1.5. The heavy plate steel grade shows fully reduced slags, i.e., the mass content of the sum of FeO and MnO is less than 2%. This steel group is silicon alloyed and is deep desulphurised with CaSi. Therefore, this type shows higher SiO_2 and sulphur contents in slag. The mean basicity amounts to 1.7.

Microanalytical Findings at Ladle Slags

On account of the widely scattered chemical composition, great differences in the mineralogical structure of the ladle slags are to be expected[5]. For microanalytical examinations on the microprobe 72 ladle slags were selected.

The slag samples were metallically embedded in an Sn-Bi alloy under pressure[6,7]. At first, each individual slag microsection was subjected to a rough preliminary evaluation by means of a light-optical microscope. This preliminary evaluation already proved that specific basicities were to be allocated to specific phases. In these microsections, characteristic microstructural areas were marked and, subsequently, the microsections were delivered to the microprobe for microanalytical evaluation.

The following four figures show typical mineralogical structures of solidified ladle slags with increasing basicity. The following symbols are used for the mineralogical phases: $C_{12}A_7$, C_3A, C_2S, C_3S, MA, C standing for CaO, A for Al_2O_3, S for SiO_2 and M for MgO.

At a basicity of 0.45, primarily separated MA-spinels occur (Fig. 2 and Table 2). Apart from Mg^{2+}, Fe^{2+}, Mn^{2+} and Ca^{2+} are integrated in the solid solution of MA-spinel as can be inferred from the zonar structure of the spinels. Another phase is formed by dendritically separated Fe-wustites. In the wustite solid solution, Mn^{2+}, Mg^{2+} and Ca^{2+} are substituted for Fe^{2+} cations. Owing to the vitreous structure, it was impossible to exactly allocate the residual melt to a mineralogical phase.

The slag microsection did not show any MA-spinels at a basicity of 1.14 (Fig. 3 and Table 3). The solid solutions of magnesio-wustite had been dendritically separated. In the magnesio-wustites, Fe^{2+}, Mn^{2+} and Ca^{2+} are partly substituted for Mg^{2+} ions. Other main components are calcium aluminates, C_3A and $C_{12}A_7$. In C_3A, SiO_4^{4-} tetrahedrons are partly substituted for AlO_4^{5-} tetrahedrons. In order to maintain a charge balance, a monovalent cation instead of a bivalent cation is to be inserted in the cation sublattice. In $C_{12}A_7$, SiO_4^{4-} tetrahedrons are substitued for AlO_4^{5-} tetrahedrons and Mg^{2+}, Fe^{2+} and Mn^{2+} ions for Ca^{2+} ions. It was not possible to clearly identify a bonding of C-A-S.

Fig. 4 and Table 4 display an example of ladle slag with a basicity of 1.67. The main components are C_3A and $C_{12}A_7$. At these basicities, a separate phase is formed by CaO_{free}, which is either dendritically separated or appears in the form of undissolved residual lime. Furthermore, small amounts of Mg-wustite occur.

At a basicity of 2.1, the calcium aluminates described above as well as high amounts of calcium silicates are detected (Fig. 5 and Table 5). In tricalcium or dicalcium silicate, small amounts of AlO_4^{5-} anion complexes are substituted for the SiO_4^{4-} tetrahedrons. In order to maintain a charge balance, $2Si^{4+}$ is to be replaced by $2Al^{3+}/Mg^{2+}$ and $3Si^{4+}$ by $3Al^{3+}/Al^{3+}$. The Mg^{2+}- and Al^{3+} cations behind the slash take sublattice positions in the carbon sublattice[8]. Moreover, MgO and CaO_{free} are found.

Quantitative Phase Analysis

The cumulative result of the qualitative and quantitative phase analysis (large-area analysis) is illustrated in the following figures, Fig. 6 to Fig. 9. The phases determined as well as their shares are plotted as a function of basicity.

At a basicity of less than 0.7, MA-spinels occur, the share of spinel with decreasing basicity increasing at the expense of the $C_{12}A_7$ share (Fig. 6). The low melting calcium aluminate, $C_{12}A_7$, occurs throughout the basicity range. The highest share occurs in a basicity range of approx. 1.0. At a basicity as of 1.2, the share of $C_{12}A_7$ considerably decreases (Fig. 7). At basicities between 1,0 and 1,6 the calcium aluminate C_3A is predominant (Fig. 8). Undissolved and separated CaO_{free} occurs at a basicity range as of 1.2 (Fig. 9).

Influence on the Melting Point of Ladle Slag

The melting point is a characteristic physical value of ladle slags that is relevant to steel making[4]. Fig 10 represents the melting point of ladle slags (hemisphere temperature according to DIN 51730) as a function of basicity. The hemisphere temperature is the temperature at which the sample body approximates the shape of an hemisphere. This figure shows three collectives:

1. At a basicity ranging from 0.4 to 0.8, the melting point ranges from 1370 to 1510°C. In this basicity range, MA-spinels are formed. This high melting point range results from these high melting spinels.

2. The second collective ranges from 1300 to 1340°C in a basicity range between 0.8 and 1.4. In this range, $C_{12}A_7$ has the highest share in the phase. This $C_{12}A_7$ has the lowest melting point among the calcium aluminates, i.e., the low melting points of the ladle slags are attributable to $C_{12}A_7$ in this basicity range.

3. As of a basicity of 1.4, another collective occurs, which ranges from 1350 to 1420°C. At this basicity high amounts of CaO_{frei}, MgO and calcium silicates are formed, with the C_3A portion prevailing. The share of the low melting $C_{12}A_7$ phase substantially decreases in this range as already shown. As of this basicity range, phase portions with higher melting points prevail.

SUMMARY

In the steel making plant of VOEST-ALPINE STAHL LINZ GmbH a wide variety of steel grades meeting various material requirements are produced. According to the relevant steel grade, the steel maker charges a ladle slag with a specific chemical composition (= basicity) for metallurgical treatment in secondary steel making.

Depending on the basicity, specific shares of cations, anions and anion complexes occur in the liquid ladle slag, which have a great impact on the slag condition through short range or long range order formation. Based on the evaluation of solidified ladle slags, this relates to the following mineralogical phases in ascending order with regard to basicity: MA-spinels, $12CaO{\cdot}7Al_2O_3$, $3CaO{\cdot}Al_2O_3$, $2CaO{\cdot}SiO_2$ and $3CaO{\cdot}SiO_2$, CaO_{free}, MgO and, depending on the degree of deoxidation of the ladle slag, (Mg,Fe)-wustites. The mineralogical structure of ladle slag is highly dependent on its basicity.

REFERENCES

[1] *Wiemer, H.-E.:* Übersicht über Verfahren und Anlagen der Sekundärmetallurgie. Stahl u. Eisen 118 (1998), Nr. 7, 27-29. –

[2] *Krauß, S.:* Sekundärmetallurgie - Voraussetzung für eine moderne Stahlerzeugung. In: Sekundärmetallurgie 96, Gerhard-Mercator Universität Gesamthochschule Duisburg (1996) 9-25. –

[3] *Cappel, J., H.-J. Ehrenberg und H.-P. Kaiser:* Verbesserung der Vergießbarkeit durch gezielte Schlackenführung in der Sekundärmetallurgie. Stahl u. Eisen 118 (1998), Nr. 7, 41-47. –

[4] *Reisinger, P., H. Preßlinger, H. Hiebler und W. Zednicek:* MgO-Löslichkeit in Stahlwerksschlacken. BHM 144 (1999), Nr. 5, 196-203. –

[5] *Reisinger, P.:* Auswirkung einer geänderten Schlackenführung auf die Pfannenwirtschaft und die Feuerfestkosten. Dissertation, Montanuniversität Leoben 1998. –
[6] *Preßlinger, H., M. Mayr und R. Apfolterer:* Quantitative phase evaluation of converter slags. steel research 70 (1999), Nr. 6, 209-214. –
[7] *Preßlinger, H., M. Mayr, G. Poferl und W. Koller:* Die quantitative Bewertung der Phasen in Konverterschlacken. BHM (1999), Nr. 7, 269-275. –
[8] Hinz, W: Silicate - Grundlagen der Silicatwissenschaft und Silicattechnik, Band 2, VEB Verlag für Bauwesen, Berlin, 1971 –
[9] *Preßlinger, H.:* Metallurgie und Verfahrenstechnik im LD-Stahlwerk zur Erzeugung hochreiner Stahlsorten. Habilitationsschrift, Montanuniversität Leoben 1993. –
[10] *Preßlinger, H., K. Antlinger, G. Poferl und W. Krieger:* Sekundärmetallurgische Aspekte bei der Herstellung von hochfesten Bau- und Röhrenstählen. BHM 134 (1989), Nr. 9, 255-264. –
[11] *Angeli, J., H. Flößholzer, K. Jandl, T. Kaltenbrunner, W. Posch und H. Preßlinger:* Qualitative and quantitative examinations of microscopic steel cleanliness in slab samples. La Revue de Métallurgie-CIT (1999), Avril, 521-527. –
[12] *Park, J. M. und K. K. Lee:* Reaction equilibria between liquid iron and CaO-Al_2O_3-MgO-FeO-MnO-P_2O_5 slag. 79. Steelmaking Conference Pittsburgh (1996), 165-172. –
[13] *Koch, E., H.-P. Narzt, H. Preßlinger, R. Steffen und H. Richter:* Verbesserung des Makroreinheitsgrades beim Brammenstrangguß. BHM 143 (1998), Nr. 9, 338-344.

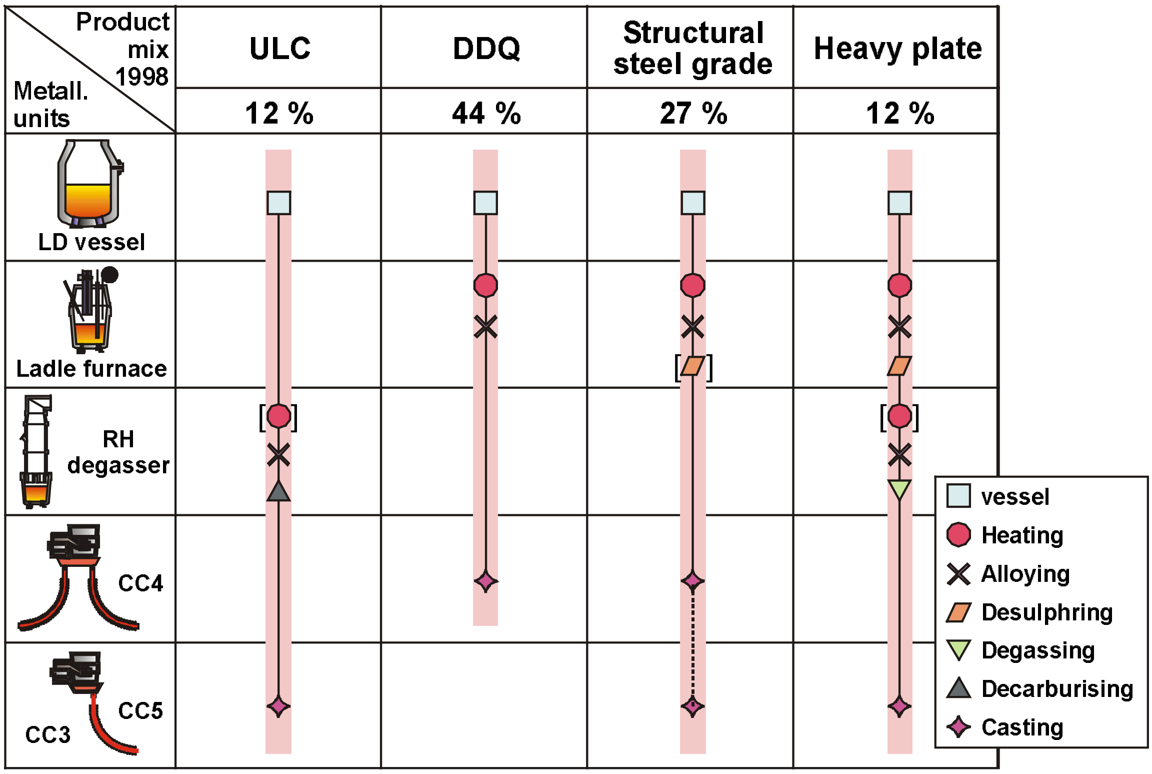

Figure 1: Programme of Production and Route of Production at VOEST-ALPINE STAHL LINZ

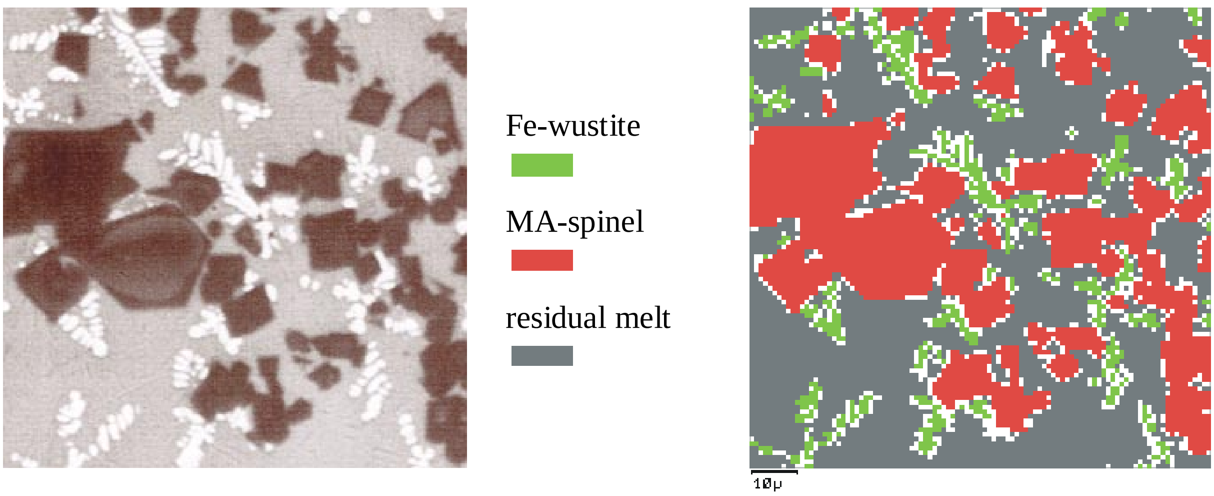

Figure 2: Back Scattered Electron Picture, Phase Map of a Ladle Slag (B=0.45)

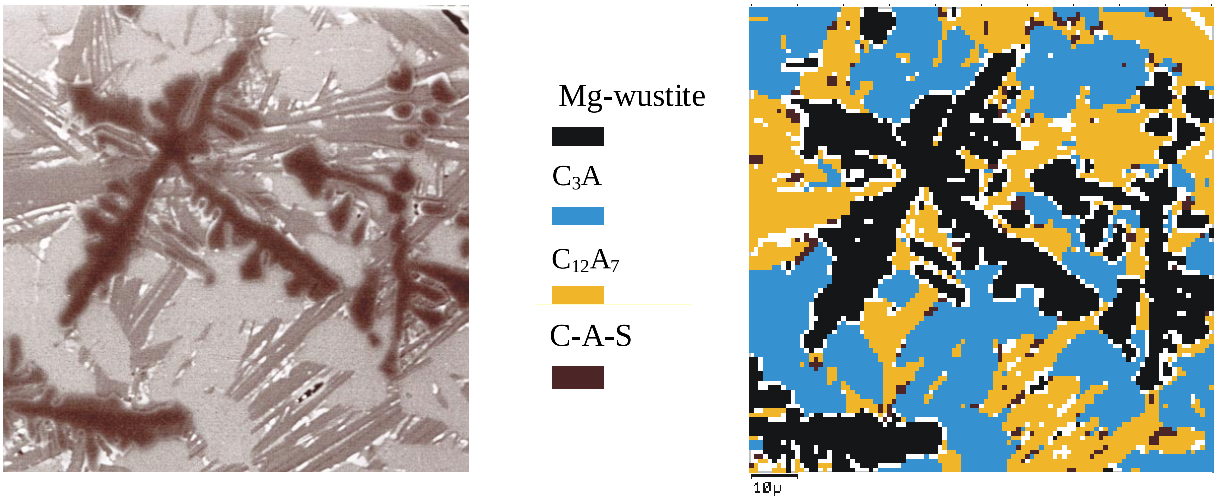

Figure 3: Back Scattered Electron Picture, Phase Map of a Ladle Slag (B=1.14)

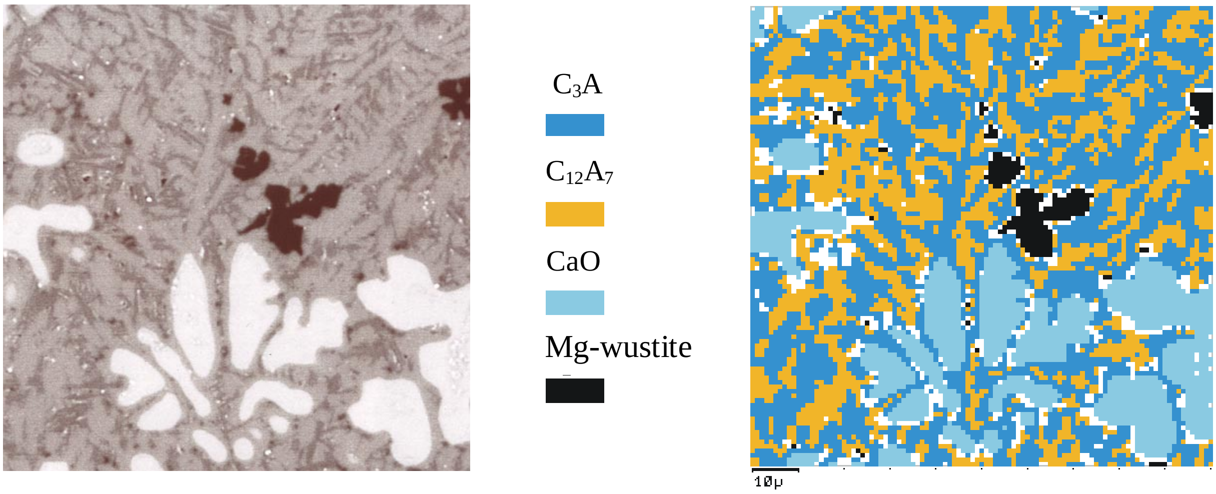

Figure 4: Back Scattered Electron Picture, Phase Map of a Ladle Slag (B=1.67)

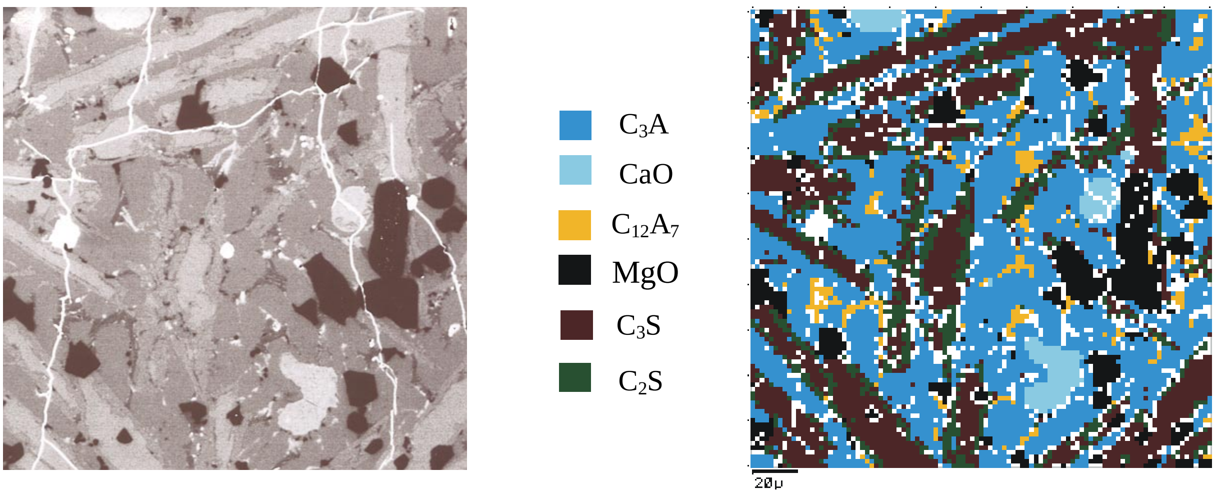

Figure 5: Back Scattered Electron Picture, Phase Map of a Ladle Slag (B=2.1)

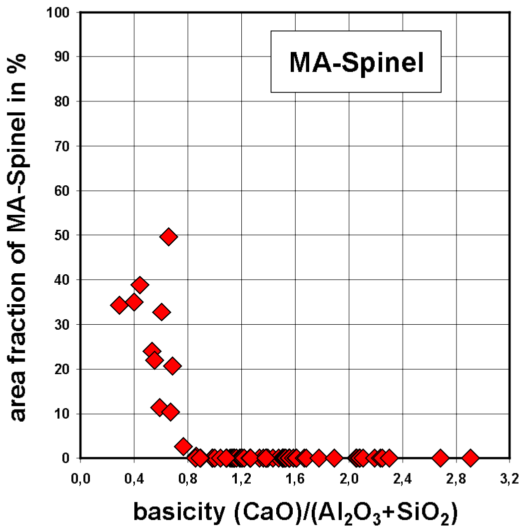

Figure 6: MA-spinel as a function of basicity

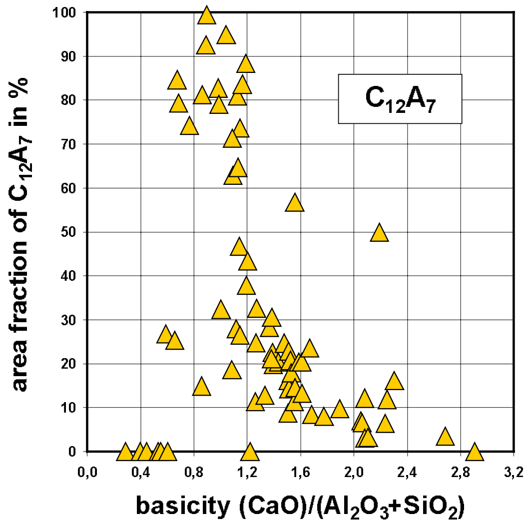

Figure 7: $C_{12}A_7$ as a function of basicity

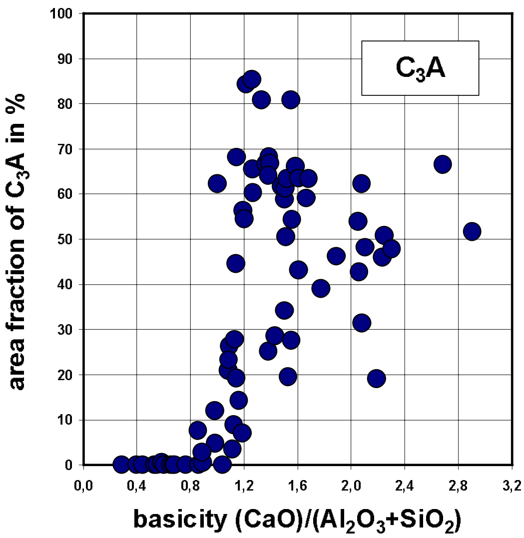

Figure 8: C_3A as a function of basicity

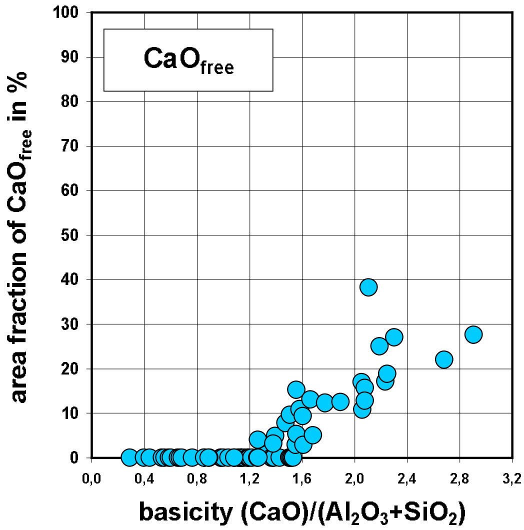

Figure 9: CaO_{free} as a function of basicity

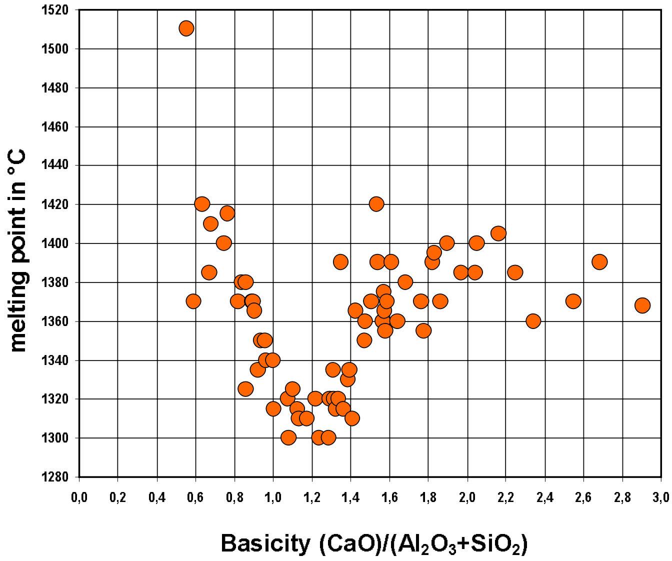

Figure 10: melting point as a function of basicity

Table 1: mass content of ladle slag components in % of different steelgrades

steelgrade	slag component							
	FeO	SiO_2	MnO	CaO	MgO	Al_2O_3	S	basicity
ULC	13,1	6,8	6,0	26,0	9,1	36,3	0,01	0,6
DDQ	5,4	6,9	4,0	39,2	9,2	34,3	0,02	1,0
Structural steel grade	3,8	4,2	2,5	50,9	8,3	29,5	0,21	1,5
heavy plate	1,0	9,6	0,5	55,1	9,9	23,3	0,35	1,7

basicity $(CaO)/(Al_2O_3+SiO_2)$

Table 2: Result of Phase Analysis; mass content of components in % (B = 0.45)

component / phase	Al_2O_3	MgO	FeO	Cr_2O_3	CaO	SiO_2	MnO	TiO_2	S	ar-%
Fe-wustite	7.58	9.94	45.05	0.05	9.04	3.95	23.58	0.81	0.0	6.86
MA-spinel	63.01	20.30	7.34	0.50	1.66	0.75	5.06	0.58	0.0	32.16
residual melt	27.47	2.04	12.22	0.05	35.67	11.42	5.44	2.34	0.0	50.13

Table 3: Result of Phase Analysis; mass content of components in % (B = 1.14)

Component / phase	Al_2O_3	MgO	FeO	Cr_2O_3	CaO	P_2O_5	SiO_2	MnO	TiO_2	S	ar-%
Mg-wustite	0.85	78.79	11.49	0.37	1.32	0.04	0.08	9.26	0.06	0.02	27.73
C_3A	35.09	0.69	0.90	0.08	58.83	0.40	3.24	1.94	0.22	0.02	32.11
$C_{12}A_7$	49.84	2.65	2.20	0.08	40.42	0.28	3.04	1.62	0.39	0.04	26.99
(C-A-S)	30.61	2.55	2.83	0.19	48.88	0.52	10.36	2.37	2.17	0.07	2.18

Table 4: Result of Phase Analysis; mass content of components in % (B = 1.67)

component / phase	Al_2O_3	MgO	FeO	Cr_2O_3	CaO	P_2O_5	SiO_2	MnO	TiO_2	S	ar-%
C_3A	33.02	1.36	0.76	0.06	57.71	0.88	4.93	0.52	0.21	0.17	43.91
$C_{12}A_7$	39.63	4.19	1.62	0.07	45.45	0.75	5.78	0.47	0.44	0.42	28.62
CaO_{free}	0.55	2.68	0.36	0.06	93.52	1.31	0.41	0.79	0.04	0.03	17.88
Mg-wustite	1.98	91.25	2.12	0.08	2.85	0.08	0.33	0.89	0.06	0.04	2.56

Table 5: Result of Phase Analysis; mass content of components in % (B = 2.1)

component / phase	Al_2O_3	MgO	FeO	Cr_2O_3	CaO	P_2O_5	SiO_2	MnO	TiO_2	S	ar-%
C_3A	32.98	0.85	0.11	0.05	57.64	0.40	3.48	0.48	0.12	0.12	39.03
$C_{12}A_7$	44.04	3.47	0.38	0.05	40.73	0.31	4.32	0.71	1.01	0.75	3.24
C_3S	1.13	1.50	0.07	0.06	68.32	0.57	23.81	0.26	0.12	0.04	24.70
C_2S	2.79	0.28	0.06	0.06	62.05	0.53	29.67	0.10	0.41	0.19	9.62
CaO_{free}	0.25	2.94	0.13	0.06	89.44	0.63	0.05	0.59	0.03	0.03	2.38
MgO	0.27	94.63	0.76	0.05	1.00	0.04	0.09	0.85	0.04	0.02	8.68