POSCH, W., PREβLINGER, H., MAYR, M., KLEPP, K., and HIEBLER, H. Sulphur bonding in solidified ladle slags. *VII International Conference on Molten Slags Fluxes and Salts,* The South African Institute of Mining and Metallurgy, 2004.

# Sulphur bonding in solidified ladle slags

W. POSCH*, H. PREβLINGER*, M. MAYR*, K. KLEPP†, and H. HIEBLER‡
**voestalpine Stahl GmbH, Linz, Austria*
*†University of Linz, Linz, Austria*
*‡University of Leoben, Leoben, Austria*

It was investigated in which form sulphur is bonded in ladle slags. For this purpose, the mineralogical phases of the ladle slags were qualitatively and quantitatively evaluated by means of a microprobe. This slag characterization allowed reconstructing the bonding of sulphur into the phases of the ladle slag. Moreover, the reaction process with regard to the ionic theory as well as the structural formula for the mechanism of sulphur bonding were discussed. The bonding of sulphur into calcium aluminate slags is determined by the sulphide ion content in the slag as well as by the ratio of (CaO)/($Al_2O_3$). Calcium sulphide separates only if the slag contains a large number of sulphide ions. When $Ca_{12}Al_{14}O_{33}$ is separated, the sulphide ion is successively integrated into the lattice. The crystal lattice of $Ca_{12}Al_{14}O_{33}$ is characterized by an open, three-dimensional anionic network composed of aluminium-oxygen tetrahedrons linking the edges. In this network, large interstitial spaces are formed, which may be filled with calcium ions on the one hand and statistically with a free oxygen or sulphide ion on the other hand.

Key Words: ladle slag, structure, phases, calcium sulphide, calcium aluminate, desulphurization

## Introduction

In modern steel shops the primary steelmaking units, i.e., converters or electric arc furnaces, are used just for the treatment of hot metal and melting of scrap. All other metallurgical objectives, such as alloying, homogenization, refining and temperature adjustment, are achieved by secondary metallurgy in the ladle or ladle furnace with top slag. The task of the ladle slag is many sided. It protects the liquid steel against oxidizing atmosphere on the one hand and is used to carry out metallurgical work on the other hand. Therefore, the ladle slag should have suitable physical and chemical properties which are characterized mainly by a low melting temperature, a low oxygen potential, as well as a high sulphur capacity. The desulphurization of liquid steels with a refining ladle slag is one of the most important processes of secondary metallurgy since, for most steel grades, sulphur is a harmful element.

The steel making plant of voestalpine Stahl GmbH has a capacity of approx. 340 000 t/month. The metallurgical process route can be described as follows: hot metal is supplied from the blast furnaces by means of torpedo cars. The three BOF converters have a capacity of 165 t each and are used in parallel. On average, 78 heats per day are produced. The converters are equipped with a bottom stirring system using argon or nitrogen and an IRIS system to prevent slag carry-over[1]. Basically, three different secondary metallurgical units are available:

- one stirring stand
- two ladle furnaces and
- two RH degassers.

At the stirring stand and the ladle furnace, aluminium and filled wires can be fed, slag forming agents added and alloys charged. Steel and slag are heated by means of three electrodes at the ladle furnace. The heating capacity is 3—5°C/min. At the RH degasser decarburization, degassing and treatment for inclusion removal can be carried out. Which of these processes is selected depends on the metallurgical requirements, e.g., the target sulphur content, the limit of hydrogen and nitrogen content, respectively, the required degree of oxide cleanliness, decarburization, modification of inclusions, or improvement of castability. The steel is then either cast on one 2-strand continuous caster or on two 1-strand casters.

Figure 1 gives a survey of the production programme and the production routes, roughly subdivided into four groups. EDDQ are heated, decarburized and precision alloyed in the RH plant. Super-EDDQ are treated in the ladle furnace and RH-plant. DDQ are heated and alloyed in the ladle furnace. For cleanness sensitive steel grades the RH-plant is used. High strength steels are heated and alloyed in the ladle furnace. HIC-resistant steels are treated on both secondary steel making units; in the ladle furnace they are subjected to calcium treatment for the purpose of desulphurisation, and on the RH plant, removal of nitrogen and hydrogen takes place.

## Characterization of ladle slags

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.

### Micro-analytical findings on ladle slags

On account of the widely scattered chemical composition,

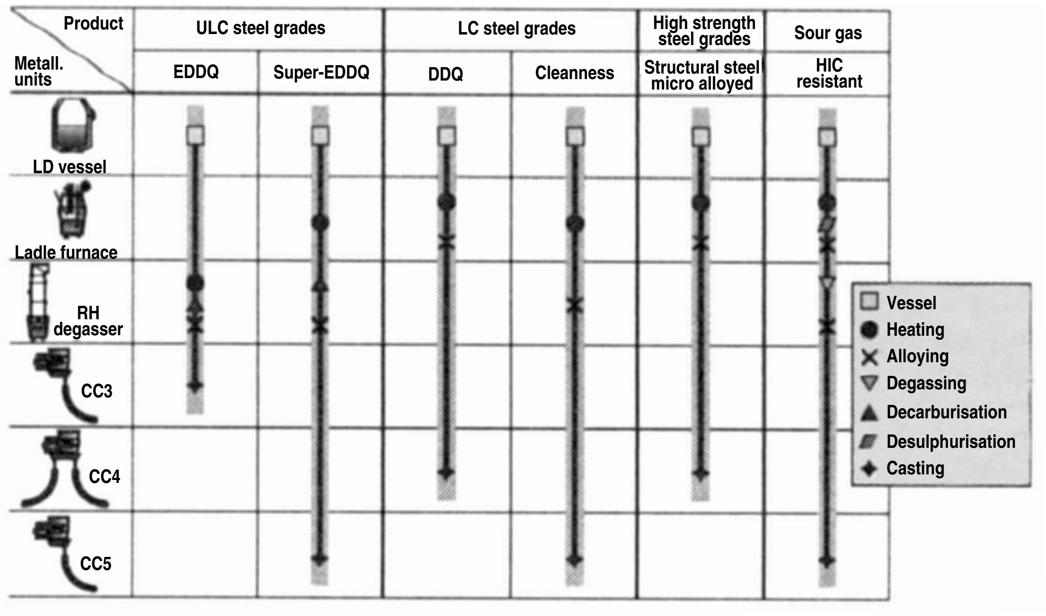


Figure 1. Production programme and production route at voestalpine Stahl GmbH

great differences in the mineralogical structure of the ladle slags are to be expected. For micro-analytical examinations on the microprobe, 72 ladle slags were selected. The programme for evaluating the phase map and phase composition is well described in literature[2–4]. In order to get a representative result for the fraction of different phases, the analysis with the microprobe is carried out on a large area (approx. 1 cm$^2$). The result of this quantitative phase analysis is illustrated in Figures 2–8. The phases determined, as well as their shares, are plotted as a function of basicity, which is defined by B=(CaO)/((Al$_2$O$_3$)+(SiO$_2$)), and slag composition (C=CaO, A=Al$_2$O$_3$, S=SiO$_2$, M=MgO).

At basicities between 1.2 and 1.6 calcium aluminate C$_3$A is prevailing (Figure 2). The low melting calcium aluminate C$_{12}$A$_7$ occurs throughout the basicity range (Figure 3). The highest fraction occurs in a basicity range between 0.8 and 1.2. When the basicity exceeds 1.2 the fraction of C$_{12}$A$_7$ decreases considerably. At a basicity of less than 0.8, MA spinels occur (Figure 4). The share of spinels increases with decreasing basicity at the expense of the C$_{12}$A$_7$ share. Undissolved and separated CaO occurs at a basicity range exceeding 1.2 (Figure 5). Dicalcium silicate C$_2$S occurs throughout the basicity range. The highest fraction occurs at basicities ranging from 1.4 to 1.6. The fraction of C$_2$S increases with increasing content of SiO$_2$ (Figure 6). Tricalcium silicate C$_3$S occurs at a basicities range exceeding 1.5 and additionally if the content of (SiO$_2$) amounts to 11 mass% (Figure 7). Magnesiowustite exists throughout the basicity range. If the ladle slag is well reduced, instead of magnesiowustite the formation of periclase occurs at a basicity exceeding 0.8 (Figure 8). At a basicity below 0.8 periclase is formed only at high contents of (MgO) because (Mg$^{2+}$) is needed for the formation of spinel.

## Precipitation of phases

Knowledge of the primary precipitation phases is essential for the optimum adjustment of the ladle slag for various metallurgical tasks. The amount of top slag forming agents added to adjust the lime saturation and the amount of raw magnesite added for (MgO) saturation should be dosed as exactly as possible in order to prevent lime and/or periclase precipitation, since slag becomes heterogeneous thereby and reactivity is thus reduced.

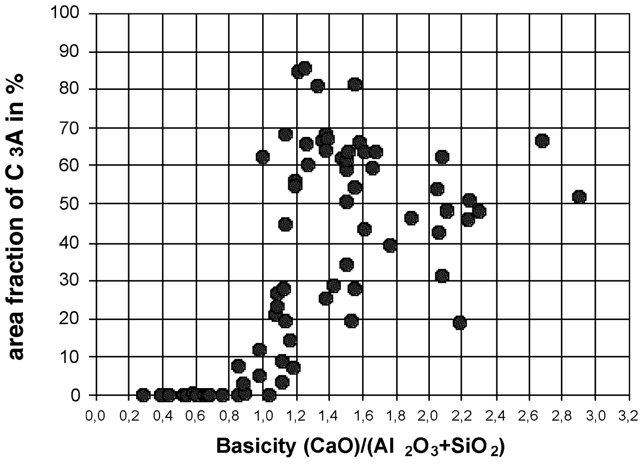


Figure 2. Area fraction of C$_3$A as a function of basicity

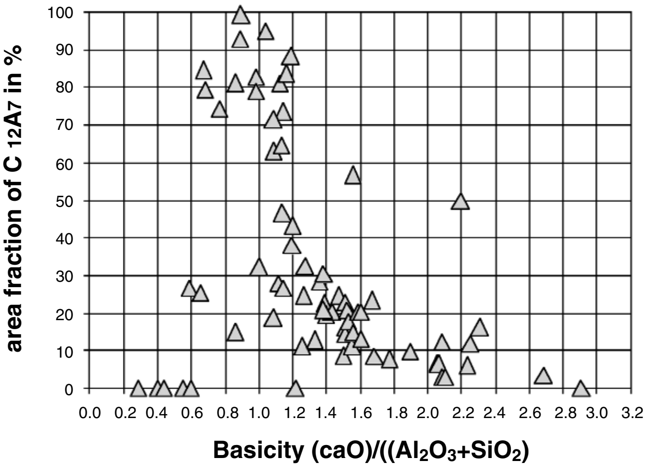


Figure 3. Area fraction of C$_{12}$A$_7$ as a function of basicity

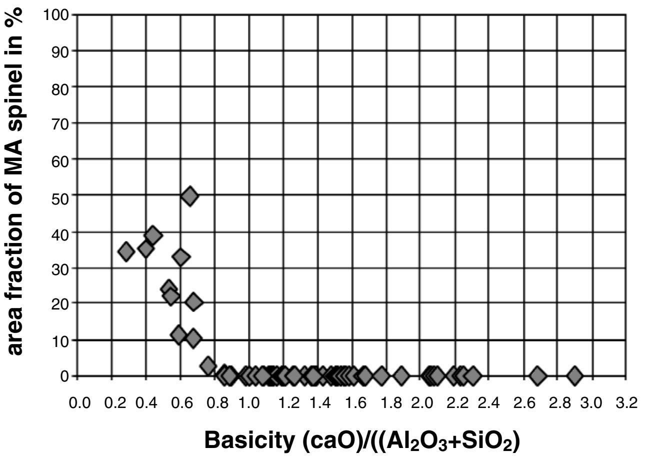


**Figure 4. Area fraction of MA spinel as a function of basicity**

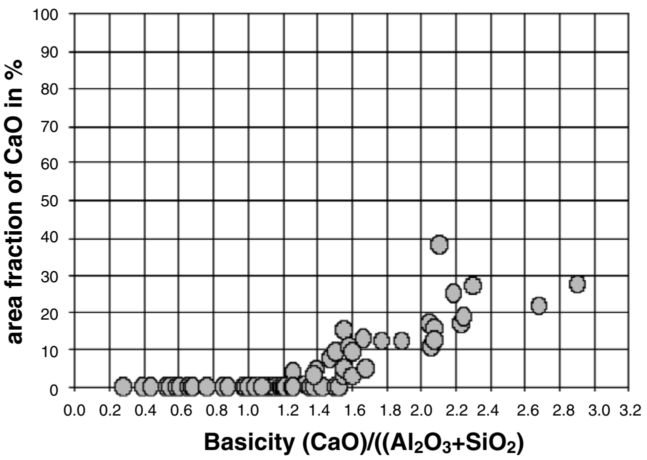


**Figure 5. Area fraction of CaO as a function of basicity**

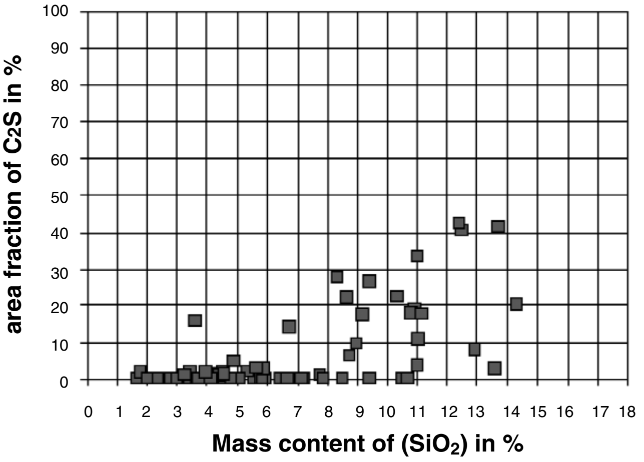


**Figure 6. Area fraction of $C_2S$ as a function of the mass content of ($SiO_2$) in %**

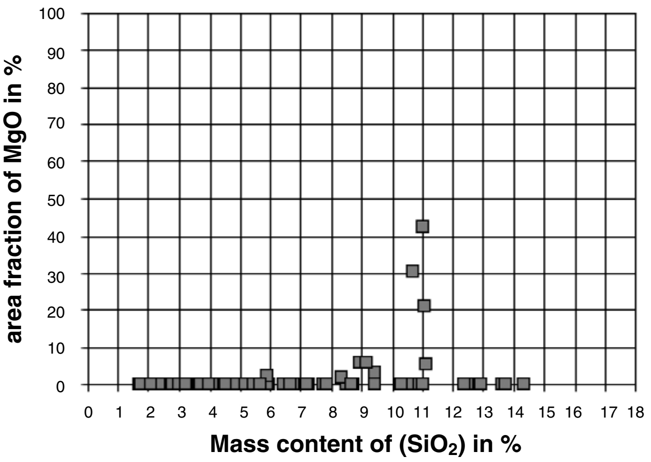


**Figure 7. Area fraction of $C_3S$ as a function of the mass content of ($SiO_2$) in %**

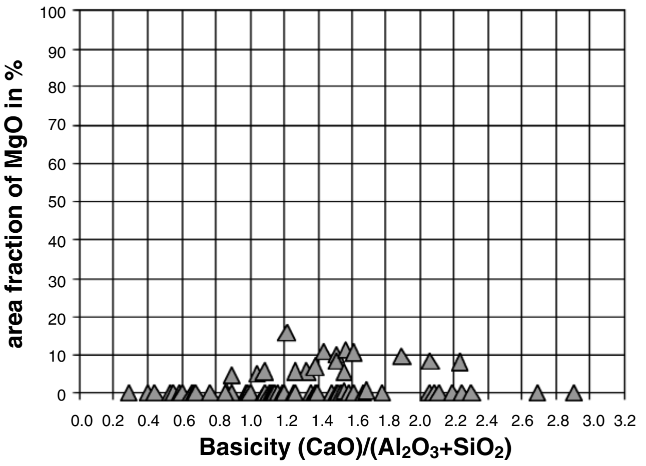


**Figure 8. Area fraction of MgO as a function of basicity**

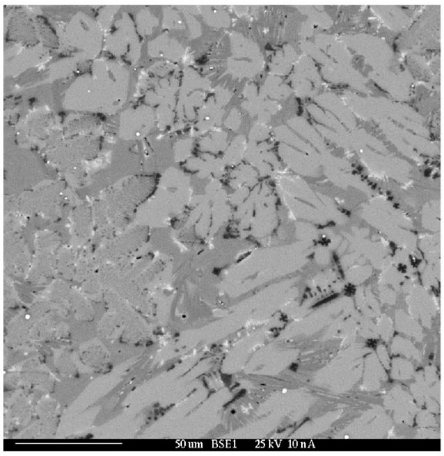
The ternary system CaO-$Al_2O_3$-$SiO_2$ generally serves as the basic system for representing phase equilibria in ladle slags. On the basis of the magnesia saturation, the ternary system is extended by the magnesia component to the quaternary system CaO-$Al_2O_3$-$SiO_2$-MgO. The position of the slags in the respective primary precipitation field indicates the phase that precipitates first. The primary precipitation phase can be derived from the graphical representation if the main components are considered. The graphical determination of the primary precipitation phases in combination with its appearance serves to draw conclusions about saturation states in the liquid slag.

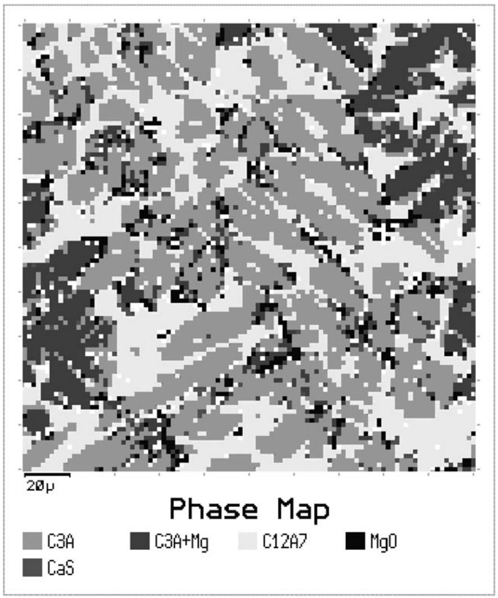
The primary precipitation phase of ladle slags depends mainly on basicity. For the most part of the investigated ladle slags it consists of periclase and, based on the high (FeO) and (MnO) contents, magnesiowustite. At a basicity of more than 1.55, besides periclase CaO occurs as the primary precipitation phase. At a basicity of less than 0.8 spinel is precipitated first.

Based on these findings the desulphurization trials in the steel making plant were carried out on a commercial scale at different basicities in order to investigate the influence on the mineralogical phases on sulphur bonding.

## Sulphur bonding in solidified ladle slags

The achievable data on the sulphide capacities of many binary, ternary and multi-component slag systems have been published in literature[5–8]. The measured results show that the sulphide capacity of slag increases with increasing temperature and concentration of basic oxides. At a constant (MgO) content, the value of $C_S$ increases considerably with increasing (CaO) content. Consequently,





| Phases | sulphurcontent | areafraction |
|---|---|---|
| C3A | 0,06 | 45,6 |
| C3A+Mg | 0,07 | 17,1 |
| C12A7 | 0,15 | 29,6 |
| MgO | 0,16 | 5,2 |
| CaS | 13,90 | 2,5 |

**Figure 9. Back scattered electron image, phase map and results of phase analysis (basicity=1.34, (S)=0.82 mass%)**

highly basic ladle slags should be used for steel desulphurization. The results of sulphur solubility in calcium aluminate slags have been summarized by Turkdogan[9] in including further data from[10–12]. Ozturk and Turkdogan have investigated calcium aluminate slags in equilibrium with liquid iron at 1600°C and 1550°C. The slags were saturated with (CaS) and (CaO) or (CaS) and (CA)/($CA_2$), respectively. The solubility of (CaS) increases with increasing temperature and increasing (CaO)/($Al_2O_3$) ratio. The solubility of (CaS) at 1600°C increases from 1.8 mass% at calcium aluminate saturated slags to up to 4.8 mass% at lime saturated slags.

Investigations of the behaviour of sulphur in liquid calcium aluminate slags prove that sulphur occurs in the sulphide form in the liquid slag under reducing conditions[13]. Sulphur bonding in solidified ladle slags should therefore also take place in the sulphide form. In literature the bonding of sulphur in solidified ladle slags is only scanty[14–15].

As a result of the desulphurization trials for aluminium killed steel grades, two characteristic ladle slags are selected describing the bonding of sulphur in solidified ladle slags. Figure 9 shows the scanning electron picture, the phase map and the phase analysis of a ladle slag with a basicity of 1.34 and a sulphur content of 0.82 mass%. The phases of this ladle slag consist of $C_3A$, $C_3A$ including $Mg^{2+}$, $C_{12}A_7$, periclase and CaS. The scanning electron picture shows that CaS is precipitated at the phase boundary of $C_3A$. Therefore it can be concluded that the precipitation of $C_3A$ starts first. Figure 10 shows a ladle slag with a basicity of 1.43 and a sulphur content of 0.29 mass%. The following phases occur: $C_{12}A_7$, $C_3A$, $C_2S$ and dendritically precipitated CaO and MgO. No CaS phases were detected. The sulphur content of the different phases shows the highest value for phase $C_{12}A_7$ (0.96 mass%).

The conclusion of this evaluation is that, besides calcium sulphide, the mayenite phase $C_{12}A_7$ integrates sulphur within its lattice. Two questions should be answered:

- In what way is sulphur integrated into the lattice of $C_{12}A_7$?
- When does the precipitation of CaS start and when is sulphur integrated into $C_{12}A_7$?

### Crystal structure of $Ca_9Al_6O_{18}$ and $Ca_{12}Al_{14}O_{33}$

To study the bonding of sulphur into the lattice of calcium aluminates $C_{12}A_7$ and $C_3A$ crystalchemical considerations are made.

The crystal structure of $Ca_9Al_6O_{18}$ is characterized by a high degree of space filling, and so it is hard to integrate sulphide ions. The crystal lattice of $Ca_{12}Al_{14}O_{33}$ is characterized by an open, three-dimensional anionic network composed of $AlO_4^{5-}$ tetrahedrons linking the edges (Figure 11). In this network, large interstitial spaces are formed, which may be filled with calcium ions on the one hand, and statistically with a free oxygen ion on the other hand. On account of the spatial conditions, substituting a sulphide ion for the free oxygen ion is the only option left for integrating sulphide. The substitution of a sulphur ion for the free oxygen ion does not lead to any fundamental changes in the geometry of the crystal lattice of $Ca_{12}Al_{14}O_{33}$. A sulphur content of 2.3 mass% results for mayenite if the free oxygen ion is substituted completely. The composition of $Ca_{12}Al_{14}O_{32}S$ results from the maximum sulphur capacity. The chemical formula for the sulphur-bonding phase generally reads $Ca_{12}Al_{14}O_{(33-x)}S_x$, where x may assume a value between zero and one.

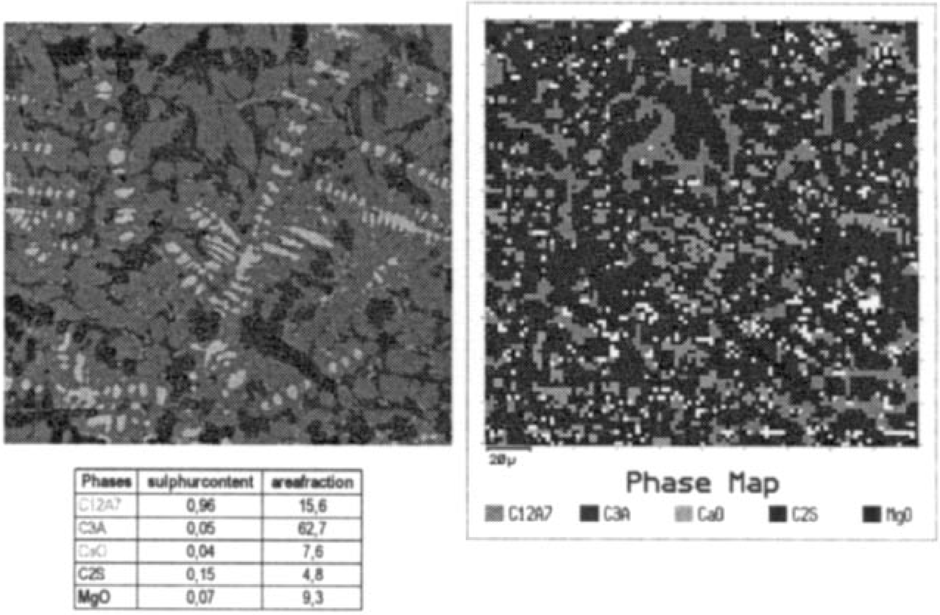
### Mechanism of sulphur bonding in ladle slags

Sulphur bonding in calcium aluminate slags is determined by two factors[16]:

- Supply of sulphide ions
- Phase composition and, as a result, the basicity and the (CaO)/($Al_2O_3$) ratio, respectively.

The sulphur content in the slag is a direct measure of the probability of formation of CaS during solidification. If the supply of sulphide ions in the liquid slag is large enough, the solubility product of CaS is exceeded and precipitates according to the following equation.

$$\left(Ca^{2+}\right)+\left(S^{2-}\right)\Leftrightarrow CaS \qquad [1]$$



| Phases | sulphurcontent | areafraction |
|---|---|---|
| C12A7 | 0,96 | 15,6 |
| C3A | 0,05 | 62,7 |
| CaO | 0,04 | 7,6 |
| C2S | 0,15 | 4,8 |
| MgO | 0,07 | 9,3 |

**Figure 10. Back scattered electron image, phase map and results of phase analysis (basicity=1.43, (S)=0.29 mass%)**

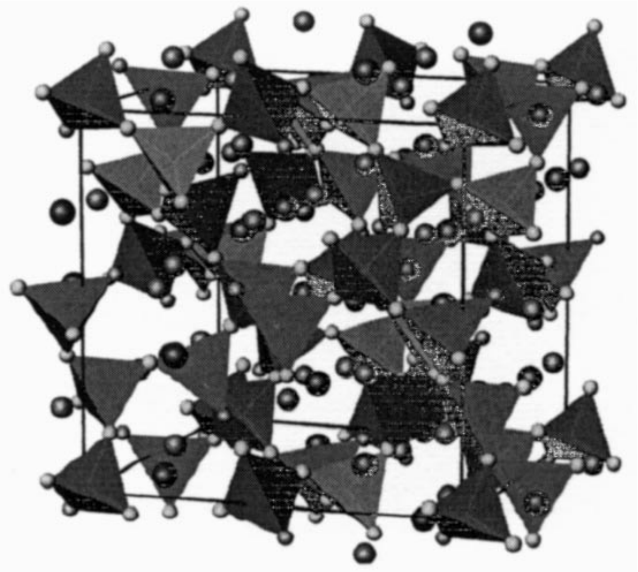


**Figure 11. The anionic tetrahedron network of $Ca_{12}Al_{14}O_{32}S$ (K. Klepp)**

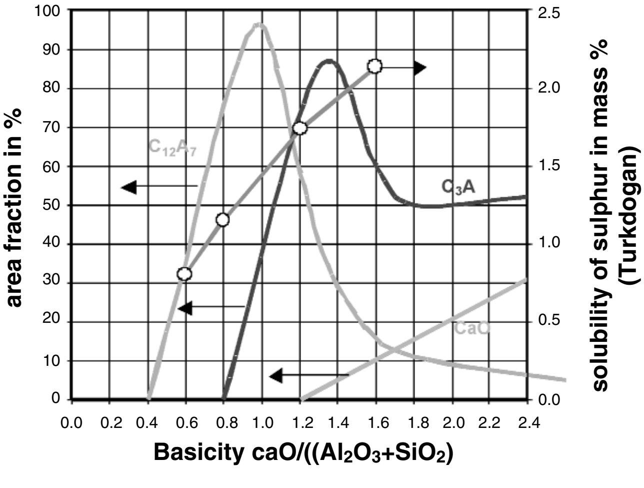


**Figure 12. Schematic diagram for the phases CaO, $C_{12}A_7$ and $C_3A$ and solubility of sulphur in calcium aluminate slags (c. f. 9)**

The $(CaO)/(Al_2O_3)$ ratio exerts an influence on the formation of CaS in so far as the sulphur solubility increases with increasing ratio, i.e., the greater the $(CaO)/(Al_2O_3)$ ratio, the more $(S^{2-})$ anions are required to exceed the solubility product.

However, if there are only a few $(S^{2-})$ anions, the above reaction does not proceed. As a result, sulphur remains dissolved in the liquid slag, and no calcium sulphide precipitates. If phases crystallize out of the liquid slag, which are not capable of integrating sulphide ions into their lattice, the sulphide ions concentrate in the residual slag and CaS is thus allowed to precipitate when the solubility product is achieved. However, if phase $Ca_{12}Al_{14}O_{33}$ precipitates, the sulphide ion is successively integrated into this phase and no CaS precipitates.

According to the ionic theory, liquid slags consist of cations, anions and anion complexes[17–20]. Crystallization starts during cooling when cations, anions and anion complexes enter into combinations with one another. As regards the crystallization of $Ca_{12}Al_{14}O_{33}$, the following reaction is possible on the basis of the available ions and taking into account a free oxygen ion in the lattice.

$$12\left(Ca^{2+}\right)+\left(AlO_4^{\;5-}\right)+11\left(AlO_2^{\;-}\right)+2\left(AlO_3^{\;3-}\right)+\left(O^{2-}\right)\Leftrightarrow Ca_{12}Al_{14}O_{33} \qquad [2]$$

Crystallization takes place by reaction of the $(Ca^{2+})$ cations on the anion complexes $(AlO_4^{5-})$, $(AlO_3^{3-})$ and $(AlO_2^{-})$ as well as a free oxygen ion $(O^{2-})$. According to the ionic theory, sulphur bonding in $Ca_{12}Al_{14}O_{33}$ can be explained by the substitution of a sulphide ion for the free oxygen ion. The sulphide ion can be integrated into the crystal lattice of $Ca_{12}Al_{14}O_{33}$ according to the following equation[16].

$$12\left(Ca^{2+}\right)+\left(AlO_4^{\;5-}\right)+11\left(AlO_2^{\;-}\right)+2\left(AlO_3^{\;3-}\right)+(1-x)\left(O^{2-}\right)+x\left(S^{2-}\right)\Leftrightarrow Ca_{12}Al_{14}O_{33-x}S_x \qquad [3]$$

Figure 12 illustrates the course of sulphur bonding once more by means of a diagram. Sulphur solubility increases with increasing $(CaO)/(Al_2O_3)$ ratio, and so calcium sulphide can only precipitate from the liquid slag at high contents of sulphide ions in the case of lime saturated slags, i.e., a sulphur content of 2.1 mass% is necessary. At a basicity of more than 1.2 the portion of $Ca_{12}Al_{14}O_{33}$ is small, and so the precipitation of CaS is the likeliest one. At basicities of less than 1.2, however, the portion of $Ca_{12}Al_{14}O_{33}$ is very high. A precipitation of CaS in this area can only take place if the sulphur content in the ladle slag reaches solubility (e.g., 1.5 mass% sulphur in the ladle slag at a basicty of 1.0).

## Conclusion

Within the scope of this investigation it was found in which form sulphur is bonded in ladle slags. For this purpose, the mineralogical phases of the ladle slags were qualitatively and quantitatively evaluated by means of a microprobe. This slag characterization allowed reconstructing the bonding of sulphur into the phases of the ladle slag.

Moreover, the reaction process with regard to the ionic theory as well as the structural formula for the mechanism of sulphur bonding were discussed. The bonding of sulphur into calcium aluminate slags is determined by the sulphide ion content in the slag as well as by the ratio of $(CaO)/(Al_2O_3)$. As this ratio increases, the solubility of sulphur increases as well. Calcium sulphide separates only if the slag contains a large number of sulphide ions. The solubility product of calcium sulphide is thus exceeded and CaS separates from the liquid slag. Calcium sulphide separation at a low content of sulphide ions is only possible if the sulphide ions in the slag are enriched by separations of phases not bonding sulphur.

When the $Ca_{12}Al_{14}O_{33}$ phase is separated, sulphide ion is successively integrated into the lattice. The crystal lattice of $Ca_{12}Al_{14}O_{33}$ is characterized by an open, three-dimensional anionic network composed of aluminium-oxygen tetrahedrons linking the edges. In this network, large interstitial spaces are formed, which may be filled with the calcium ions on the one hand and statistically with a free oxygen ion on the other hand.

The substitution of a sulphur ion for the free oxygen ion does not lead to any fundamental changes in the geometry of the crystal lattice.

The chemical formula for the sulphur-bonding phase generally reads $Ca_{12}Al_{14}O_{(33-x)}S_x$, where x may assume a value between zero and one.

## References

1. BORZ, M. and ÖRTELT, P. *AISE, Annual Convention Proceedings*, September 23–26, 2001, Cleveland, Ohio.
2. POSCH, W., PREẞLINGER, H., MAYR, M., JUNGREITHMEIER, A., and PISSENBERGER, E. *BHM*, 145. Jg. (2000), Heft 5, pp. 168–175.
3. PREẞLINGER, H., MAYR, M., ANTLINGER, K., and HIEBLER, H. *Radex-Rundschau*, Heft 1 1989, pp. 12–25.
4. POSCH, W., PREẞLINGER, H. and HIEBLER, H. *Ironmaking and Steelmaking* 2002, vol. 29, no. 4.
5. TURKDOGAN, E.T. *Physicochemical properties of molten slags and glasses*, The Metals Society, London, 1983.
6. Verein Deutscher Eisenhüttenleute: *Slag Atlas*, 2nd Edition, Verlag Stahleisen GmbH, Düsseldorf, 1995.
7. NZOTTA, M.M., DU, S., and SEETHARAMAN, S. *Met. Trans.*, 30B 1999. pp. 909–920.
8. NZOTTA, M.M., DU, S., and SEETHARAMAN, S. *ISIJ International*, 38, 1998. pp. 1170–1179.
9. TURKDOGAN, E.T. *Ironmaking and Steelmaking*, vol. 12 no. 2, 1985. pp. 64–77.
10. OZTURK, B. and TURKDOGAN, E.T. *Metal Science*, vol. 18, 1984. pp. 299–305.
11. SHARMA, R.A. and RICHARDSON, F.D. J*ournal of the Iron and Steel Institute*, 198, 1961. pp. 386–390.
12. KOR, G.J.W. and RICHARDSON, F.D. *Journal of the Iron and Steel Institute*, 206, 1968. pp. 700–704.
13. FINCHAM, C.J.B. and RICHARDSON, F.D. *Research Group in Extraction Metallurgy*, Royal School of Mines, London, S.W. 7, November 1953. pp. 40–62.
14. Patsiogiannis, F. and Pal, U.B. *ISIJ International*, vol. 36, no. 4, 1996. pp. 402–409.
15. ANDERSSON, M., HALLBERG, M., JONSSON, L., and JÖNSSON, P. Tagungsband: *Sixth International Conference on Molten Slags, Fluxes and Salts*, Stockholm, Sweden—Helsinki, Finland, 12–17 June 2000, paper 119.pdf
16. Posch, W. Dissertation, Montanuniversität Leoben 2001.
17. Frohberg, M.G. and Kapoor, M.L. S*tahl u. Eisen 91* Nr. 4, 1971. pp. 182–189.
18. FROHBERG, M.G. and KAPOOR, M.L. *Archiv für das Eisenhüttenwesen* Heft 2, 1970. pp. 209–213.
19. Schulz, H.P. *Archiv für das Eisenhüttenwesen*, Heft 9, 1964. pp. 803–819.
20. Frohberg, M.G., Papamentellos, D., and Patel, P. *Archiv für das Eisenhüttenwesen* Heft 9, 1969. pp. 651–656.