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PHOSPHORUS- AND SULPHUR-CONTAINING PHASES IN BOF-SLAGS

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Synopsis: The necessity to minimize the slag volume, to adjust lowest phosphorus contents in steel and to utilize the converter slag, as far as it is possible, also for desulphurization requires an efficient slag practice. In the present work results of investigations on solidified converter and laboratory slags, obtained with the microanalyzer, are presented. The factor responsible for the binding of phosphorus in converter slags is the formation of dicalcium silicate, whereas for the binding of sulphur it is the dicalcium ferrite.
In slags from laboratory melts with an SiO_2-content below 1 wt-% phosphorus is detected in a separate calcium phosphate phase.

Key words: dephosphorization; desulphurization; EPMA; phase analysis; converter slag; slagging practice

1. Introduction

In the LD-process as used in Europe the highest possible percentage of scrap is sought for economic reasons. This makes it impossible to minimize the amount of phosphorus in the hot metal by means of a pretreatment, whereby physical heat is lost.

Therefore the goal is to optimize dephosphorization and desulphurization by using a suitable slagging practice with the lowest possible amount of slag and the smallest loss of iron.

Besides other factors the LD-process with bottom blowing is decisively influenced by the composition and the reactability of the slag. The reactions which take place between the metal bath and the converter slag during blowing determine the final metallurgical results.

Let us consider dephosphorization. An initial phosphorus content of 0,06 wt-% in the hot metal can be reduced in the converter to under 0,005 wt-% by oxidation and appropriate slagging practice using lime additions of about 40 kg/t steel. This is a dephosphorization rate of over 90 %.[1,2)
For a better understanding of the results of our work the methodology of phase identification will be discussed first.

2. Method of phase analysis by an electron probe microanalyzer

The present work is essentially based on a method of phase analysis using an electron probe microanalyzer (EPMA). It enables both an identification of all phases detectable with the microanalyzer in a slag sample and the determination of the average composition of each phase as well as the establishment of a phase map showing the distribution of phases. A detailed description has already been given in publications. 3,4)

As a first step, an analysis carried out, using "Concentration Mapping"(CM) (FIG. 1).

The result obtained is a large number of quantitative analyses point grid. This data can be represented, for example, in the form of "concentration maps".For the second step, a suitable quaternary system is selected in which all analysis values are normalized to 100% total amount and arranged in the appropriate concentration tetrahedron. For graphical representation, the tetrahedron is cut into slices, parallel to the base. In the various slices, accumulations of analysis points can be distinguished. The locations of these "point clouds" in the tetrahedron represent the regions of the phases, whereby phase identification is supported.

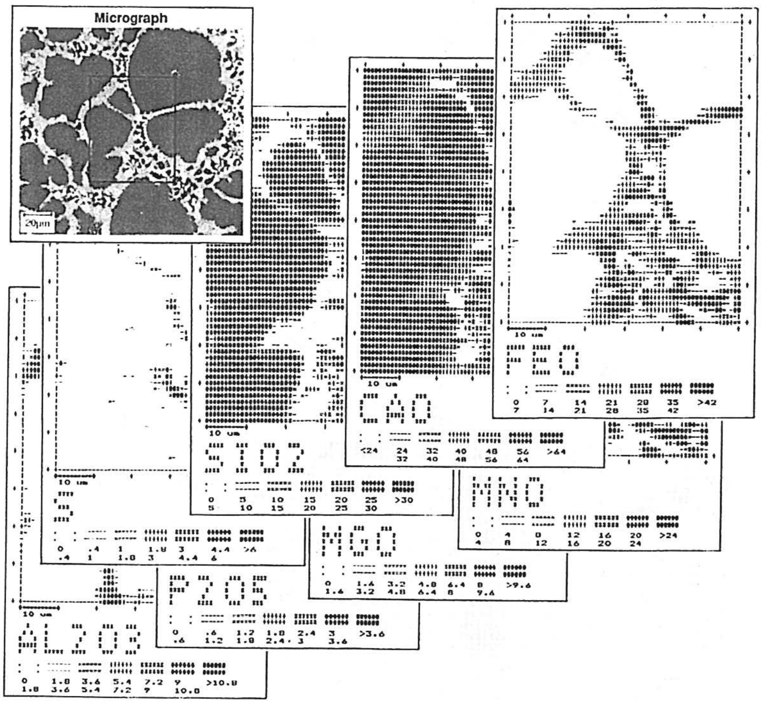


Fig. 1 Concentration Mapping (CM) analysis

The last step involves the specification o a certain region within the tetrahedron for each discerned phase. Thus, each analysis point can be assigned to a specified phase. From this, a map of the phase distribution (phase map) can be subsequently plotted and the average composition of the individual phases determined.

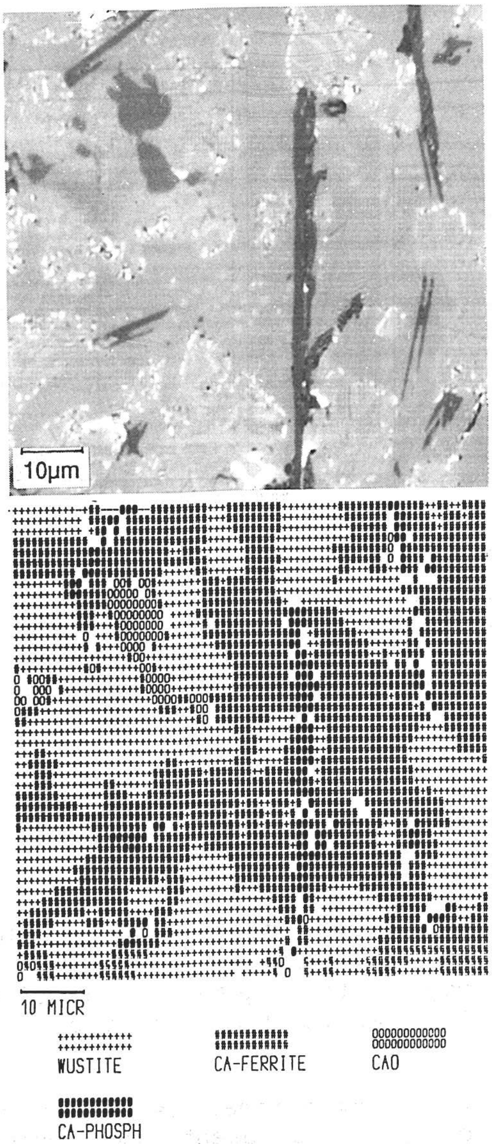
The essential advantage of this method over the conventional technique of point analysis is that the results obtained are highly representative, which is especially important is slags because of their heterogeneity. It provides information with a high degree of certainty concerning the behavior of elements with regard to their distribution to the various phases.

3. Experimental Procedures

For purposes of environmental protection and utilization of valuable secondary raw materials, briquettes made from the dust caught in the primary and secondary filters are reintroduced into the converters. Because of the composition of these briquettes, and their relatively large quantity (up to 3000 kg/ melt) a change in the composition of the slag occurs which must be investigated using selected samples.

3.1 Evaluation of a laboratory slag

According to metallographic and microanalytical evaluations, the laboratory slag with a chemical composition of 35 wt-% CaO, 0,8 wt-% SiO_2 43 wt-% Fe_{tot}, 1 wt-% Al_2O_3, 3 wt-% MgO, 0,9 wt-%, P_2O_5 and 0,1 wt-% S consists of 50 vol-% dicalcium ferrite, 41 vol-% wustite, 3,5 vol-% calcium phosphate and 2,5 vol-% calcium oxide, (Fig. 2).



Phase \ Component	FeO	MnO	SiO_2	CaO	Al_2O_3	MgO	P_2O_5	S
WUSTITE	73,41	1,87	0,43	22,95	0,24	3,14	0,20	0,10
CA - FERRITE	47,34	0,32	1,21	42,79	3,78	0,22	1,25	0,11
CAO	18,95	1,28	1,21	74,27	0,26	0,69	0,60	0,22
CA - PHOSPH	19,38	0,19	2,72	51,22	1,23	0,08	23,05	0,52

Fig.2 Micrograph, phase map and average composition of a laboratory slag

Mn and Mg are also contained in the wustite. Phosphorus is bonded into a separate calcium phosphate (CnP-)phase.[5] It should be noted here that a similar phosphate phase was found in another slag microsection which was identified with the aid of X-ray diffraction analysis as iron oxide apatite because of its typical appearance.[6]

3.2 Evaluation of the slag samples after 25% of the blowing time

Wustite, primarily precipitated out upon solidification of the slag dominates the area of the microsection which was analyzed. In the evaluation of the phase map of this typical early slag, the interrelationship among FeO, MnO and MgO can be clearly identified.

The heterogeneous matrix shows several phases called silicates for short: Along with a calcium silicate which approaches the composition of dicalcium silicate as refining continues and the dissolution of lime increases, and which already in an early stage bonds phosphorous (SILIC-HI-P), there are further silicate phases which have less P-, but various S-content (SILIC-LO-P/S), (SILIC-HI-S).

3.3 Evaluation of the slag samples after 50% of the blowing time

The micrograph of this sample shows large primary solidified calcium silicates which have almost reached the stoichiometric composition of dicalcum silicate (C_2S) and bonded more than 5% P_2O_5.

In the evaluation of the phase map, a transition area is identified which is labeled as a mixed phase of wustite and calcium silicate.

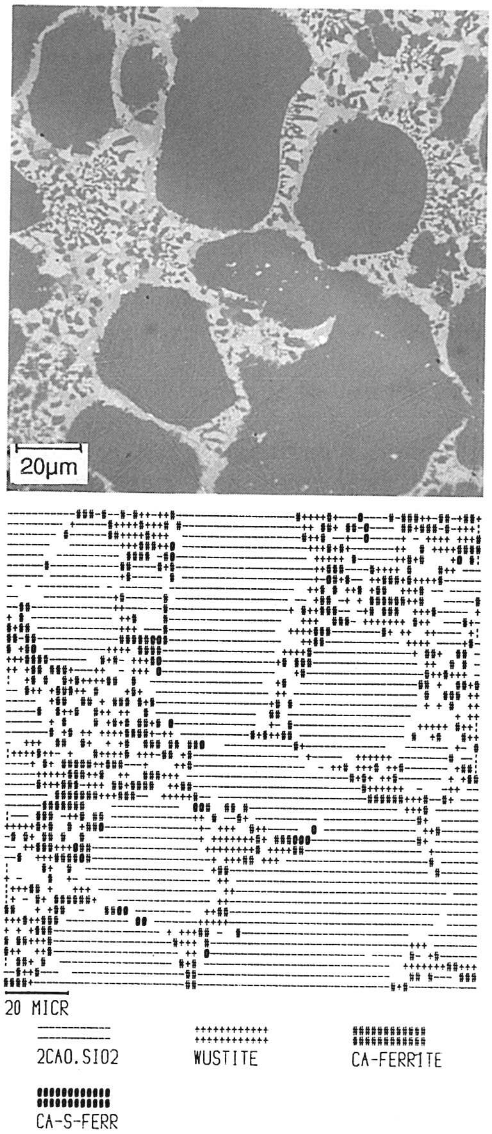
It seems interesting to note a small phase band (AL-S-Rich) which permits us to identify a clear correlation between Al and S, and which has up to 13% Al_2O_3 with a sulphur content of 0.23%.

3.4 Evaluation of the slag samples after 75% of the blowing time

At this point in the blowing process the converter slag was stiff and crumbly so that it was very difficult to obtain a sample, and the samples which were taken could not be evaluated. For this reason we did without an evaluation of the slag after 75% of the blowing time in this test series.

3.5 Evaluation of the slag samples at the end of blowing

The average chemical composition of the phases of a slag at the end of blowing is presented in Figure 3.



Phase \ Component	FeO	MnO	SiO_2	CaO	Al_2O_3	MgO	P_2O_5	S
2CAO.SIO2	2,20	0,50	31,60	63,30	0,20	0,20	3,00	0,05
WUSTITE	44,20	17,10	4,30	26,90	0,30	5,80	0,40	0,11
CA - FERRITE	25,70	10,00	5,90	47,60	2,00	3,10	1,00	0,22
CA - S - FERRITE	26,40	4,90	7,10	49,70	2,50	1,10	0,80	4,60

Fig.3 Micrograph, phase map and average composition of a converter slag

From this table it can be seen that the dicalcium silicate (C_2S) is of nearly stoichiometric composition and on average has picked up about 3% P_2O_5. Other phases shown in the map, such as calcium ferrite and wustite solid solutions, however, contain considerably less P_2O_5. Sulphur is for the most part bonded in a phase similar to calcium ferrite, however it is not distributed homogeneously, but rather has high values in small areas (CA-S-FERRITES).

4. Formation of a converter slag during the blowing period

The slag formation of a representative charge is shown in Figure 4 in a projection onto the base area of a tetrahedron which forms the quasi-quaternary system with P_2O_5 on top. After 25% of the blowing time the slag is homogeneous and liquid. The phase map of the solidified structure shows olivines, which contain up to 3.5% P_2O_5, and wustite. At about the half of the blowing time-the slag has dissolved more and more lime and FeO has decreased-there is a split into two basically different paths. The path of the phosphorus-rich slag phase leads over increasing P-concentrations to dicalcium silicate. CaO and SiO_2 produce a stable bond, which then crystallizes out of the slag melt and holds phosphorus dissolved in a solid solution. FeO and MnO remain in the low-phosphorus slag melt which moves in the direction of the FeO-MnO corner.At the three quarters point in the blowing time the slag is very heterogeneous because of dicalcium silicate precipitates. The liquid iron-rich phase dissolves the remaining lime, whereby this part of the slag then moves toward lime saturation. At the end of blowing the slag consists of dicalcium silicate in an almost stoichiometric composition and of a liquid lime- and iron-rich melt from which wustite and dicalcium ferrite precipitate upon solidifying.

This slag can also bond sulphur. In the phase maps, in very limited areas, large enrichments of sulphur can be seen, and for this reason the sulphur-rich calcium ferrite was also identified as a separate phase. As a result, laboratory tests were carried out with higher sulphur content and the sulphur-rich phase was classified as($2CaO.Fe_2O_3.FeS$) using the electron probe microanalyzer,stoichiometric calculations and ionic theory approach.[7]

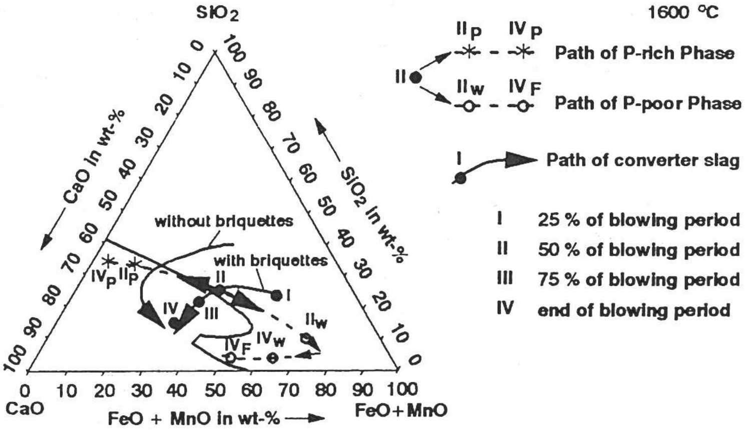


Fig.4 Formation of a converter slag during blowing period

5.Considerations of ionic theory regarding the course of dephosphorization

The process of the slagging of phosphorus can best be described using the ionic theory.[8-11]
In the phase boundary reaction metal/slag the anion complexes (PO_4^{3-}) are formed in conjunction with the dissolved oxygen in the melt and the oxygen ions in the slag. These can form chains in the acidic slag with the (SiO_4^{4-}), and partially can substitute and polymerize the (SiO_4^{4-}). This explains why the largest part of phosphorus is picked up and held in the slag already in the first half of blowing although the basicity has only reached 1.5. With increasing basicity the chains are broken by the (Ca^{2+})-cations. (PO_4^{3-}) becomes more active in this way and reduction of phosphorus into the melt occurs, supported additionally by the reduction of manganese which takes place simultaneously. When in one place sufficient lime is dissolved, the stable dicalcium silicate phase is formed in the slag, which crystallizes out. Phosphorus is dissolved and is in a stable bond in solid solution.

6. Considerations of ionic theory regarding the course of desulphurization

According to ionic theory [8-14] sulphur becomes under oxidizing conditions changed into the form of ions during the first step by absorption of electrons at the phase boundary of metal bath/slag. The electrons needed are supplied, for example, through emission of electrons when Fe changes to Fe^{2+}. The Fe^{3+}-ions produced by emission of electrons from Fe^{2+} are not stable in the slag complex. With the free oxygen anions O^{2-} present it forms the anion complex $Fe_2O_5^{4-}$ in step 2.
Such $Fe_2O_5^{4-}$ anion complexes form dicalcium ferrite with $2Ca^{2+}$. Dicalcium ferrite is responsible in the following way for the incorporation of sulphur:

The incorporation of sulphur anions in the crystallites during solidification depends on the number of Fe^{2+}-cations present in the liquid converter slag. If the number of Fe^{2+}-cations present is low because crystallization of wustite has already occured, sulphur is incorporated in the crystal lattice of the dicalcium ferrite as represented by the equation

$$(2 + x)\ (Ca)^{2+} + (Fe_2O_5)^{4-} + x(S)^{2-} = Ca_{(2+x)}\ Fe_2O_5S_x$$

If - for example, by adding oxides as slag-forming agents or by afterblowing - sufficient Fe^{2+}-cations are present in the liquid converter slag sulphur is also incorporated - according to equation

$$(S)^{2-} + (Fe)^{2+} + (Fe_2O_5)^{4-} + 2(Ca)^{2+} = Ca_2Fe_3O_5S$$

in a separate phase - a dicalcium-sulphur-ferrite compound.

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