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COMPOSITION CHANGE DURING THE SLAG FORMATION BOTH IN THE BLAST FURNACE AND THE ELECTRIC ARC FURNACE

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Synopsis: In iron and steelmaking the composition of slags is essential for technological control of processes. In blast furnace, primary slag with various FeO contents depending on burden composition is formed. In steelmaking, the foaming slag can be formed by using scale as steel-plant waste material. In stainless steelmaking various chromites are formed depending on the slag composition.

Key words: Blast furnace slags, EAF slags, foaming, mineralogical composition of slags

1. Introduction

Raw materials in steelmaking are pig iron and ferroalloys. In all the three processes liquid slags are used. During the reduction in the blast furnace the primarily formed slag is rich in FeO. Content of the other oxides depends on the composition of burden. In the zone where burden softens and melts its pulsating volume change was observed. Partially molten burden penetrates between the coke lumps [1], [2], [3]. On contact points with coke burden bloates during reduction and thus the volume is increased. Shape depends on the available space between coke lumps. When some portion of iron is reduced the primary slag inside contracts. The walls of such bloated section are very thin. Other layer consists of iron, on inner side is slag with the varying composition. In the molten slag which passes tuyeres on its way into hearth there is already up to 10% FeO.

During steelmaking in EAF several types of slags are used. In the melting and refining stage they can be represented by the $CaO-SiO_2-FeO$ phase diagram, if reactions with refractory lining are taken into account, $CaO-SiO_2-FeO-MgO$ is favourable. Their composition highly depends on their basicity. In this stage foaming slags with 15 to 20% FeO are used [4].

In making stainless steel, slags contain calcium silicates free, CaO, chromite or calcium chromite. If slags contain 12 to 15% MgO then $(FeO,MgO)\cdot Cr_2O_3$ is formed. CaO is enveloped by calcium chromite on the solid liquid interface during the dissolution in such slags. Chromium yield from the refining slag depends on the basicity and the slag composition.

2. Primary Blast Furnace Slags

In investigations of cooled blast-furnace burden, three zones are described: in the first one the burden is loose and single lumps are separated from each other; in the second zone initial softening and melting is commencing; while the third zone consists of coke layers through which primary slag rich in FeO and reduced iron are streaming. Final blast furnace slags contain 85 to 95% CaO, SiO_2, MgO and Al_2O_3. In cooled blast-furnace slags various minerals can be found after the crystallization of such slags. These minerals are e.g. melilite, dicalcium silicate, monticellite, mervinite, spinel. In amorphous matrix also alkalies can be found.

Primary slags are rich in FeO, since its content is even more than 50%. As such slag streams down over coke, reduction process takes place, and thus its volume is increased due to formation of carbon monoxide. In this burdens of cooled blast furnaces stalactite-like forms of burden where found. Similar constituents in burdens were mentioned also by Japanese researchers [5], [6], [7]. Stalactite - iron stalactite consists of metal on the external side which is in contact with coke while on internal side the metallic wall contains still slag. Fig. 1 represents such a stalactite [8], [9], [10].

Fig. 1 Shape of iron stalactite

We were interested whether such stalactites are formed only during the burden cooling-down in the furnace, or the phenomena of volume increase occur also in the blast-furnace reduction process. Sampling probes enabled to take samples from a smaller blast furnace (with a 3.5 m diameter hearth) at the transition from bosh to belly, and from the tuyeres level. Table 1 presents chemical compositions of primary slags from the belly region, while Table 2 gives composition of samples from the tuyere region or tuyere level.

Those sample exhibited bloated portions of burden, having various shapes with very thin walls. In laboratory experiments of sinter reduction in graphite crucible, a short-lasting volume increase of partially melted sinter, having spherical shape, was observed. After reaching certain volume, the bubble burst, and the cycle was pulsatingly repeated.

Table 1 Chemical analysis of slag in the blast-furnace belly

$Fe_{tot.}$	$Fe_{met.}$	FeO	CaO	MgO	SiO_2	Al_2O_3	K_2O
53÷67	3÷60	6÷55	9÷12	0,7÷3,0	8÷16	0,6÷4,2	0,4÷7,0

Table 2 Chemical analysis of slag at the tuyere level

FeO	CaO	MgO	SiO_2	Al_2O_3	K_2O
1,6÷9,0	30÷45	4,0÷6,5	32÷40	9÷12	0,2÷3,5

Fig. 2 presents how primary slag with about 30% FeO was streaming down through a coke layer, and due to simultaneous reduction process its volume was increased filling the gaps between coke lumps. Thus a phase was formed, consisting of molten iron with slag on internal wall. Fig. 3 is giving a detail of bubble which was trapped between the coke lumps.

Also in reduction of rich iron ore with a low amount of gangue, consisting mainly of SiO_2, an extensive volume increase of ellipsoidal shape, about 5 cm long and 2 to 2.5 cm in diameter, was observed in the region of forming liquid phase at 1400°C. Wall of that bubble consisted also of fayalitte $2FeO \cdot SiO_2$, and metallic iron.

With synthetic samples containing 75% Fe_2O_3, and having various basicity, the volume increase was measured during the reduction process in 40% CO and 60% N_2 atmosphere at 1370°C. Fig. 4 presents time variation of volume increase applying sinter with basicity CaO/SiO_2 = 0.8, which was about 300%, while Fig. 5 gives the volume increase with sinter of CaO/SiO_2 = 1.8, which was about 500%. Fig. 6 gives a schematic presentation of stalactite formation.

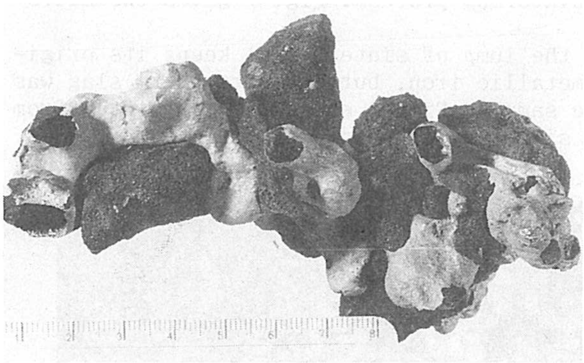

Fig. 2 Formation of foaming slag in coke layer

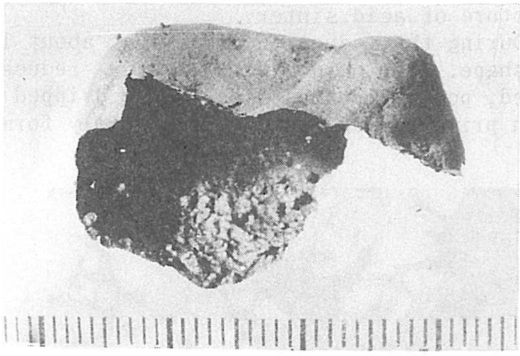

Fig. 3 Section of bloated slag

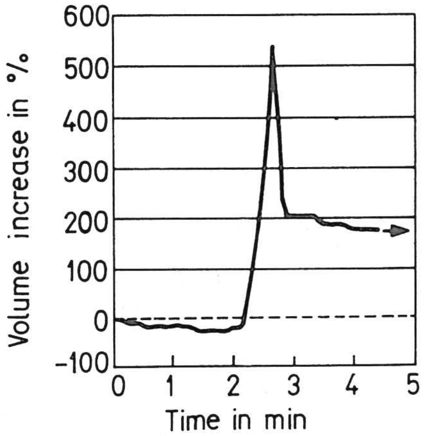

Fig. 4 Volume increase of partially melted sample. CaO/SiO_2 = 0.8, Temp. 1370°C

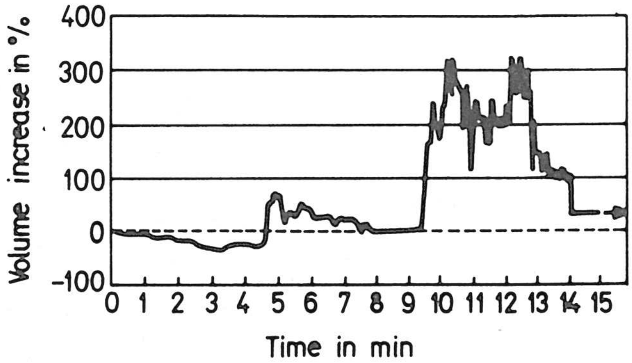

Fig. 5 Volume increase of partially melted sample CaO/SiO_2 = 1.8, Temp. 1370°C

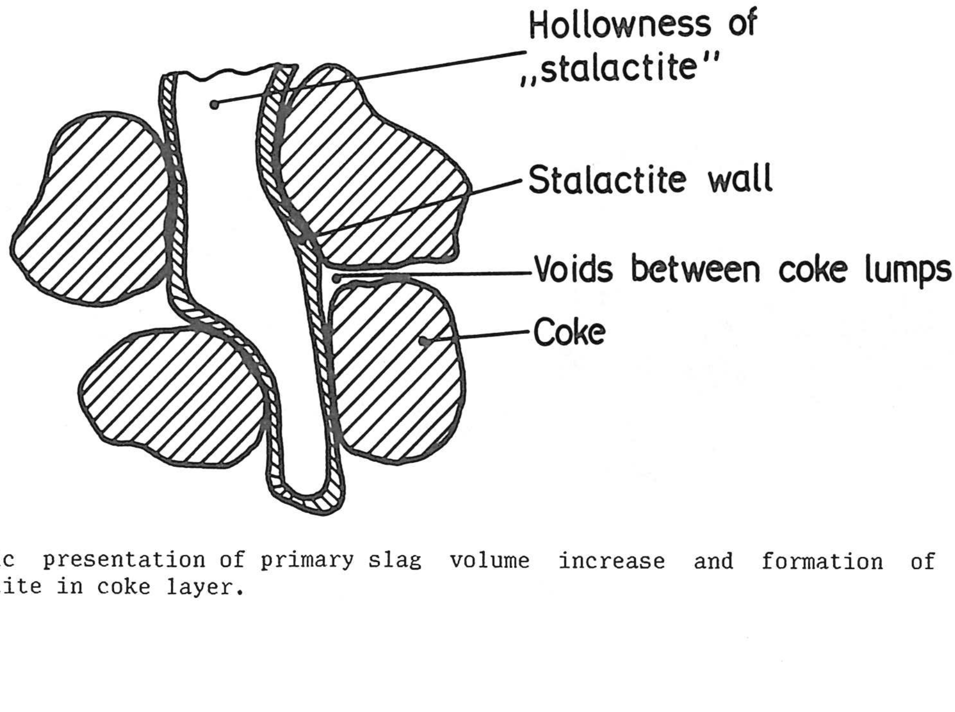

Fig. 6 Shematic presentation of primary slag volume increase and formation of iron stalactite in coke layer.

Primary slags are formed already during the sintering process. Fig. 7 gives the microstructure of acid sinter.

During the reduction process at about 1250°C the lump of sinter still keeps its original shape. Iron oxides were already reduced to metallic iron, but on spots where slag was formed, pores appeared since slag dripped of the sample. Fig. 8 shows reduced sinter from which primary slag, which was actually formed in sintering process, dripped off.

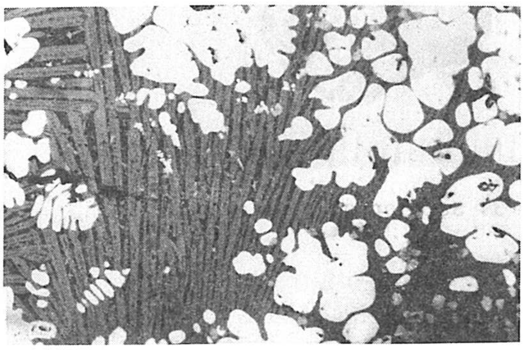

Fig. 7 Microstructure of acid sinter

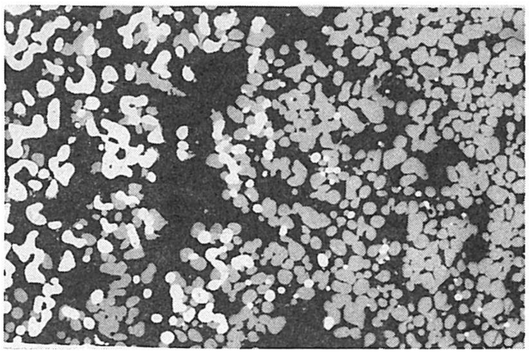

Fig. 8 Partially reduced acid sinter

3. Foaming slags

In steelmaking the refining slags e.g. in EAF are similar to those in the blast furnace regarding to the FeO content. Application of foaming slags in EAF, covering the arc, saves electric energy. Foaming slags are actually liquid slags with dispersed gaseous bubbles. Single bubbles are separated from each other by thin slag walls. Formation of carbon monoxide and dioxide takes place in metal bath, on metal-slag interface, and in slag. Additions of dolomite ($CaCO_3 \cdot MgCO_3$) to EAF for formation of slag increase the amount of evolved carbon dioxide [11], [12], [13], [14].

Our investigations had intention to test the increased use of scale in EAF in order to increase metal yield, therefore mixture of scale and ground electrode or coke was added into EAF for formation of foaming slag. FeO content in slags was up to 35%. Good foaming of slag to achieve height of 30 to 40 cm demands contents above 15%. Foaming slags were applied for dephosphorisation of melt, and also lower content of Cr in the melt was achieved. Foaming slags leaving the furnace contain also droplets of steel.

Fig. 9 shows macropicture of foaming slag, and in Fig. 10 metallic droplets are visible. Micropicture of bubble wall is presented in Fig. 11. The bubble wall contained also crystals of periclease and chromite next to calcium silicate. Table 3 presents chemical compositions of EAF slags.

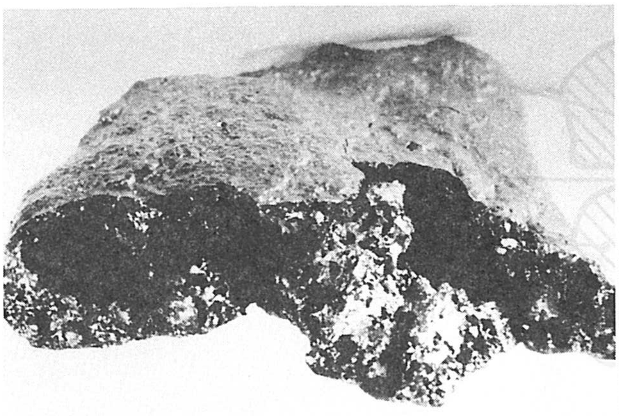

Fig. 9 Microstructure of foaming slag

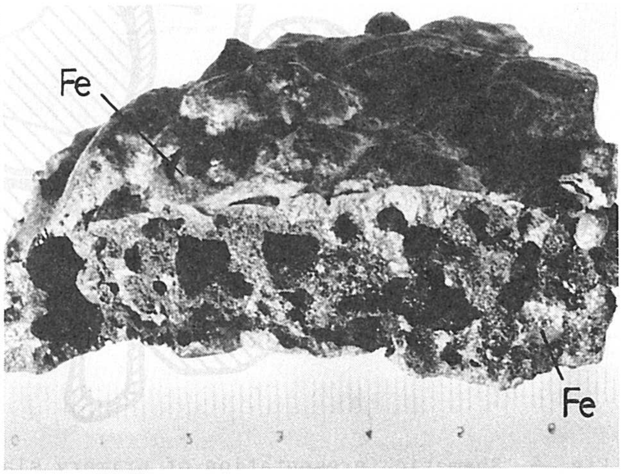

Fig. 10 Metal drops in slag

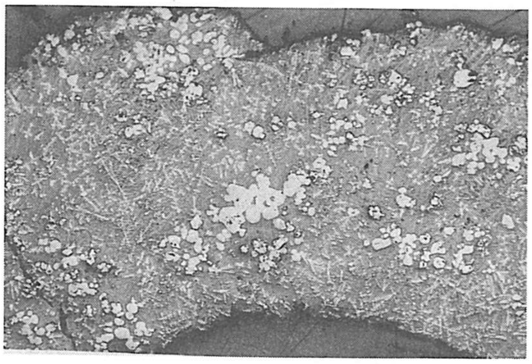

Fig. 11 Micropicture of the bubble wall

Table 3 Chemical analysis of foaming slags

	CaO	MgO	SiO_2	Al_2O_3	FeOn
1	42,7	5,1	12,8	6,3	25,8
2	41,9	8,4	13,4	4,6	23,6
3	46,7	9,6	15,6	3,5	15,1

4. Stainless-steelmaking slags

In melting alloyed burden slags contain high amount of chromium oxide due to oxidation of chromium. Oxide in solidified slags is in form of chromite, $FeO\cdot Cr_2O_3$, or calcium chromite, $CaO\cdot Cr_2O_3$, or even picrochromite, $MgO\cdot Cr_2O_3$. In basic slags calcium chromite has preference. Picrochromite is formed in MgO-containing slags. In such slags also forsterite crystals, $2MgO\cdot SiO_2$, can be found.

In VOD slags in stainless steelmaking also $FeO\cdot Cr_2O_3$, $MgO\cdot Cr_2O_3$, or $(FeO, MgO)\cdot Cr_2O_3$ solid solution appear next to $2CaO\cdot SiO_2$ and $3CaO\cdot SiO_2$, and undissolved CaO, i.e. in slags containing over 15% MgO, while in basic slags there is $CaO\cdot Cr_2O_3$. Beside chromites there are also $3CaO\cdot MgO\cdot 2SiO_2$ and $2CaO\cdot MgO\cdot 2SiO_2$. Slag compositions can be represented by the quaternary $CaO-SiO_2-MgO-Cr_2O_3$ diagram (Fig. 12).

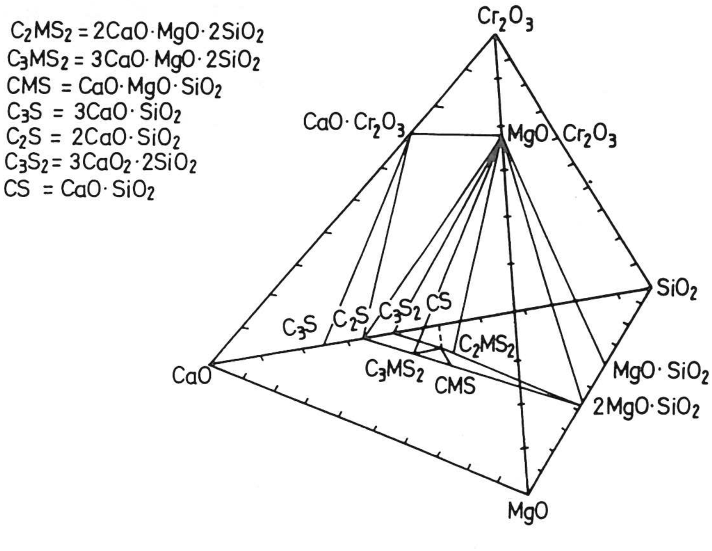

Fig. 12 Minerals in slags in stainless-steelmaking

After the refining stage of melt, the slags are in the most cases heavy flowable due to higher amounts of chromites (Fig. 13). During the dissolution of CaO in those slags, calcium chromites (Fig. 14 and 15) are formed already on the solid-liquid interface.

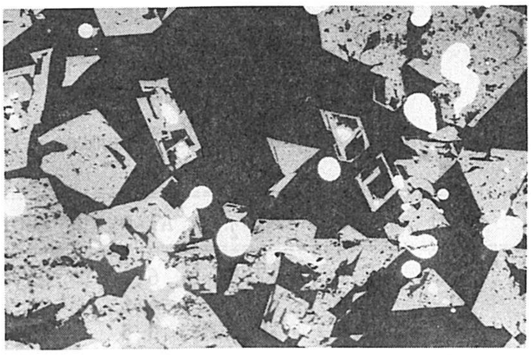

Fig. 13 Chromite in slag

Fig. 14 CaO-slag interface

5. Conclusions

Composition of slags being formed during the reduction in blast furnace, their increase in volume are foaming as they are in contact with coke, are presented.
For formation of foaming slags in the refining stage in EAF scale and ore can be used.
In stainless-steelmaking, slags can contain $MgO \cdot Cr_2O_3$, $CaO \cdot Cr_2O_3$, and $FeO \cdot Cr_2O_3$, or their solid solutions.

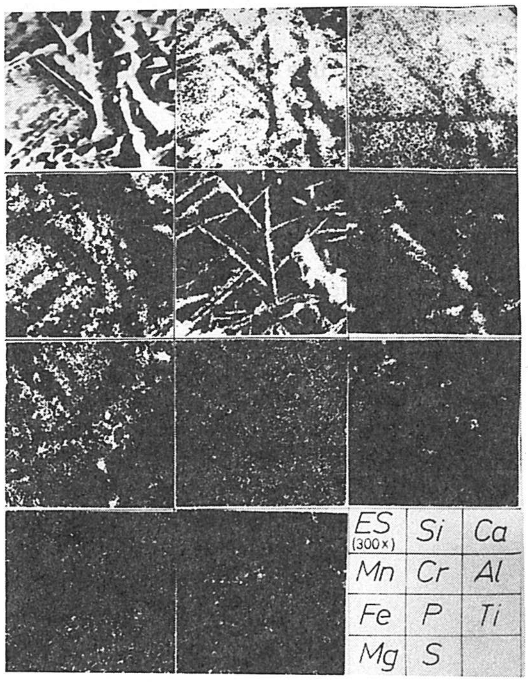

Fig. 15 Elements distribution on CaO-slag interface

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