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Melting Behaviour of Ferronickel Slags

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The industrial manufacturing of ferronickel in electric furnaces produces large amounts of slag with strong acidic character and high melting points, which seriously stresses the furnace refractory lining. In this study, the melting behavior of synthetically produced ferronickel slags on magnesia as refractory material was determined by means of a hot stage microscope. Therefore, slags comprising the main oxides SiO_2 (35–70 wt.%), MgO (15–45 wt.%) and Fe_2O_3 (5–35 wt.%) were melted in a graphite crucible and afterwards analyzed by a hot stage microscope. The design of experiments, which was created by the statistic software MODDE®, included 20 experiments with varying slag compositions as well as atmospheres. The evaluation of the test results occurred at three different characteristic states of the samples like the softening point according to DIN 51730 and the temperatures at which the area of residual cross-section of the samples amounted to 30% and 40%, respectively, of the original value depending of their SiO_2/MgO ratio and iron oxide content. Additionally, the thickness of the zone influenced by the slag was measured and evaluated.

INTRODUCTION

Ferronickel represents an irreplaceable alloying additive for stainless steels and also plays an important role for other materials like nickel-based and other steel alloys.[1,2] For the metallurgical production of this ferroalloy, wet laterite with a low nickel content of about 1.5–3% is used. Such a typical oxidic nickel resource consists of 40% SiO_2, 25% MgO, 1% Al_2O_3, 15% Fe, 5% O (bounded) and about 11% chemically combined water. The dominating ferronickel production route for oxidic ores includes a rotary kiln and an electric arc furnace with subsequent raffination. Nickel constitutes a relatively noble metal and so it is possible to separate it from the gangue through a carbothermic reaction. Because of the high water content of lateritic ores, a drying process exhibits an advantage prior reduction. After the pretreatment in rotary kilns, electric arc furnaces are widely applied for smelting. Additionally to the raw ferronickel containing about 20 wt.% nickel, large amounts of a very acidic slag with a high melting point are also produced. This provides a challenge to the

metallurgical plant operators and the refractory producers. After the smelting process, the raw ferronickel has to be refined, e.g., in a converter to generate a saleable product.[1–3]

The chemical and physical properties of slags act as important parameters in metallurgy and strongly influence the process control. Consequently, the slag represents not an unwanted by-product but an additional phase, which takes part in chemical reactions that protects the metal against absorption of tramp elements and collects harmful elements from the metal. Therefore, concentrated attention is paid on slag properties like viscosity, density, chemical activity and miscibility, which influence the process.[4,5]

To get a better understanding of the behavior of liquid slags, two different models, the molecular and the ionic theories, can be used. The molecular theory assumes that the oxides are uncharged molecules but it reaches its limits concerning the electrical resistance of liquid slags. During the melting of the slags, the electric conductibility makes an abrupt rise and so slags must consist of positively and negatively charged ions as the ionic

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theory postulates. The ionic model distinguishes between non-metallic oxides having an acidic character and metallic compounds which can be basic or amphoteric. Compounds like SiO_2 build stable crystal systems and also in molten form long-chained silicon oxygen complexes composed of SiO_4^{4-} tetrahedrons. The high binding energy of these covalently bonded atoms causes a very high stability and so they do not break down even in liquid form. The SiO_2 molecules absorb O^{2-} ions representing acceptors in the following acid/base reaction:[5,6]

$$SiO_2 + 2O^{-2} \rightarrow SiO_4^{4-}$$
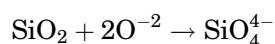
Basic oxides, like CaO or MgO, build ionic compounds which exhibit in solid state a lattice similar to NaCl. When these crystals fuse, their lattice become destroyed and a dissociated electrolytic melt with a disordered composition is generated. Their basic characteristics results from acting as donators:[6]

$$CaO \rightarrow Ca^{2+} + O^{2-}$$

The integration of the alkali- and alkaline earth groups breaks down the three-dimensional Si-O-Si network. The addition of more MeO causes a shortening of the silicate chains, until they appear only as orthosilicates, SiO_4^{4-}. In consideration of the ionic theory, the ferronickel slags consists of two main components, SiO_2 and MgO:[6]

$$2MgO + SiO_2 \rightarrow 2Mg^{2+} + SiO_4^{4-}$$
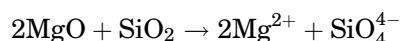
The ferronickel slags exhibit melting points of around 1500°C and are tapped at temperatures about 50°C above the melting point to achieve a good separation between slag and metal. Both oxides (MgO and SiO_2) are entirely transferred to

the slag and so the ore has a direct influence on the slag composition. In Fig. 1, the melting temperatures of different industrial slags are shown as a function of their SiO_2/MgO ratios and FeO contents. Thus, the slag composition has a direct influence on the melting point and moreover on the required process conditions.[7]

In this study, the melting behavior of different slags in reducing, neutral or oxidising conditions is investigated. Also, the impact of these slags on magnesia refractories was investigated. The results should provide a basis to improve the course of the process flow and optimize the slag metallurgy in the production of ferroalloys.
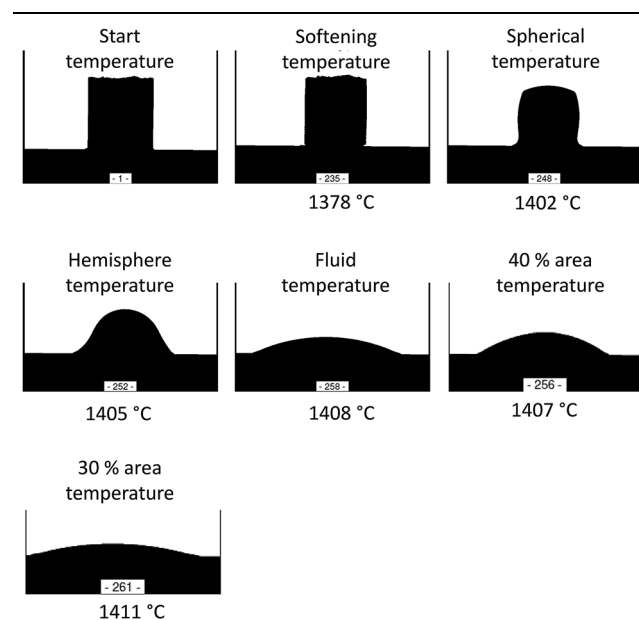

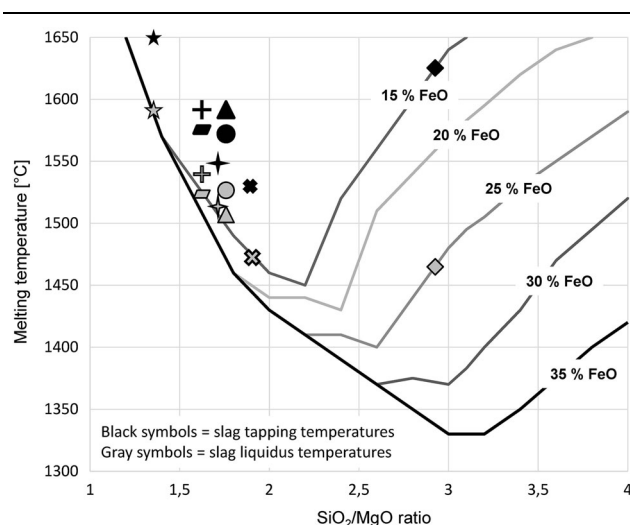Fig. 2. Silhouettes of a sample during heating-up in the hot stage microscope.

Fig. 1. Melting points of slags as a function of the SiO_2/MgO ratio with the corresponding tapping temperatures of different producers.[7]
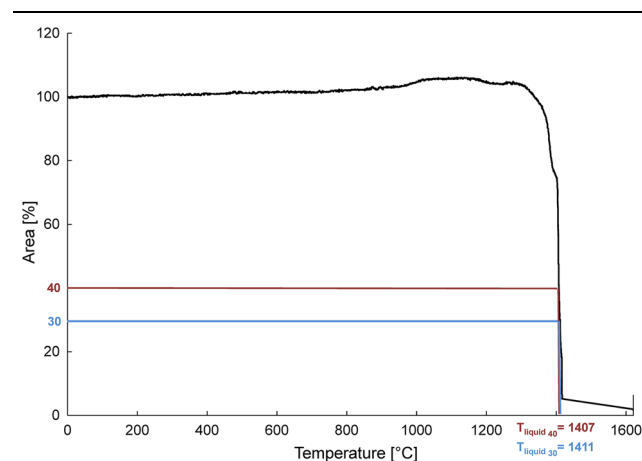

Fig. 3. Cross-section area results of a sample melted in the hot stage microscope.

MATERIALS AND METHODS

Method of Analysis by a Hot Stage Microscope (HSM)

A hot stage microscope was used to analyze the melting behavior of the synthetically produced ferronickel slags. The cylindrical samples were melted by the HSM and software identified characteristic temperatures according to DIN 51730. One of these represents the softening temperature, at which first indications of softening (edge rounding, start of swelling) occur. At a hemisphere temperature, the sample exhibits a shape similar to a hemisphere and its height is half as large as the
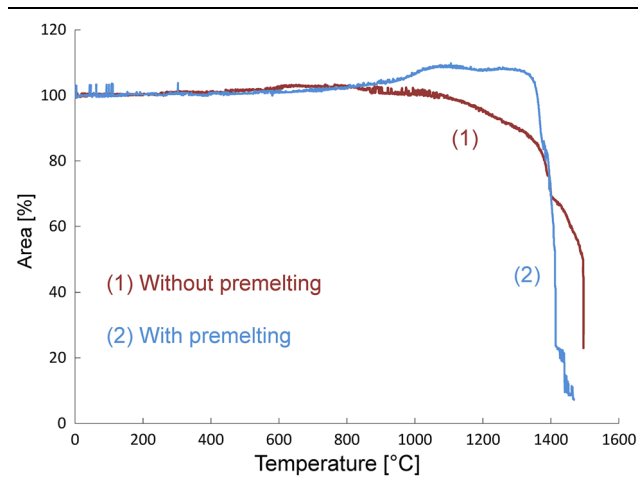

Fig. 4. Comparison of the melting behaviour of a synthetic slag with and without premelting.

length of its baseline. Furthermore, the flow temperature is reached when the height of the sample is one-third of its height at hemisphere temperature. However, not all slags yielded results for the flow temperature by this method. So, the evaluation of the measured data was done by the method of Schnideritsch.[8] Silhouettes at softening, spherical and other characteristic points (see Fig. 2) were compared in order to determine the minimum temperature for complete melting of the sample. Figure 3 shows its cross-sectional area over temperature, including the modified definition of the liquidus temperature at 30% and 40%, respectively, of the residual cross-section area, because no hemisphere or fluid temperature was identifiable.[8]

Preparation of Synthetic Slag

In this section, the preparation and characterization of the synthetic slags that only consist of the three main oxides of ferronickel slags, namely MgO, SiO_2 and Fe_2O_3, is explained. The resultant slag samples served for the subsequent investigation in the HSM. A swing mill, an induction furnace and a hot stage microscope for the investigation of their melting behaviors were used.

Test Procedure

Before mixing the slag components, quartz was purified with 10% HCl followed by annealing. Then, a swing mill served for homogenization of the powder mixture. The following melting process in the induction furnace occurred in a graphite crucible because of its resistance to acidic slags. After reaching the liquidus temperature of the slag, it was

Table I. Design of experiments

No. of trial	Slag	MgO (wt.%)	SiO_2 (wt.%)	Fe_2O_3 (wt.%)	Gas	Fe^{2+}/Fe_{tot} (–)	Fe^0/Fe_{tot} (–)
N1	S1	45	35	20	−1	0.38	0.61
N2	S1	45	35	20	1	0.38	0.61
N3	S2	15	70	15	1	0.09	0.14
N4	S3	15	50	35	−1	0.07	0.01
N5	S3	15	50	35	1	0.07	0.01
N6	S4	45	50	5	−1	0.48	0.26
N7	S5	25	70	5	−1	0.12	0.08
N8	S5	25	70	5	1	0.12	0.08
N9	S2	15	70	15	0	0.09	0.14
N10	S6	15	63	22	−1	0.06	0.01
N11	S4	45	50	5	0	0.48	0.26
N12	S7	30	35	35	0	0.87	0.09
N13	S7	30	35	35	0	0.87	0.09
N14	S8	25	40	35	1	0.55	0.02
N15	S9	38	57	5	1	0.16	0.03
N16	S10	29	52	19	−1	0.17	0.03
N17	S10	29	52	19	0	0.17	0.03
N18	S10	29	52	19	0	0.17	0.03
N19	S10	29	52	19	0	0.17	0.03
N20	S10	29	52	19	0	0.17	0.03

Table II. Experimental results

No. of trial	Softening temperature (°C)	Sphere temperature (°C)	Hemisphere temperature (°C)	Fluid temperature (°C)	Temperature of 30% residual area (°C)	Temperature of 40% residual area (°C)	Area (mm²)
N1	–	–	–	–	–	–	0.97
N2	–	–	–	–	–	–	1.31
N3	1532	–	1559	1579	1571	1566	8.73
N4	1356	–	1621	–	1427	1415	5.24
N5	1384	–	1622	–	1448	1445	
N6	1542	–	1562	1594	–	1621	4.79
N7	1548	–	1583	1594	1586	1578	7.06
N8	1531	–	1574	1584	1577	1573	10.27
N9	1534	–	1620	–	1572	1567	7.35
N10	1523	–	1593	–	1535	1530	4.23
N11	1534	1543	1550	–	–	1622	11.65
N12	1387	–	1434	1592	1569	1508	4.21
N13	1380	–	–	–	1583	1523	
N14	1375	1402	1405	1408	1411	1407	5.45
N15	1525	1531	1535	1538	1538	1537	6.74
N16	1447	–	1469	1481	1484	1476	3.68
N17	1411	–	1441	1471	1478	1470	4.58
N18	1370	1416	1436	1476	1487	1469	5.33
N19	1399	–	1433	1463	1463	1460	5.4
N20	1396	1421	1439	1467	1467	1457	5.26
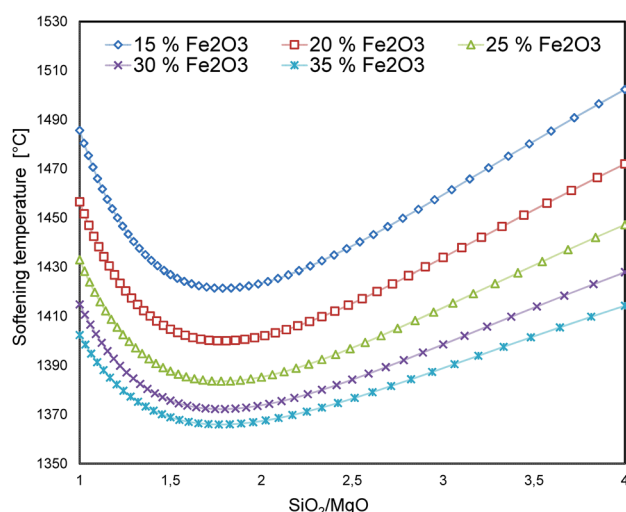
Fig. 5. Dependence of the softening temperature of the SiO₂/MgO ratio and the Fe₂O₃ content in neutral CO₂ atmosphere.

quenched on a steel plate at room temperature to achieve high cooling rates. Afterwards, a swing mill ground the solid slag to obtain a fine slag powder.

The focus of this work comprised the analysis of the melting behavior of the slag by the hot stage microscope. For that, a small slag cylinder was pressed and positioned on a MgO plate. Besides the investigation of the melting behavior of the slags, the corrosion of the magnesia by them, which should simulate the real smelting process, was also determined. For that, a heating of the furnace by 10 K/min up to a temperature of 1700°C occurred, which corresponds to a sample temperature of about 1620°C. After that, the temperature remained constant for 1 h to determine the interaction between the slag and the refractory.

Pre-test to Define Proper Test Conditions

To find the best experimental conditions closest to the real process, some pre-tests were necessary. One of them comprised the detection of suitable atmospheres. Therefore, a reducing atmosphere with 2% H_2 and 98% Ar was checked, but its high reduction potential resulted in the generation of pure iron drops out of the Fe oxide contained in the slag. After several tests, it was found that a mixture of 60% CO and 40% CO_2 [corresponding to p(O_2) = 1.13 × 10⁻⁷ bar at a temperature of 1620°C] was the best atmosphere for closest to real processing.

Some tests also investigated the effect of plate material carrying the slag sample. Due to the fact that the magnesia plate did not show a significant influence on the melting behavior of the slag compared to a Pt/Rh plate, magnesia served for the following investigations because it allowed the simulation of refractory corrosion.

Additionally, tests with and without premelting of the synthetic slag were performed in the HSM, which illustrated a strong difference in melting behavior (see Fig. 4). For the following experiments, premelted synthetic slag powder was applied to approximate real slags.

Design of Experiments

The design of the experiments can be seen in Table I, which includes 20 tests with different slag compositions and varying gas atmosphere in which −1 indicates a gas mixture of 60 vol.% CO and 40 vol.% CO_2, 1 synthetic air and 0 pure CO_2. Due to the pre-melting of the slag in a graphite crucible,

partial reduction of iron oxide took place, the extent of which varied strongly with the slag composition. Therefore, Table I quantifies this effect by the ratios of Fe(II) oxide as well as metallic iron to total iron content. However, the heating of the samples by the HSM in above-mentioned controlled atmospheres compensates these varying oxidation states.

RESULTS AND DISCUSSION

Experimental Results

Table II shows the characteristic softening temperatures and temperatures for 30% and 40%, respectively, residual cross-section area as well as the infiltration area. The tests N1 and N2 achieved no results, because of a too high melting point of slag S1 of more than 1620°C, which constitutes the heating limit of the hot stage microscope. Finally, the area of the slag infiltration was manually determined by an optical stereo microscope.

Statistical Evaluation and Interpretation of the Results

The experimental results were evaluated by the statistic software MODDE® 11, which also served for the design of the experiments. The statistical analysis includes the following parameters:
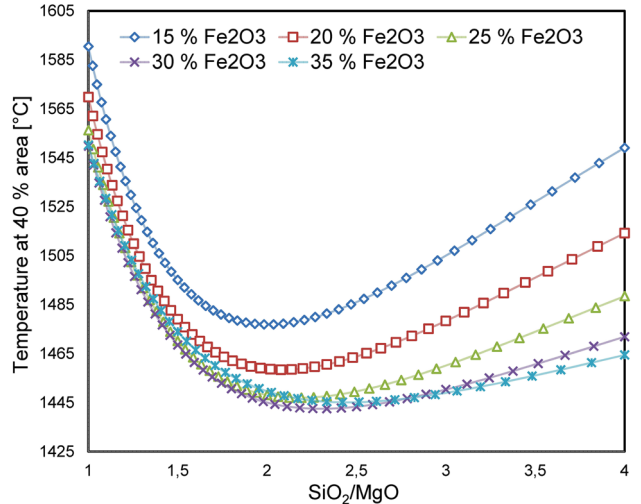
- Softening temperature

Fig. 6. Dependence of the 40% residual area of the SiO_2/MgO ratio and the Fe_2O_3 content in neutral CO_2 atmosphere.
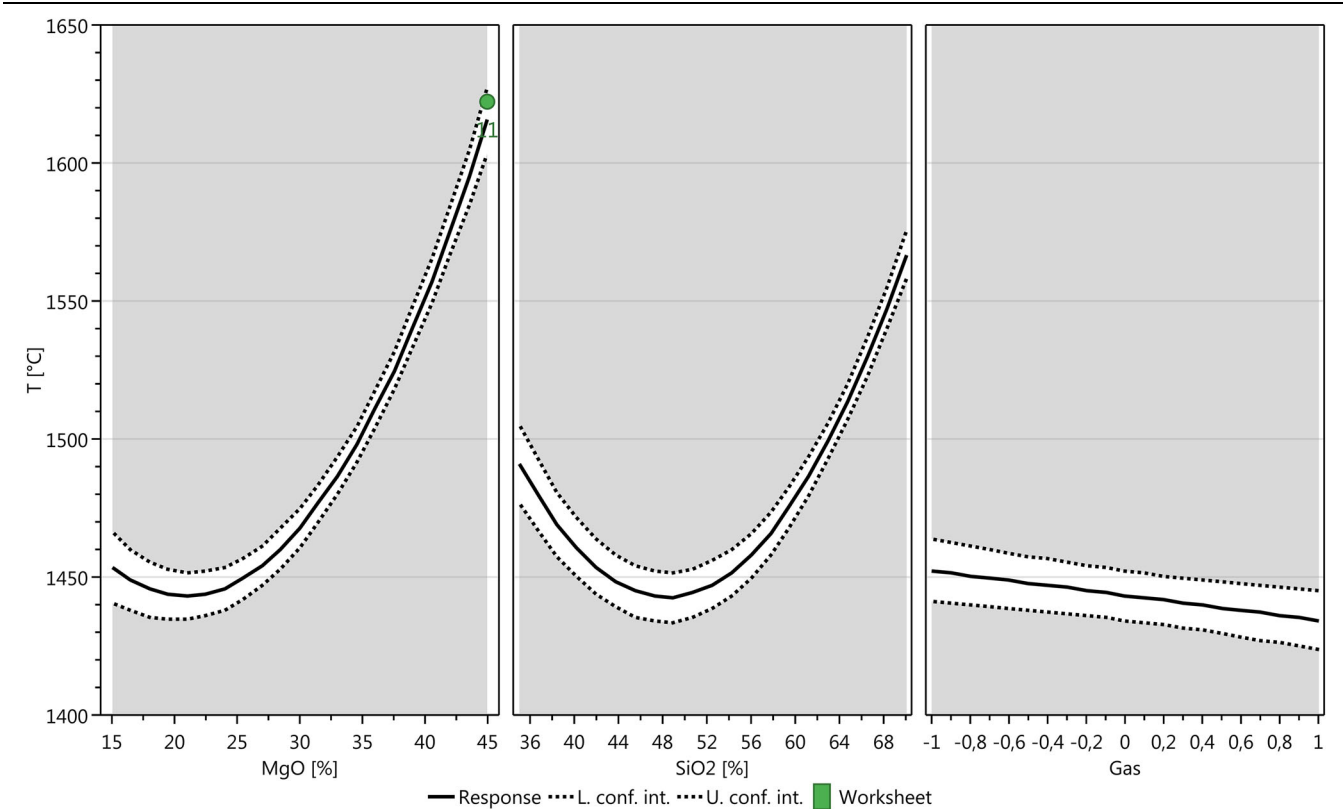

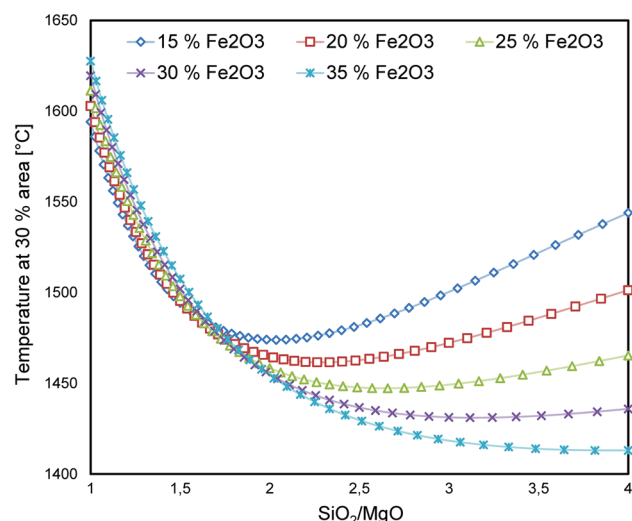Fig. 7. Representation of the 40% residual area temperature for 50% SiO_2, 20% MgO and gas = 0.

Fig. 8. Dependence of the 30% residual area of the SiO_2/MgO ratio and the Fe_2O_3 content in neutral CO_2 atmosphere.

- Temperature for 40% residual area
- Temperature for 30% residual area
- Area of slag infiltration zone

Figure 5 presents the softening temperature dependent on the Fe_2O_3 content. An increasing content of iron oxide resulted in a declining softening temperature. At a constant iron oxide concentration, the lowest temperatures appeared in a range of about 1.5–2 for the SiO_2/MgO ratio.

During heating the furnace, the samples will reach that temperature at which the areas of their silhouettes amount to 40% of the original area. It is assumed that the liquidus temperature is reached at this point. This temperature (see Fig. 6) exhibits the same trend in dependence on the slag composition as the published data from literature (see Fig. 1), indicating that the lowest temperature is at a SiO_2/MgO-ratio between 2 and 3.

The next diagrams (see Fig. 7) show the influence of the MgO and SiO_2 content as well as the gas composition on the melting point. The first diagram illustrates the melting temperature in dependence on the MgO content by a fixed SiO_2 content of 50% and the atmosphere 0 (pure CO_2), the second in dependence on the SiO_2 content by a fixed MgO concentration of 20% as well as the atmosphere 0, and the last one the influence of the atmosphere on the melting temperature at a slag composition of 50% SiO_2, 30% Fe_2O_3 and 20% SiO_2. In both cases, an increase of the MgO and the SiO_2 content resulted in higher melting temperatures. The influence of the atmosphere on the melting behavior is very low and in the range of the model inaccuracy.

A similar trend is shown in Fig. 8 at the temperature for a residual cross section area of 30%. The amount of iron oxide in the synthetic slag exhibits a larger impact on the liquidus temperature at higher SiO_2/MgO ratios. At low SiO_2/MgO ratios, the iron oxide content has only a very low influence on the temperature.

Affected Zone of the Refractory by the Slag

The statistical evaluation of the size of infiltration zones results in a clear rise of the area with increasing SiO_2/MgO ratios due to the influence of the slag. The area of infiltration appears about three times larger at a ratio of 4 than at a ratio of 1, whereas the effect of iron oxide content is considerably smaller.

CONCLUSION

The enormously large slag amounts, their acidic character and high melting temperatures challenge ferronickel and refractory producers. To achieve a better understanding of how the slag acts in the electric furnace, its melting behavior and the corrosion of the refractory caused by the slag was the main topic of this research. Therefore, the analysis by the hot stage microscope proves an excellent method for the determination of its melting behavior. The slags show minimum melting temperatures within the investigated range from 1.5 to 3 for the SiO_2/MgO ratio. The influence of the iron oxide content, which depends in real processes on the reducing conditions in the furnace, indicates that the melting temperatures fall with rising iron oxide contents. In detail, the comparison of Figs. 5 and 8 indicate that the iron oxide content influences both characteristic temperatures at high SiO_2/MgO ratios but only the softening temperature at low ones. Several effects cause this diverging behavior, which can be described in detail by thermodynamical calculations (e.g., FactSage). Depending on their composition, diverse solid phases are stable within the melting ranges of these slags, which exhibit differing solubilities for iron(II) oxide and iron(III) oxide. However, the ratio between these both components in the liquid phase also depend on temperature and gas atmosphere. The corrosion of magnesia-based refractory rises with increasing SiO_2/MgO ratios, whereas the iron oxide has no strong influence on the corrosion.

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