

Corrosion Mechanisms of Refractory Materials Used in Secondary Metallurgy

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In the present work dissolution mechanisms of refractory materials after contact with slags of the secondary metallurgy are discussed. Post mortem samples of the RH-degasser as well as samples from dynamic and static corrosion tests were investigated. There are many empirical observations existing, concerning the wear of refractory materials in the mentioned vessels but still, a fundamental scientific understanding of the ongoing corrosion processes is missing. This work provides important considerations concerning these wear mechanisms. The results enable an estimation of chemical dissolution in dependence of the steel grade and its corresponding slag. These fundamentals allow an extension of service life by influencing the prevalent process parameters and selecting suitable refractory materials. Moreover they provide impulses for the development of new or improvement of already existing refractory materials.

the spinel is added as a grain fraction (spinel containing castable) or formed in an in situ reaction of magnesia and alumina during service (spinel forming castable) [1, 2]. In this paper some exclusive results regarding the corrosion of alumina spinel castables are discussed. The composition of a spinel containing (CI) and a spinel forming castable (CII) are given in Tab. 2. The aim of this investigation was to reveal, which slag type has the most aggressive behaviour against the examined castables. Further emphasis was put on the question which castable shows a superior slag resistance.

The second refractory material investigated, were magnesia chromite bricks. Usually the various parts of the RH vessel are lined with different grades of magnesia chromite bricks. For areas of severe wear – such as the inner lining of the snorkels and the lower part of the vessel – high quality direct bonded bricks, bricks based on magnesia

1 Introduction

The work deals with the scientific investigation of dissolution of refractories in contact with steelmaking slags. The main focus was put on the characterisation of the melting behaviour of the different ladle slags, the examination of reaction products formed at the interface between refractory material and slag and additionally on the determination of the solubility of different refractory oxides within the slags. The slags were investigated thermochemically – using the software package FactSage – mineralogical-

ly and microanalytically. For the chemical composition of the slags see Tab. 1. S1 is a slag used for the production of an ULC (ultra low carbon) steel quality and S2 for a LC (low carbon) steel quality. S3 is the slag with the highest basicity and used for the production of acid resistant steel. Further investigations comprised the examination of post mortem samples from dynamic and static corrosion tests as well as samples taken directly from the mentioned vessels.

Alumina spinel castables are widely used in steel ladle linings below the slag line. Either

Tab. 1 Slag composition

	Composition Slag S1 [mass-%]	Composition Slag S2 [mass-%]	Composition Slag S3 [mass-%]
FeO	23,3	5,5	0,3
SiO ₂	8,1	8,7	5,7
CaO	26,3	42,8	54,8
MgO	13,2	11,3	9,3
Al ₂ O ₃	21,7	28,0	29,9
MnO	7,4	3,7	–
C/(S+A)	0,88	1,17	1,54

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Tab. 2 Composition of the castables

	Castable I Spinel containing [mass-%]	Castable II Spinel forming [mass-%]
FeO	0,2	0,1
SiO ₂	0,3	0,5
CaO	1,3	1,0
MgO	3,2	7,9
Al ₂ O ₃	95,0	90,5

Tab. 3 Magnesia chromite refractory composition

	Composition Magnesia chromite brick [mass-%]
MgO	59
SiO ₂	0,5
Fe ₂ O ₃	12
Al ₂ O ₃	7
Cr ₂ O ₃	21
CaO	0,5
C/S	1

chromite co-clinker and bricks based on fused magnesia chromite grain are applied. The samples investigated here belong to the latter group. In the present work post mortem samples from the RH degasser (service conditions app. 1630 °C) and samples after a rotary slagging test at 1700 °C have been compared. Both have been in contact with a highly basic Al₂O₃ rich slag, used for the treatment of acid resistant steel qualities (see Tab. 1, slag S3) [1, 2]. The refractory composition as per data sheet is given in Tab. 3. Main emphasis was put on the question of the amount of liquid phase that forms during service. Refractory wear is discussed as a function of the distance from the hot face in both cases.

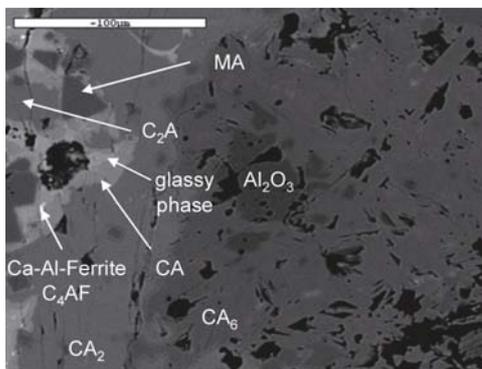


Fig. 1 SEM image of castable I in contact with slag S1; the left margin is nearest to the hot face

2 Experimental procedure

For a mineralogical evaluation of the castables cup tests with the different combinations refractory/slag have been carried out at 1620 °C. After testing, the specimens were investigated using reflected light microscopy and afterwards SEM and EDX examinations. Additionally FactSage calculations have been performed for a thermochemical assessment of the interactions between refractory and slag. The emphasis was put on the interactions of the various combinations refractory/slag to determine the phases in equilibrium in dependence of the amount of refractory material added. The calculations consider only the composition of the fines, as this fraction is supposed to react first in contact with slag [3].

Regarding the magnesia chromite samples, a rotary slagging test with the mentioned magnesia chromite brick (sample A) at 1700 °C has been performed for five hours with an acid resistant steel slag. After testing microsections of the brick (residual thickness 72 mm) from the hot face to the cold end were taken. The samples were prepared for light microscopic and afterwards scanning electron microscopic (SEM) and energy dispersive X-ray spectroscopic (EDX) examinations again using standard ceramographic grinding and polishing techniques. Additionally microsections from a post mortem sample from the lower vessel of the RH degasser were prepared in the same manner (sample B). The residual thickness of the sample was app. 80 mm. Besides the standard EDX evaluation, chemical profiles using EDX techniques from the hot face to the cold end were compiled in both cases. Moreover a thermal simulation provided information about the temperature gradients at service and during the testing conditions, respectively. The information of the chemical profiles together with the data from a thermal simulation enabled the estimation of the amount of liquid that forms during service conditions as a function from the distance to the hot face.

3 Results

3.1 Mineralogical evaluation of alumina spinel castables

Fig. 1 documents the transition area of castable I in contact with slag S1. Phases observed are CA₆, CA₂ and CA. Additionally spinel MA, which is embedded in the CA₂

matrix, a small amount of corundum, which has not reacted to CA₆ completely, as well as small amounts of a calcium aluminate ferrite and a glassy phase have been identified. The formation of this secondarily formed spinel occurs near the transition zone. It shows the characteristic cubic shape and is inhomogeneously distributed at some distance from the interface.

3.2 Thermochemical investigations concerning the interactions between refractory and slag

Fig. 2 and 3 illustrate the calculated phase distribution in dependence of the refractory content in weight percent relatively to the total amount of slag and refractory at 1620 °C and 1680 °C, respectively. Zero percent represents the composition of the particular slag and 100 percent the phase composition of the refractory material.

In contact of castable I with slag S1 at 1620 °C spinel precipitation is observed at 29,6 % followed by CA₂ at 63,6 % and CA₆ at 71,3 %. Hence 70,4 % slag is required to completely dissolve castable I. Moreover the figures reveal that the slag is already saturated in MgO at both temperatures. The fines consist of 10,6 % CA₆, 48,6 % Al₂O₃, 37,7 % spinel and 3,1 % of liquid. At 1680 °C the spinel precipitation is shifted to higher amounts of castable (39,5 %), indicating that less slag (60,5 %) is necessary for a complete dissolution of the castables fines fraction. CA₂ is no longer stable and therefore already low additions of slag form an extensive amount of liquid. At 1680 °C, an addition of 25 % slag leads to a complete dissolution of the intermediately formed calciumaluminates rising the amount of liquid to values of > 70 %. At both examined temperatures dissolution of alumina may occur indirectly, i.e. calciumaluminate layers will be formed. In service the flow conditions in the ladle must be considered, as a more intense bath movement increases the dissolution rate. If the dissolution rate is higher than the rate of reaction to CA₆ and CA₂ respectively, direct dissolution of Al₂O₃ may be expected.

A comparison of castable I and II at 1680 °C in contact with slag S2 (Fig. 4 and 5) reveals that with increasing basicity of the slag, the amount of slag necessary for an entire dissolution of refractory fines decreases significantly. Spinel is primarily responsible for the

corrosion resistance of the castables and gets more easily dissolved in CaO rich slags. To clarify the dependence of the solubility on the composition of the fines and on different C/S ratios, variable ratios A/M for the reactive components of the refractory material have been regarded. The results are summarized in Figs. 6 and 7. The ordinate represents the maximum amount of refractory material dissolved in 100 g slag and the abscissa the molar ratio A/M of the refractory. Additionally the molar ratios of the two examined castables are labelled. A rising temperature is linked to a strong increase of the refractory material dissolved. For higher basicities there is minimum of the solubility at A/M ratios of 2 to 2,5. For more acidic slags this minimum is shifted to values of $A/M < 0,5$. Moreover the diagrams reveal that the amount of refractory material dissolved decreases in slags with lower basicities. The solubility of the refractory material in slags with lower C/S ratios shows an even higher dependence on the temperature.

3.3 Mineralogical evaluation of magnesia chromite rotary slagging test sample

Fig. 8 shows a light microscopic overview of the first microsection of the sample A. The adherent slag and the adjacent corroded microstructure are clearly visible. The first app. 20 mm of the sample are characterised by an entire change of the brick's original microstructure. Chromites are decomposed to a great extent. Reaction products are spinel solid solutions between picrochromite and spinel MA. Minor phases occurring near the hot face are mainly calciumaluminate ferrites as well as calcium aluminates (CA directly at the hot face and $C_{12}A_7$ from the transition zone to a depth of app. 20 mm). Fig. 9 documents a spot about 14 mm from the hot face. Appearing minor phases are calciumaluminate ferrites (C_4AF), marginal amounts of C_2S and again high amounts of a spinel solid solution between picrochromite and spinel MA. These spinel solid solutions occur primarily at the grain boundaries of the chromite residues. Chromite precipitates have already decomposed to a high extent.

Fig. 10 shows a plot based on SEM investigations and chemical profiles using mass balance equations to determine the composition for the first 30 mm of sample A. Direct-

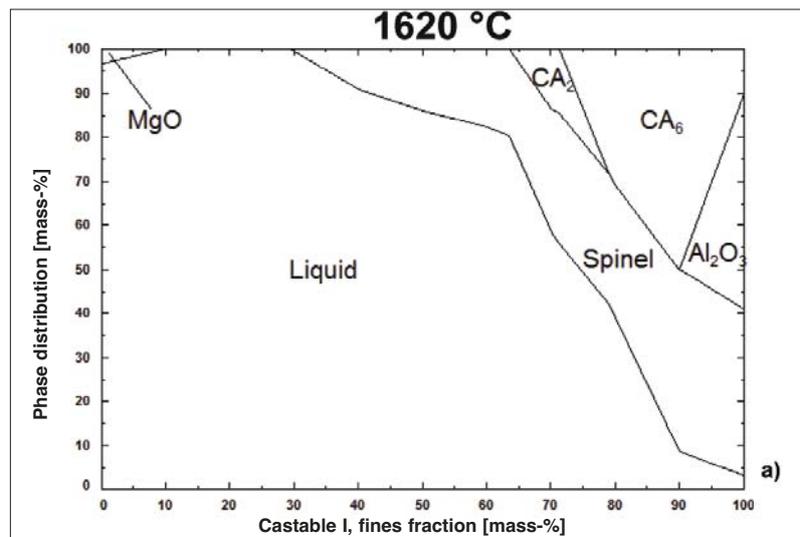


Fig. 2 Equilibrium between fines of castable I and slag S1 at 1620 °C (a)

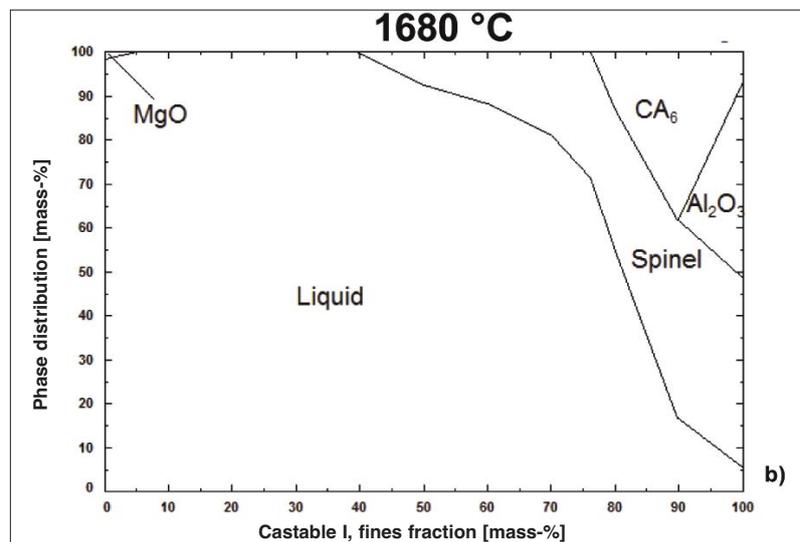


Fig. 3 Equilibrium between fines of castable I and slag S1 at 1680 °C (b)

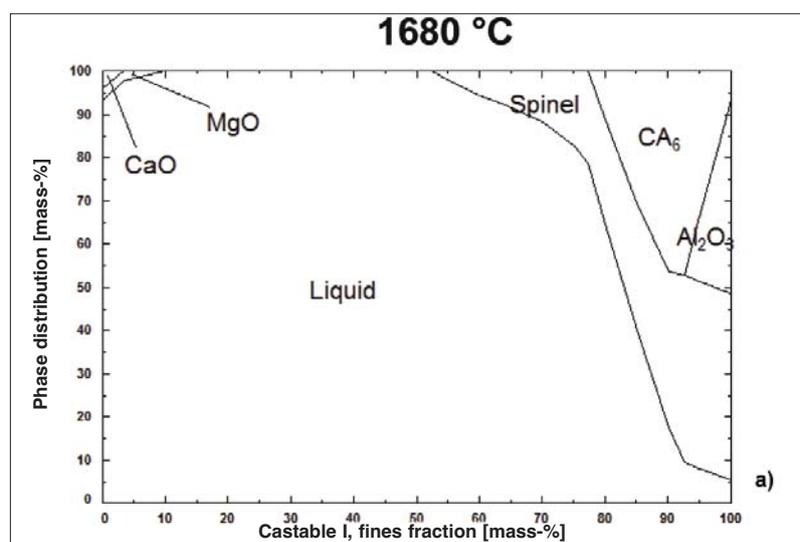


Fig. 4 Equilibrium between fines of castable I and slag S2 at 1680 °C (a)

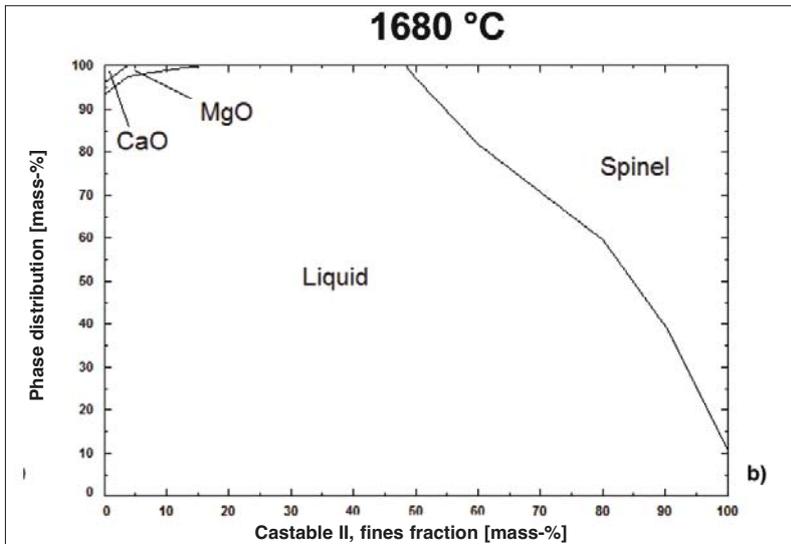


Fig. 5 Equilibrium between fines of castable II and slag S2 at 1680 °C (b)

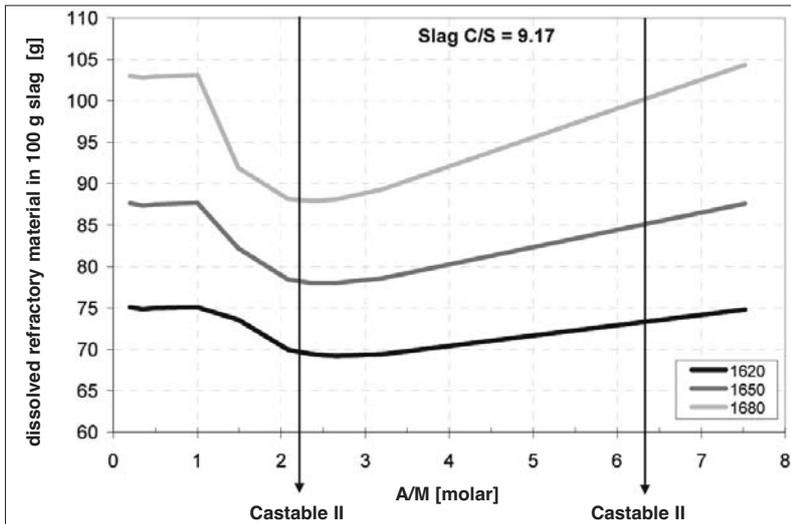


Fig. 6 Dissolved refractory material in 100g slag in dependence of A/M ratios for C/S = 9,17

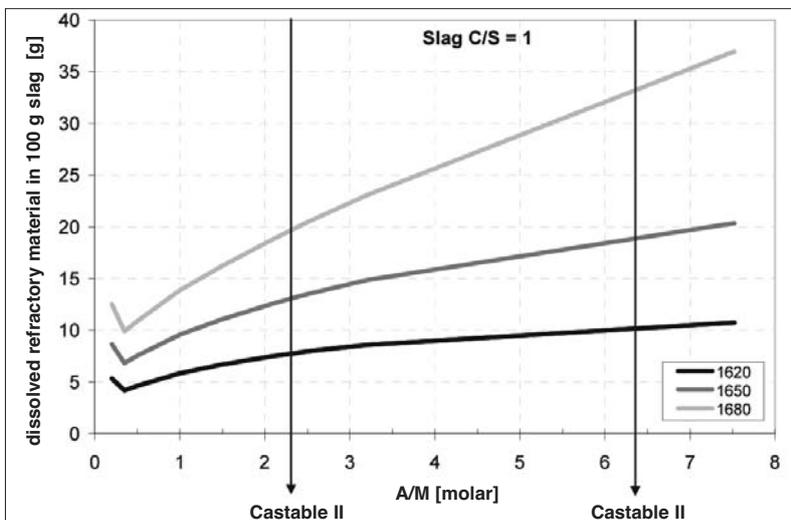


Fig. 7 Dissolved refractory material in 100 g slag in dependence of A/M ratios for C/S = 1

ly at the hot phase calciumaluminate CA and spinel MA, which are both embedded in a predominantly gehlenite matrix, were detected. The transition zone delivered calciumaluminate ($C_{12}A_7$) together with calciumaluminate ferrite and spinel solid solutions. At about 15 mm, C_2S appears for the first time. The amount of C_2S increases in greater distances from the hot face.

Fig. 11 illustrates a spot app. 43 mm from the hot face. The results are similar to the solution of the mass balance equations displayed in Fig. 10. Although the microstructure appears less corroded, still considerable amounts of minor phases are present. The amount of C_2S has increased and the amount of calciumaluminate ferrites has decreased compared to the former investigated spots. At this distance to the hot face small amounts of C_3MS_2 appear for the first time, indicating the beginning of a change in the brick's C/S ratio.

The results of the chemical microanalysis using a quantitative EDS are shown in Fig. 12. All main oxides were plotted in dependence of the distance from the hot face. On the right hand side of the diagram (100 mm) the nominal composition of the virgin brick is depicted. The first app. 10 mm represent the adherent slag layer followed by the infiltrated brick. The first few centimetres of the residual brick are characterised by an increase of Al_2O_3 and CaO. Between 20 to 40 mm the C/S ratio in the residual brick increases. In greater distances from the hot face the C/S ratio is decreasing again. This was also proven mineralogically by the appearance of C_3MS_2 as a second silicatic minor phase.

Fig. 13 shows a SEM image of sample B. The investigated spot is located app. 10 mm from the hot face. Also in this case high amounts of a spinel solid solution next to calciumaluminate ferrite were detected. C_2S was not found in this area.

Fig. 14 displays a spot app. 30 mm from the hot face. Like in sample A, C_2S was detected in greater distances from the hot face. Compared to Fig. 9 the amount of calciumaluminate ferrites was smaller and the amount of the silicatic minor phase C_2S increased. Besides, amounts of calciumaluminate ($C_{12}A_7$) were found. It was shown that even in greater distances especially the chromite precipitates are still severely degraded.

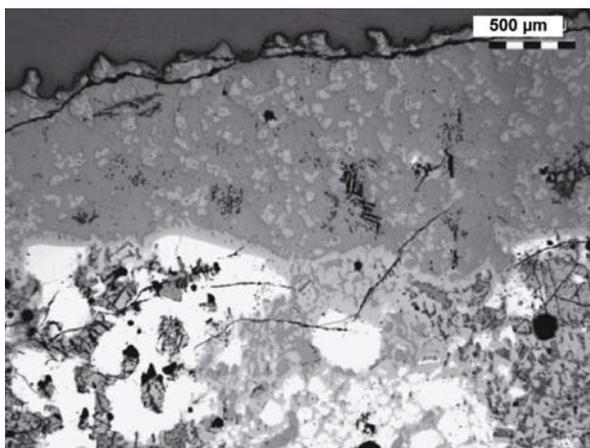


Fig. 8 Light microscopic overview of sample A, directly at the hot face

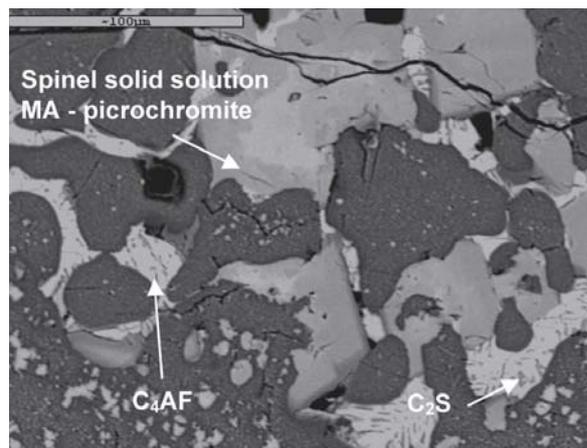


Fig. 9 SEM image of sample A; spot app. 14 mm from the hot face

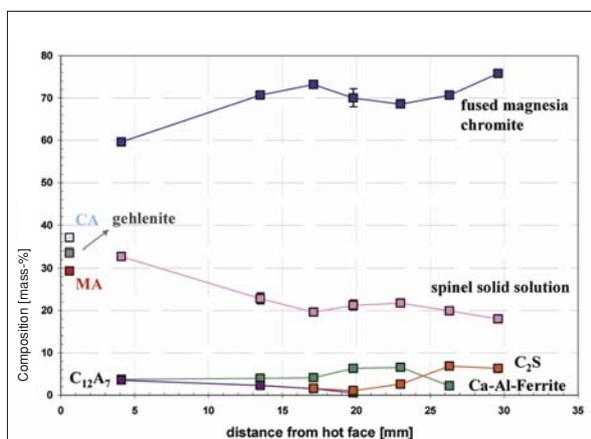


Fig. 10 Distribution of brick composition for the first 30 mm from the hot face

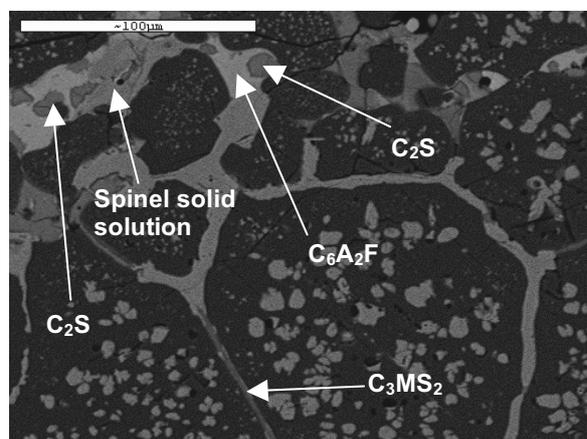


Fig. 11 SEM image of sample A; spot app. 43 mm from the hot face

3.4 Thermochemical assessment for the magnesia chromite samples

Supplementary investigations comprised a thermal simulation using the software DIANA [4]. The thermal simulation delivered the necessary information for the subsequent thermochemical calculations using the software package FactSage [5]. Those calculations included the determination of the amount of liquid formed in dependence from the distance to the hot face. The results of the calculation are shown in Fig. 15. The abscissa represents the distance from the hot face in mm and the two ordinates show the amount of liquid formed, relating to 100 g refractory material and the temperature of the samples in dependence of the distance from the hot face, respectively. A considerable amount of liquid phase formation during service was

calculated for sample B up to distances of app. 50 mm.

Within sample A there exists a smaller temperature gradient and therefore liquid phase formation was calculated till the cold end. But even for sample A at about 50 mm a considerable decrease of the amount of liquid phase formed was calculated. The results of the calculations agree well with the microscopical and SEM investigations, which confirm the formation of liquid phase.

4 Conclusion

4.1 Alumina spinel castables

It was shown that spinel is primarily responsible for the corrosion resistance of the examined castables. Castables with higher amounts of spinel in the fines are supposed to show a better slag resistance. Thermochemical calculations revealed that at lower temperatures the formation of calciumalu-

minate layers has a positive effect on the corrosion resistance, as these layers inhibit the direct dissolution of Al_2O_3 in the slag. Under service conditions the flow velocity of the slag relatively to the lining has to be considered. Indirect dissolution of Al_2O_3 can only be expected if the velocity of the slag is relatively low. For a more intense slag movement the dissolution rate of the reaction products will increase. If it is higher than the rate of reaction to CA_6 and CA_2 , respectively, direct dissolution of Al_2O_3 may be expected.

Additionally thermochemical calculations concerning a comparison of the dissolved refractory material in slags with different C/S ratios revealed, that slags with higher basicities show a more aggressive behaviour and that lower A/M ratios in the fines, i.e. higher spinel contents, have a positive effect on the solubility.

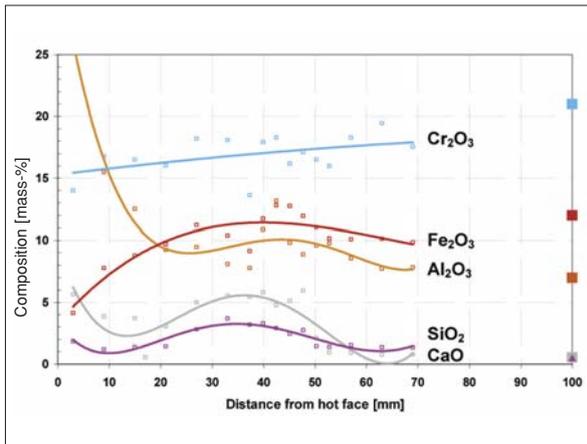


Fig. 12 Chemical profile of sample A in dependence of the distance from the hot face

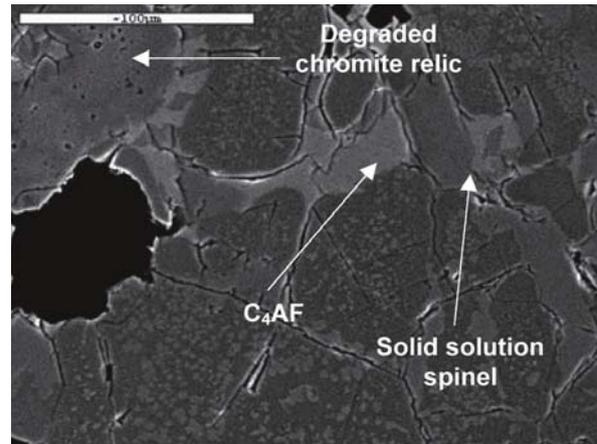


Fig. 13 SEM image of sample B; spot app. 10 mm from the hot face

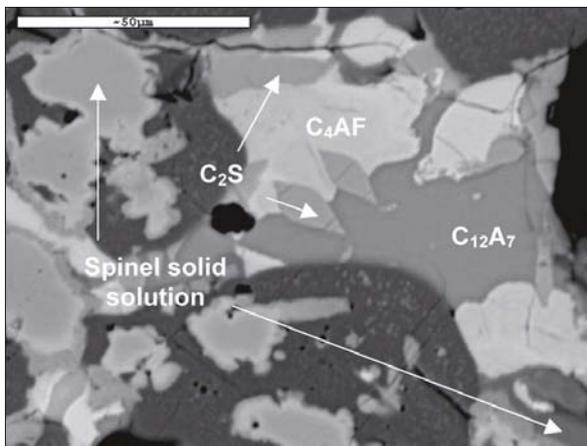


Fig. 14 SEM image of sample B; spot app. 30 mm from the hot face

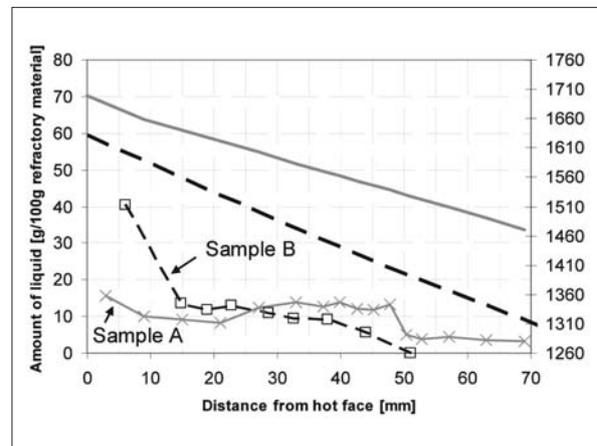


Fig. 15 Amount of liquid formed in dependence of the distance from the hot face

4.2 Magnesia chromite refractories

Two post mortem samples of a magnesia chromite brick – one from a rotary slagging test (sample A) and one directly from a RH-degasser (sample B) – have been investigated. Both samples were in contact with a highly basic acid resistant steel slag.

The investigations comprised mineralogical, thermal and thermochemical methods. The application of chemical profiles together with the data from a thermal simulation enabled the investigation of the local equilibrium conditions in the samples using the software package FactSage.

The combination of the mentioned methods allowed a characterisation of the corrosion processes occurring during service. Near the hot face in both cases the reaction products

were mainly spinel solid solutions between picrochromite and spinel MA. Other minor phases were – in dependence of the distance from the hot face – calciumaluminates (near the hot face) and calciumaluminat ferrites (even in greater distances from the hot face), as well as C_2S and C_3MS_2 . It was shown, that within the samples in both cases there exist areas of a higher C/S ratio, followed by a decrease at a depth of app. 50 mm.

Moreover in both samples severe chromite corrosion was detected. The investigation revealed that the infiltration of CaO , Al_2O_3 and partly SiO_2 especially near the hot face led to a considerable change in the brick's microstructure. This formation of low melting minor phases is primarily responsible for an accelerated wear by erosion.

Moreover it was proven, that the investigation from a rotary slagging test delivered comprehensible results compared with the sample from a RH degasser.

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