Corrosion Mechanism of Commercial MgO–C Refractories in Contact with Different Gas Atmospheres

Sune JANSSON,¹⁾ Voicu BRABIE²⁾ and Pär JÖNSSON³⁾

1) Arvika Gjuteri AB, SE-671 82 Arvika, Sweden. E-mail: sune.jansson@arvikagjuteri.se

2) Dalarna University, SE-781 88 Borlänge, Sweden. E-mail: vbr@du.se

3) Division of Applied Process Metallurgy, Royal Institute of Technology, SE-100 44 Stockholm, Sweden. E-mail: par@mse.kth.se

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Corrosion of MgO–C refractories in different gas atmospheres consisting of air, Ar, CO or Ar/CO was studied in laboratory experiments. In total, 103 experiments were carried out in the temperature range 1 173 to 1 773 K and for holding times between 2 to 120 min. The reaction rate of the MgO–C material was determined from measurements of the weight loss of the samples. The results showed that the refractory weight loss increased with an increased temperature or an increased holding time. The thermodynamic conditions and the experimental results showed that magnesium gas and carbon monoxide gas should form during ladle refining of steel when the refractory material consists of MgO–C. It was suggested that the reaction rate is directly dependent on the oxygen potential in the ambient atmosphere.

KEY WORDS: MgO–C refractory; oxidation-reduction; gas atmosphere; corrosion rate; corrosion mechanism.

1. Introduction

Carbon bonded magnesia (MgO–C) refractory materials are used in the linings of ladles when refining steel. They inhibit slag penetration into the brick structure, as a result of the low wettability of graphite by slag. In addition, they inhibit the brick from thermo-mechanically spalling (surface splitting of the lining) due to graphite's high thermal conductivity and low thermal expansion. Although graphite has a high chemical stability when it is in contact with a molten slag, it is easily oxidized by iron oxide in the slag, ambient gas and MgO (MgO–C reaction). The gas-phase oxidation is caused by oxygen and carbon dioxide in the ambient atmosphere reacting with the carbon in the refractory. This type of oxidation is significant during the heating of ladles as well as the transportation of ladles. However, several studies have shown that the formation of a slag layer on the brick surface will decrease the decarburization tendency.^{1–4)}

In MgO–C brick, carbon is also oxidized by magnesia according to the following reaction:

Equation (1) can be obtained by combining the following two reactions:

The free energy changes for Eqs. (1)–(3) in the temperature range 298–2 000 K can be calculated as follows using standard reference tables⁵⁾:

$$\Delta G_1 = -615\,600 + 1\,118.23T - RT \ln P_{\text{Mg}} - RT \ln P_{\text{CO}} \dots\dots (4)$$

$$\Delta G_2 = -730\,000 + 204T + RT \ln \frac{1}{P_{\text{Mg}} \cdot P_{\text{O}_2}^{1/2}} \dots\dots (5)$$

$$\Delta G_3 = -114\,400 - 85.77T + RT \ln \frac{P_{\text{CO}}}{P_{\text{O}_2}^{1/2}} \dots\dots\dots (6)$$

where P_{Mg} is the partial pressure of Mg, P_{O_2} is the partial pressure of O_2 and P_{CO} is the partial pressure of CO.

On the basis of the thermodynamic arguments, the rate of the internal oxide–carbon reactions would be expected to increase with increasing temperature and to decrease at a given temperature with an increase in either P_{Mg} or P_{CO} in the ambient atmosphere.¹⁾ The influence of the temperature and the partial pressure of Mg(g) and CO(g) on reaction (1) is also illustrated in **Fig. 1**. Magnesium is characterized by a high affinity to oxygen and a very stable oxide. At a temperature of 2 120 K and 1 atm, the MgO and CO lines cross each other, as illustrated in the figure. This means that magnesium oxide can be reduced by a reaction with carbon and form magnesium gas according to reaction (1).

Sunayama and Kawahara⁶⁾ have studied decarburization of resin-bonded magnesia–carbon refractory in the temperature range from 1 473–1 673 K in $\text{N}_2\text{--O}_2$ and Ar--O_2 atmospheres. After kinetic analysis, it was suggested that the

Fig. 1. Equilibrium relation for magnesium and carbon monoxide.⁴⁾

Fig. 2. Effect of temperature on the oxidation rate in atmosphere with oxygen partial pressure of 3.7×10^2 Pa and 2.1×10^4 Pa.⁶⁾

overall oxidation process was controlled by the diffusion of oxygen through the decarburized layer. The confirmation of a dense layer formation on the surface of the sample was achieved by the observation of the cross section of the sample after the oxidation test. It is interesting to note that the authors observed an increase in the oxidation rate when the oxygen potential pressure changes from 3.7×10^2 Pa to 2.1×10^4 Pa, as illustrated in Fig. 2. Furthermore, they found that when the temperature reached 1673 K the oxidation rate became constant.

Komarek *et al.*⁷⁾ studied the reaction between magnesia and graphite in vacuum by measuring the amount of carbon monoxide formed during the reaction. They observed that the reaction was phase-boundary controlled. Furthermore, that a linear time law was obtained for all experiments. They considered that the reaction proceeds over the gas phase by dissociation of the oxide into atomic oxygen followed by the rate controlling step, desorption of CO from the graphite surface. Gulyanitzkii and Chizhikov⁸⁾ made similar experiments as Komarek *et al.*⁷⁾ by determining the corrosion by measuring the weight loss. They concluded that the rate controlling step was the gas phase reaction involving carbon oxides.

Fruehan *et al.*⁹⁾ studied the rate of reduction of MgO by carbon in Ar, He and CO atmospheres at 1748–1873 K. The amount of carbon remaining in the refractory was determined after cooling of the samples. In addition, the weight loss was determined for all samples. They noticed that the weight loss in general showed a linear behavior

Fig. 3. The rate of weight loss for an MgO-C sample in Ar and CO at 1823 K.⁹⁾

with time and that the reaction rates (determined using Eq. (1)) corresponded well with the weight loss. According to Fruehan *et al.*⁹⁾ the mass transfer of the dissolution of solid phase into gas phase can be calculated as follows:

$$\ln \left(1 - \frac{w_0 - w_t}{w_0} \right) = -k \cdot t \dots\dots\dots (7)$$

where w_0 is the weight of the sample before the test, w_t is the weight of the sample after time t .

Seiltveit²⁾ has also investigated the loss of weight of the refractory material in an inert gas atmosphere at temperatures greater than 1723 K. The results show that the loss of weight depends on the reaction between carbon and solid or liquid oxide phases, and the main components of the refractory material.

Leonard *et al.*¹⁾ performed laboratory experiments with carbon-bearing BOF refractory at temperatures between 1473 and 1873 K and in air, He and CO atmospheres. They found that the reaction rates increased with increased temperature and decreased with an increased p_{MgO} and/or p_{CO} at a constant temperature. Also, according to Leonard *et al.*¹⁾ in the interior of the sample reaction (1) proceeds to the right and Mg(g) diffuses towards the free surface of the sample encounters a much higher oxygen potential and it is oxidized to MgO which condenses as a dense layer. The reaction rate is reduced substantially. The process within the sample was no longer occurring in an open system. The reactions continue, but probably by counter diffusion of CO and oxygen across the dense layer.

In general, it can be concluded from previous research that an inert atmosphere is beneficial for decreasing the corrosion of carbon-bonded magnesia refractory. As illustrated in Fig. 3, the loss of weight occurs during a shorter time and with an increased rate than in CO atmosphere if the pressure is 1 atm.⁹⁾

In the present work, the focus is on the oxidation rate of commercial carbon-bonded magnesia refractory for different temperatures, holding times and atmospheres (air, Ar, CO or Ar/CO). In the first part of the paper, the experimental procedure is described. Thereafter, the experimental results are presented and discussed.

Table 1. Test parameters.

Temperatures, K	Holding time, minutes	Gas atmospheres
1173; 1373; 1573; 1773	2-120	Air; Argon; Carbon monoxide; Mix of Ar and CO (25/75; 50/50; 75/25)

Fig. 4. Experimental apparatus.

2. Experimental Work

The reaction between carbon-bonded magnesia refractory and gas atmospheres was studied using the experimental set-up shown in Fig. 4. An alumina tube is placed inside the furnace, through which the gas can be supplied during the experiments. A Pt-basket containing the refractory sample which is to be studied was placed in the alumina tube. The refractory test samples were cut from a commercial MgO-C brick with the following chemical composition: MgO=96.8 wt%; CaO=1.8 wt%; SiO₂=0.6 wt%; Fe₂O₃=0.3 wt% and carbon retained=5.5 wt%. The samples had a density of 3.1 g/cm³ and a porosity of 5%. The test samples had a diameter of 13 mm and a length of 20 mm.

Initially, the samples were preheated to 773 K before testing so that the volatile elements in the samples would not disturb the results. The preheating was carried out in an inert argon atmosphere.

When the furnace reached the desired temperature for the specific experiment, the samples were placed in the Pt-basket. The different holding times for the experiments were 2–120 min and the temperatures were 1 173–1 773 K. In addition, experiments were carried out using gas atmospheres consisting of air, Ar, CO or different mixtures of Ar and CO. The test parameters used in the experiments are summarized in Table 1.

During the tests, the gas being studied was flushed through the furnace at a rate of 2 L/min. The argon gas and the carbon monoxide gas were cleaned by letting the gas pass through a gas-cleaning system consisting of a column of silica gel, a column of magnesium per chlorate, a column of ascarite, and a column of magnesium chips at 773 K. The air was cleaned using a particle filter and a moisture trap.

After the experiments, the refractory samples were removed from the furnace. The weight of the samples was measured and the weight loss was determined as:

$$\Delta W = W_0 - W_t \dots \dots \dots (8)$$

where W_0 is the weight before the tests and W_t is the weight

after time t . The estimated error of the balance was ± 1 mg.

Cross sections of the oxidized samples were examined by using an optical microscope (Leica Quantimet 500) and a Scanning Electron Microscope, SEM (JEOL JSM 820) with an Energy Dispersive X-ray Spectrometer, EDS (Link ISIS 300).

3. Results and Discussion

After the experiments, the influence of the gas atmosphere and temperature on the weight loss of the commercial MgO-C samples was studied. In addition, the influence of oxide layers, formed on the refractory surface, on the reaction rate of Eq. (1) was studied.

3.1. The Influence of the Gas Atmosphere on the Weight Loss

Table 2 and Fig. 5 show the weight loss as a function of time for MgO-C samples at 1 573 K and different ambient atmospheres. It is observed that in air the samples lose weight as a result of the oxidation reaction of carbon with oxygen according to reaction (3). The curves of weight loss as a function of time show a parabolic dependence.

Samples tested in argon and CO atmospheres reach a linear rate of weight loss in 45 and 30 min respectively. The weight loss in air at 1 573 K is 6 times higher than that for samples in Ar and 10.5 times than that in CO. The experimental results and microscopic observations indicate that the magnesia reduction by carbon is dominant for the test conditions when the atmosphere is characterized by a low oxygen potential.

The loss of weight in Ar at 1 773 K is 1.5 times higher than for the CO samples, while Fruehan *et al.*⁹⁾ reported a difference between Ar and CO samples of 5 times. The difference between the values in the present study and their value depends on the experimental conditions and the materials investigated. Fruehan used samples with lower carbon contents (2.55% C) and a dimension of 15×15×40 mm. The present samples have a carbon content of 5.5% and a geometry corresponding to a 13 mm diameter and a 20 mm length.

The examinations in an optical microscope showed that the samples were decarburized during the tests. The decarburized zone for the tests at 1 573 K lasting for 30 min were measured to be 0.26 mm for the CO experiment, 0.64 mm for the argon experiment, and 3.07 mm for the air experiment, see Fig. 6. The boundary between the decarburized and undecarburized zones was quite clear, as seen in Fig. 6. It was difficult to estimate the decarburized zone for the experiments that were carried out at 1 373 K using Ar and CO, since the separation between the decarburized and undecarburized zone was indistinct. Thus, for these experiments no values are given in Table 2. The decarburized zone was measured using an optical microscope equipped with image distance analysis. The experimental error was estimated to be ± 0.02 mm. Figure 7 shows the decarburization zones

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Test Nr	Time min	Temp K	Air %	CO %	Air %	CO %	Decarburized zone				Test Nr	Time min	Temp K	Air %	CO %	Air %	CO %	Δ w mg	dw/dt mg/sec	k mg/sec	Decarburized zone mm
							Δ w mg	dw/dt mg/sec	k mg/sec	mm											
1	2	1773	100	0	66	6.90 x 10 ⁻⁵	0.550	0.29	53	60	1573	50	50	77	0.021	2.69 x 10 ⁻⁶	0.50				
2	5	1773	100	0	69	2.89 x 10 ⁻⁵	0.230	0.32	54	90	1573	50	50	80	0.015	1.86 x 10 ⁻⁶	0.68				
3	10	1773	100	0	77	1.61 x 10 ⁻⁵	0.128	0.40	55	120	1573	50	0	93	0.013	1.62 x 10 ⁻⁶	0.80				
4	15	1773	100	0	88	1.23 x 10 ⁻⁵	0.098	0.52	56	2	1573	0	100	23	0.192	2.40 x 10 ⁻⁵	0.08				
5	20	1773	100	0	90	9.43 x 10 ⁻⁶	0.075	0.65	57	5	1573	0	100	37	0.123	1.55 x 10 ⁻⁵	0.11				
6	30	1773	100	0	93	6.50 x 10 ⁻⁶	0.052	0.78	58	15	1573	0	100	48	0.053	6.69 x 10 ⁻⁶	0.19				
7	45	1773	100	0	104	4.85 x 10 ⁻⁶	0.039	0.87	59	30	1573	0	100	56	0.031	3.90 x 10 ⁻⁶	0.26				
8	60	1773	100	0	108	3.78 x 10 ⁻⁶	0.030	0.91	60	60	1573	0	100	63	0.018	2.20 x 10 ⁻⁶	0.33				
9	90	1773	100	0	120	2.80 x 10 ⁻⁶	0.022	1.09	61	90	1573	0	100	76	0.014	1.77 x 10 ⁻⁶	0.46				
10	105	1773	100	0	119	2.38 x 10 ⁻⁶	0.019	1.17	62	120	1573	0	100	81	0.011	1.41 x 10 ⁻⁶	0.58				
11	120	1773	100	0	121	2.12 x 10 ⁻⁶	0.017	1.36	63	2	1573	0	100	133	1.108	1.40 x 10 ⁻⁴	0.59				
12	5	1773	75	25	70	2.93 x 10 ⁻⁵	0.233	0.26	64	5	1573	0	100	195	0.650	8.23 x 10 ⁻⁵	0.83				
13	15	1773	75	25	80	0.089	1.12 x 10 ⁻⁵	0.43	65	15	1573	0	100	321	0.357	4.55 x 10 ⁻⁵	1.98				
14	30	1773	75	25	82	0.046	5.72 x 10 ⁻⁶	0.67	66	30	1573	0	100	467	0.259	3.34 x 10 ⁻⁵	3.07				
15	90	1773	75	25	96	0.018	2.24 x 10 ⁻⁶	0.99	67	60	1573	0	100	513	0.143	1.84 x 10 ⁻⁵	completely				
16	2	1773	50	50	50	0.417	5.22 x 10 ⁻⁵	0.15	68	90	1573	0	100	606	0.112	1.46 x 10 ⁻⁵	completely				
17	5	1773	50	50	53	0.177	2.22 x 10 ⁻⁵	0.19	69	120	1573	0	100	630	0.088	1.14 x 10 ⁻⁵	completely				
18	15	1773	50	50	66	0.073	9.20 x 10 ⁻⁶	0.31	70	2	1373	100	0	12	0.100	1.25 x 10 ⁻⁵	-				
19	30	1773	50	50	78	0.043	5.44 x 10 ⁻⁶	0.47	71	5	1373	100	0	43	0.143	1.80 x 10 ⁻⁵	-				
20	60	1773	50	50	81	0.023	2.83 x 10 ⁻⁶	0.69	72	15	1373	100	0	46	0.051	6.41 x 10 ⁻⁶	-				
21	90	1773	50	50	89	0.016	2.07 x 10 ⁻⁶	0.77	73	30	1373	100	0	75	0.042	5.23 x 10 ⁻⁶	-				
22	120	1773	50	50	99	0.014	1.73 x 10 ⁻⁶	0.84	74	60	1373	100	0	87	0.024	3.04 x 10 ⁻⁶	-				
23	5	1773	25	75	49	0.163	2.05 x 10 ⁻⁵	0.17	75	90	1373	100	0	99	0.018	2.31 x 10 ⁻⁶	-				
24	15	1773	25	75	61	0.068	8.50 x 10 ⁻⁶	0.28	76	120	1373	100	0	107	0.015	1.87 x 10 ⁻⁶	-				
25	30	1773	25	75	64	0.036	4.46 x 10 ⁻⁶	0.41	77	2	1373	50	50	8	0.067	8.34 x 10 ⁻⁶	-				
26	60	1773	25	75	76	0.021	2.65 x 10 ⁻⁶	0.58	78	5	1373	50	0	27	0.090	1.13 x 10 ⁻⁵	-				
27	90	1773	25	75	82	0.015	1.91 x 10 ⁻⁶	0.66	79	15	1373	50	0	33	0.037	4.59 x 10 ⁻⁶	-				
28	120	1773	25	75	94	0.013	1.64 x 10 ⁻⁶	0.73	80	30	1373	50	0	52	0.029	3.62 x 10 ⁻⁶	-				
29	2	1773	0	100	41	0.342	4.28 x 10 ⁻⁵	0.12	81	60	1373	50	0	74	0.021	2.58 x 10 ⁻⁶	-				
30	5	1773	0	100	44	0.147	1.84 x 10 ⁻⁵	0.15	82	90	1373	50	0	76	0.014	1.77 x 10 ⁻⁶	-				
31	15	1773	0	100	56	0.062	7.81 x 10 ⁻⁶	0.24	83	120	1373	50	0	87	0.012	1.52 x 10 ⁻⁶	-				
32	30	1773	0	100	62	0.034	4.32 x 10 ⁻⁶	0.32	84	2	1373	0	100	7	0.058	7.29 x 10 ⁻⁶	-				
33	60	1773	0	100	68	0.019	2.37 x 10 ⁻⁶	0.40	85	5	1373	0	100	23	0.077	9.60 x 10 ⁻⁶	-				
34	90	1773	0	100	85	0.016	1.98 x 10 ⁻⁶	0.52	86	15	1373	0	100	28	0.031	3.90 x 10 ⁻⁶	-				
35	105	1773	0	100	88	0.014	1.76 x 10 ⁻⁶	0.58	87	30	1373	0	100	44	0.024	3.06 x 10 ⁻⁶	-				
36	120	1773	0	100	87	0.012	1.52 x 10 ⁻⁶	0.60	88	60	1373	0	100	56	0.016	1.95 x 10 ⁻⁶	-				
37	2	1773	0	100	301	2.508	3.20 x 10 ⁻⁴	2.89	89	90	1373	0	100	69	0.013	1.60 x 10 ⁻⁶	-				
38	5	1773	0	100	321	1.070	1.37 x 10 ⁻⁴	3.21	90	120	1373	0	100	78	0.011	1.36 x 10 ⁻⁶	-				
39	15	1773	0	100	448	0.498	6.40 x 10 ⁻⁵	completely	91	2	1373	0	100	41	0.342	4.28 x 10 ⁻⁵	0.52				
40	30	1773	0	100	550	0.306	3.96 x 10 ⁻⁵	completely	92	5	1373	0	100	168	0.560	7.07 x 10 ⁻⁵	0.77				
41	60	1773	0	100	621	0.173	2.24 x 10 ⁻⁵	completely	93	15	1373	0	100	236	0.262	3.33 x 10 ⁻⁵	1.54				
42	2	1573	100	0	38	0.317	3.97 x 10 ⁻⁵	0.14	94	30	1373	0	100	382	0.212	2.72 x 10 ⁻⁵	2.24				
43	5	1573	100	0	58	0.193	2.43 x 10 ⁻⁵	0.21	95	60	1373	0	100	446	0.124	1.59 x 10 ⁻⁵	2.86				
44	15	1573	100	0	78	0.087	1.09 x 10 ⁻⁵	0.46	96	90	1373	0	100	479	0.089	1.14 x 10 ⁻⁵	3.28				
45	30	1573	100	0	85	0.047	5.93 x 10 ⁻⁶	0.64	97	120	1373	0	100	512	0.071	9.19 x 10 ⁻⁶	completely				
46	60	1573	100	0	93	0.026	3.25 x 10 ⁻⁶	0.75	98	5	1173	0	100	108	0.360	4.53 x 10 ⁻⁵	0.54				
47	90	1573	100	0	106	0.020	2.47 x 10 ⁻⁶	1.03	99	15	1173	0	100	207	0.230	2.91 x 10 ⁻⁵	0.79				
48	120	1573	100	0	112	0.016	1.96 x 10 ⁻⁶	1.25	100	30	1173	0	100	325	0.181	2.30 x 10 ⁻⁵	2.02				
49	2	1573	50	50	25	0.208	2.61 x 10 ⁻⁵	0.10	101	60	1173	0	100	410	0.114	1.46 x 10 ⁻⁵	2.33				
50	5	1573	50	50	43	0.143	1.80 x 10 ⁻⁵	0.14	102	90	1173	0	100	448	0.083	1.07 x 10 ⁻⁵	2.91				
51	15	1573	50	50	58	0.064	8.08 x 10 ⁻⁶	0.21	103	120	1173	0	100	456	0.063	8.15 x 10 ⁻⁶	3.02				
52	30	1573	50	50	73	0.041	5.09 x 10 ⁻⁶	0.41													

for different reaction times and atmospheres at 1573 K. It was observed that the sample is completely decarburized after 60 min in an air atmosphere but only 10% of the sample is decarburized in a CO atmosphere.

3.2. The Influence of Temperature on the Weight Loss

Figure 8 shows the weight loss as a function of temperature and gas atmospheres for experiments, which were conducted for 30 min. The weight loss is seen to increase in a linear manner with an increasing temperature. It is also seen that the weight loss for the Ar, Ar+CO and CO experiments is considerably lower than that for the air experiments. The reaction rate constant can be calculated using the Arrhenius equation¹⁰⁾:

$$k = A \cdot \exp(-E_a/RT) \dots \dots \dots (9)$$

where A is a pre-exponential term (frequency factor), E_a is the activation energy (J/mol), R is the gas constant

Fig. 5. The weight loss as a function of time for different atmospheres at 1573 K.

Fig. 6. Pictures of cross-section for different samples at 1573 K during 30 min, a) CO, b) Ar and c) air. The scales in the pictures indicates 1 mm between the lines.

Fig. 7. The effect of holding time on the decarburised zone for different atmospheres at 1573 K.

($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature (K). By taking the natural logarithm of both sides of this equation, the following equation is obtained:

$$\ln k = -\frac{E_a}{RT} + \ln A \dots \dots \dots (10)$$

In Fig. 9, the logarithm of the rate constant is plotted *versus* $1/T$ in a so called “Arrhenius plot”.¹⁰⁾ The figure is based on the data in Table 2. The activation energy was determined from the slopes of the lines in the figure. The results were the following: 101.9 kJ/mol for the tests in air, 87.3 kJ/mol for the tests in argon, 93.3 kJ/mol for the tests in a 50%Ar+50%CO atmosphere and 90.4 kJ/mol for the tests in CO. These activation energy values are higher than those of 38–37 kJ/mol reported by Sunayama and Kawahara.⁶⁾ However, they are lower than those reported by Komarek *et al.*⁷⁾ (249 kJ/mol) and Fruehan *et al.*⁹⁾ (657 kJ/mol). In general, it seems that the large variation of the activation energy data for different experiments depends on the experimental conditions and materials investigated. Komarek⁷⁾ studied the reaction between oxides and graphite in a vacuum furnace. They used oxide powder thoroughly mixed in the graphite crucible, covered with a layer of graphite powder. In the present study, samples are cut from an industrial brick. Thus, it is assumed that they are not homogeneous as the samples used in earlier laboratory studies by, for example, Komarek *et al.*⁷⁾

3.3. The Influence of Oxide Layers on the Reaction Rate

The examination of the samples using SEM in combination with EDS showed that a MgO layer had been formed at the surface of the samples. The layer is considered to be formed by reactions (1) and (2). More specifically, magne-

Fig. 8. Weight loss as a function of temperature for different gas atmospheres at 30 min.

sium vapor formed by the reaction (1) diffuses through the pores in the decarburized layer toward the surface and reacts with oxygen from the atmosphere and forms MgO(s) according to reaction (2). After formation of the initial scale of MgO, the rate of reaction is controlled by diffusion of magnesium and CO through the MgO scale resulting in the parabolic oxidation rate. The dense layer formation will decrease the decarburization of the MgO–C lining by retarding the diffusion of carbon and oxygen across the layer.

It is interesting to observe that the decrease of the oxygen potential in the refractory pore atmosphere contributed to a decrease of the carbon oxidation (see Fig. 5 and Ref. 4)) and as a result the oxide layer formation decreased. When an oxide layer has formed at the surface of the sam-

ples the diffusion of reacting elements through the layer decreases and then the carbon oxidation and MgO reduction decreases. The reduction in the reaction rate was easier to observe in the tests with air atmosphere than in the other tests.

According to Fruehan *et al.*⁹⁾ the rates shown in Figs. 3 and 5 are slower in the CO atmosphere compared to those in the CO+Ar or Ar atmospheres, as the back reaction (see reaction (1)) for oxidation of magnesium by carbon monoxide becomes significant. Thus, the reaction is probably controlled by the oxidation of carbon.

Komarek *et al.*⁷⁾ considered that the most probably reaction proceeds by dissociation of MgO. However, Gulyanitzkii *et al.*⁸⁾ concluded that the reduction is primarily due to intermediate reactions in the gas phase involving carbon oxides and not due to the reduction of MgO vapor or dissociation of MgO into the Mg and O and subsequent reaction with C.

The porosity of the MgO layer was much less than the original MgO grains. The chemical composition determination showed that the MgO layer consisted of approximately the same elements as the original MgO grains (~70 wt% Mg, 28 wt% O, 1 wt% Si and 1 wt% Ca). EDS mapping images of the examined layers are shown in Figs. 10 and 11. Figure 10 shows that the original pores that initially were impregnated with carbon have now been decarburized. The

Fig. 9. The temperature's effect on the reaction rate constant for the reduction of MgO by C at 2 min.

Fig. 10. X-ray mapping images of cross-section of a sample that has been in argon atmosphere at 1773 K for 105 min.

Fig. 11. X-ray mapping images of cross-section of a sample that has been in argon atmosphere at 1773 K for 105 min.

amount of carbon remaining in the pores is small. Instead, calcium, silicon and aluminium were found in the pores and they probably derive from impurities in the bulk. From the mapping images shown in Fig. 11 it is clear that the MgO layer on the surface of the sample has less porosity than the original MgO grains, which can be observed at the side of the MgO layer. It is not clear whether the MgO layer has recently been formed as a secondary layer or if it is magnesium gas that has been reoxidised in pores and cracks and in that way formed a less porous layer. The MgO layer has also been formed between the original MgO grains and thereby filled up cavities present between the grains. The MgO layer had a thickness of 50–100 μm and was found around all the test samples.

A CaO layer was also found on the outside of the MgO layer. Its thickness was 5–10 μm and it was also present around all the test samples. This layer has probably been formed from calcium gas originating from impurities inside the refractory material and which has been oxidised at the surface. Both the MgO and CaO layers make the reaction rate inside the refractory material decrease, since the reaction's products must diffuse through the layers in order for a further reaction to proceed. The formation of these layers is most likely dependent on the temperature, because they were not observed at the lower experimental temperatures.

In the CaO layer, small amounts of aluminium and silicon were found. They probably have their origin from impurities inside the refractory material. The SEM/EDS examinations of the cross-sections of the samples also showed some metallic phases inside the refractory material. The chemical composition of these metallic phases was analysed using dot analysis. A working distance of 25 mm and an acceleration voltage of 20 kV were used in all EDS determinations. In addition, the SEM/EDS was calibrated using a cobalt standard. The metallic phases were spread out over the whole cross-section of the sample and they varied in size. The metallic phase could be as little as one single grain between the original MgO grains or as a phase that has filled out a crack in the original MgO grain. **Figure 12** shows a SEM image of a metallic phase that has filled out cracks in an original MgO grain. The analysis spectrum from the EDS is shown in **Fig. 13**. The metallic phase seems to consist of zirconium, calcium and silicon. The other elements that were determined were ignored, since they were only found in very small quantities and probably had their origin from the surrounding matrix. Several dot analyses were carried out and the mean value showed that the metallic phase consists of 70 wt% zirconium, 28.5 wt% calcium and 1.5 wt% silicon. The zirconium, calcium and silicon come from impurities in the refractory material. Other metallic phases that were found were pure iron and aluminium and a mixture of some of these metals. Most of them probably come from oxides that have their origin in impurities in the refractory material that have been reduced by carbon to metallic phases.

The metallic phase of aluminium can react with carbon monoxide and form aluminium oxide and carbon. Yamaguchi *et al.*¹¹⁾ described how aluminum can work as an antioxidant to suppress carbon oxidation as in the following reaction:

Fig. 12. SEM backscatter image in the metallic phase that has been in air atmosphere at 1 573 K during 15 min.

Fig. 13. EDS analysis spectrum for a metallic phase that has been in air atmosphere at 1 573 K for 15 min.

Al reacts with $\text{CO}_{(\text{g})}$ to form $\text{Al}_2\text{O}_{3(\text{s})}$ and $\text{C}_{(\text{s})}$ and compensates the decrease of carbon. At the same time, the formed Al_2O_3 plays a role in the densification and the formation of a protective layer near the surface of the refractories, which suppresses the diffusion of oxygen into the refractories.

4. Conclusions

The rates of reactions of commercial MgO–C refractories in different atmospheres consisting of air, Ar, CO or Ar/CO were studied using laboratory experiments. In total, 103 experiments were carried out at temperatures ranging from 1 173 to 1 773 K and at holding times ranging from 2 to 120 min. The reaction rate of the MgO–C material was determined by measuring the weight loss of the samples. The internal oxidation-reduction is assumed to increase with increasing temperature and to decrease at a certain temperature with either an increase in the partial pressure of magnesium or carbon monoxide. In the beginning of the oxidation-reduction, the reaction rate is controlled by the diffusion of reactants through the gas boundary layer near the surface of the samples. Furthermore, when an oxide layer is formed, the diffusion through the oxide layer determines the reaction rate.

The primary findings of the investigations are summarized below.

(1) The weight loss in an air atmosphere was up to 6 times greater than in an Ar atmosphere and 10.5 times greater than in a CO atmosphere. Other investigations have

shown a greater difference in weight loss between Ar and CO than the present results. This is due to differences in the experimental conditions and materials investigated.

(2) The results show that the weight loss from the samples principally comes from the loss of carbon and oxygen.

(3) The samples are completely decarburized after a 60 min holding time in an air atmosphere, but only 10% is decarburized after a 60 min holding time in a CO atmosphere.

(4) The activation energy was found to be 87–101 kJ/mol. These data are lower than those reported by Fruehan *et al.* (675 kJ/mol) and Komarek *et al.* (249 kJ/mol), but slightly higher than those reported by Sunayama *et al.* (37–38 kJ/mol).

(5) If the diffusing rate decreases in the system, the reaction rate decreases consequentially.

(6) The carbon loss and the reduction of oxides that occurs as a result of the internal reactions at higher temperatures lead to the formation of cavities between the refractory grains and the remaining carbon structure. These cavities imply that the total porosity in the refractory increases, which can lead to a reduction in the mechanical strength and, in combination with other mechanisms, lead to disintegration of the refractory material. Overall, the results indicate that decarburization and deterioration of the refractory materials occur during the heating up of the ladles in the steelmaking processes.

(7) The layer that forms on the surface of the samples consists of oxygen, magnesium, aluminum, silicon and calcium.

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