

Properties and corrosion of alumina-magnesia-carbon refractories

A post-firing expansion of alumina-magnesia-carbon (AMC) refractories can close joints and densify the brick structure. Many positive reports on their use in torpedo and steel ladles have been reported. A slag layer on the refractory surface has been found to be the best protection for preventing carbon loss. Corrosion resistance of bauxite-based AMC refractories has been found to be poor in comparison to alumina-based refractories however, the combination of a MgO-C lining and a calcium-alumina slag results in the lowest corrosion.

Jürgen Pötschke, Gerald Routschka
DIFK Deutsches Institut für Feuerfest und Keramik GmbH

Alumina-magnesia-carbon (AMC) bricks are resin bonded and made from corundum or bauxite, magnesia and graphite. The magnesia and carbon contents are 5–35% and about 10%, respectively. If an AMC brick is heated, then spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$) forms and the resulting post-firing expansion can close joints and densify the brick structure. Many reports have demonstrated the positive results of AMC bricks in torpedo and steel ladles.

The current work characterises different grades of AMC bricks in the range of AC to MC and examines their oxidation and corrosion behaviour.

Materials and experiments

Table 1 gives a summary of the brick grades examined. All materials have been manufactured by the refractory industry using their raw materials. In order to study the formation of spinel, linear changes, development of open porosity and

No.	raw material	MgO* [%]	C[%]	As delivered	
				Bulk density g/cm ³	Open porosity %
1	sintered corundum	0	10	3.05	9.1
2	bauxite	5	10	2.88	11.9
3	bauxite	10	10	2.88	12.1
4	sintered corundum	5	10	3.02	8.1
5	sintered corundum	10	10	3.07	7.9
6	sintered corundum + Al	5	10	3.09	7.0
7	sintered corundum + Al	6	6	3.18	4.0
8	sintered corundum + Al	33	8	3.01	6.1
9	fused corundum	7.4	7.5	3.22	6.7
10	sintered corundum	29.4	10	3.21	3.1
11	fused magnesia	98	10	3.11	2.4
12	bauxite	14	7	3.15	3.3
13	bauxite	28	10	3.08	3.0
14	fused brown corundum + Al	28	10	3.18	4.0

● Table 1 Characteristics of tested bricks (* ignited material)

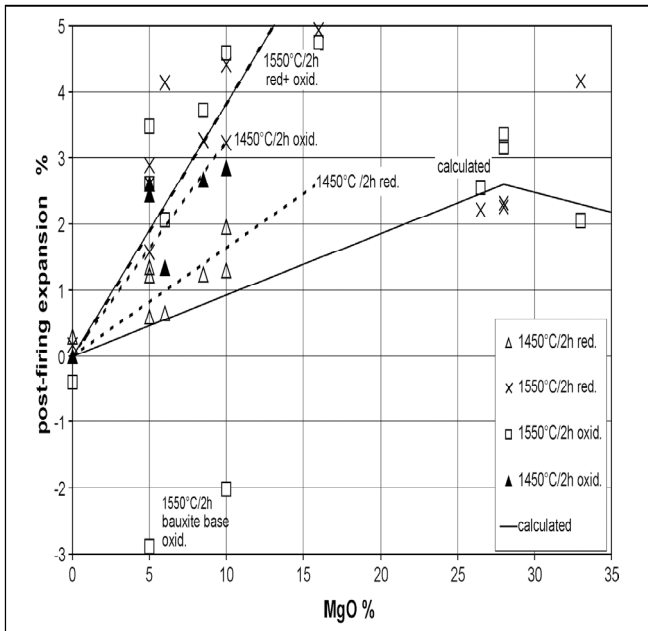
strength, cylindrical samples were drilled out of the bricks, coked at 1,000°C/5 h and subsequently fired at 1,250°C, 1,450°C and 1,550°C/2h, either under reducing conditions (embedded in coke) or under oxidising conditions (air) after complete burn-out of carbon at 1,100°C.

Properties

Formation of spinel The X-ray diffraction analysis of the fired samples showed no significant differences in the amount of spinel formed either under reducing or oxidising firing conditions. At 1,550°C/2h the formation of spinel is complete and the amount of spinel corresponded approximately with the theoretically expected value, or was slightly lower: 23% MgO + 77% Al_2O_3 . The normal composition of spinel is 28% MgO + 72% Al_2O_3 .

Post-firing expansion The post-firing expansion due to the formation of spinel begins at about 1,200°C and is completed at 1,550°C/2h. At 1,550°C similar expansions occur under both firing conditions, with the exception of the bauxite-based bricks with low MgO content – they show a remarkable shrinkage in oxidising atmosphere caused by formation of a high amount of melting phase (see Figure 1).

At 1,450°C/2h, the post-firing expansion of the carbon-containing material (embedded in coke) is



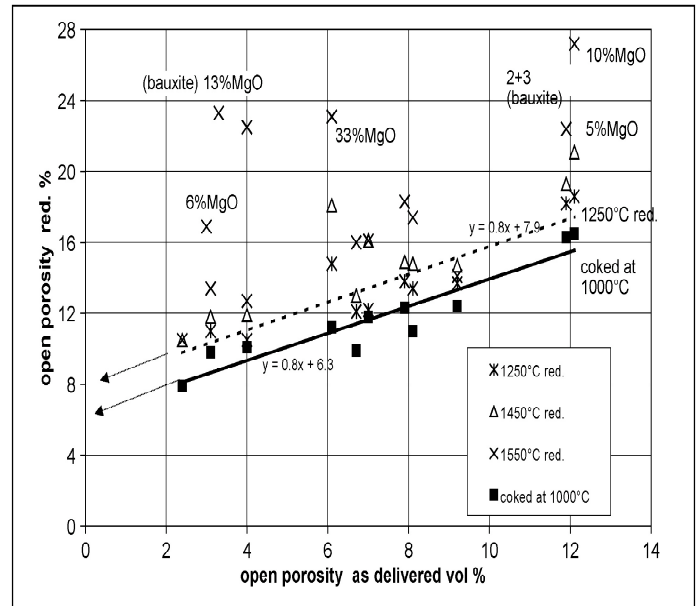
● Figure 1 Relationships between post-firing expansion and MgO content of the AMC bricks under different firing conditions

noticeably lower than in the carbon-free material (fired in air). This may be due to the more elastic behaviour of the carbon-containing brick structure. At higher firing temperatures, however, sintering embrittles the brick structure. In Figure 1, the line for the theoretical post-firing expansion by the formation of spinel is plotted for comparison. The brick type with an excess of Al₂O₃ with respect to spinel (less than 20% MgO) shows a much higher post-firing expansion than theoretically expected, otherwise the expansion of the brick type with an excess of MgO (above 28% MgO) corresponds with theory.

It can be deduced that in the first case the brick pore structure cannot take up the expansion and consequently cracks, and a separation of grains occurs. In bricks with an excess of MgO the expansion seems to be compensated by the better sinterability of the MgO compared to Al₂O₃.

Open porosity A correlation between open porosity of the brick as delivered and after coking and firing up to 1,250°C under reducing conditions was found (see Figure 2). At higher firing temperatures the scatter of porosity measurements may be due to the different post-firing expansion of the materials. Coking of the as-delivered bricks results in an increase in porosity of 6% at 1,000°C, and by about 8% at 1,250°C.

The burning out of 10% carbon raises porosity by about 15%. The porosity of the oxidised fired bricks at 1,250°C ranges between 24–30% and, at higher temperatures porosity, can reach 35%, depending on the post-firing expansion.



● Figure 2 Relationships between open porosity as delivered and after firing under reducing conditions

Development of strength In Figure 3, characteristic changes in cold crushing strength of some selected bricks after firing under reducing and oxidising conditions are plotted. When embedded in coke up to 1,450°C, the strength remains constant or tends slightly towards a lower value. Brick No. 7 shows that high strength up to 1450°C can be achieved by special manufacturing measures. Sintering and formation of the melting phase is hindered by the presence of carbon in the brick. The strength of the carbon-free material was found to be low up to 1,250°C – as expected. With increasing firing temperature, a low or marked increase in strength is observed, depending on the composition and sinterability of the brick matrix and formation of melting phase (see brick on bauxite base).

An influence of the antioxidant Al could not be proven.

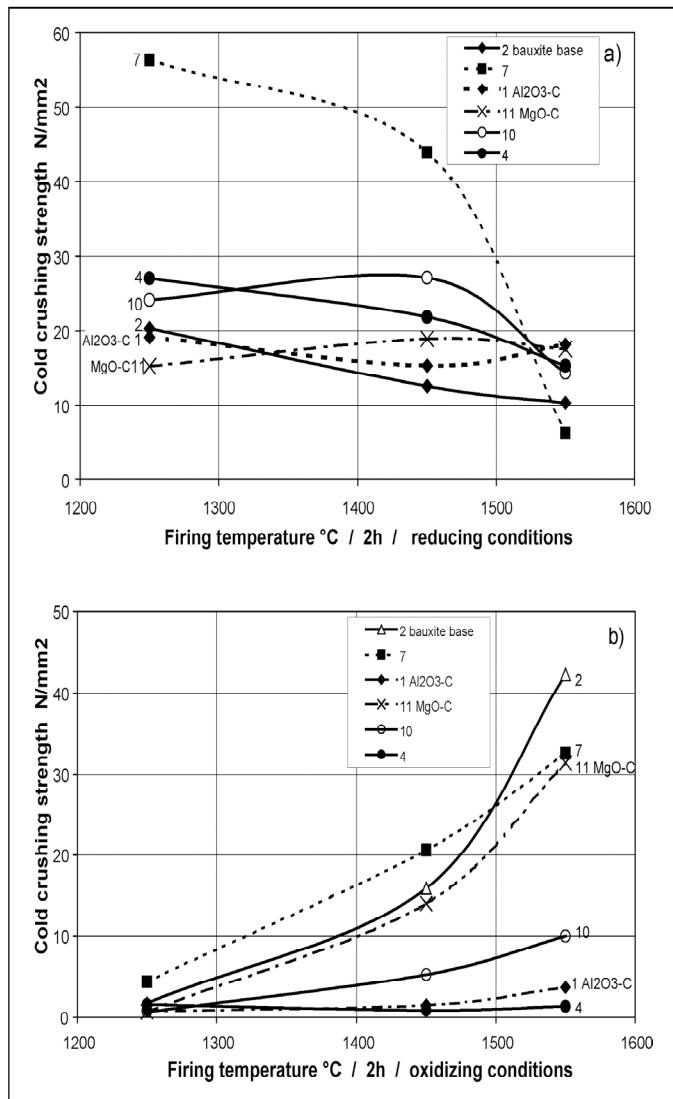
Oxidation At sufficiently high temperatures the oxidation of carbon according to the chemical reaction:



is controlled by the diffusion of oxygen through the pores of the decarburised surface layer. The oxidised depth Δx for the slab-geometry is:

$$\Delta x = (2 \alpha \cdot t)^{0.5} \tag{2}$$

The kinetic oxidation coefficient α [cm²/h] may be described as:



● **Figure 3** Change of cold crushing strength with increasing firing temperature under reducing and oxidising conditions

$$\alpha = 7 \cdot 10^{-5} \cdot \varepsilon (1.84 \sqrt{\varepsilon} - 0.3) \cdot \text{CO} \cdot T_K^{0.79} \quad (3)$$

where ε is the open porosity of the decarburised layer, CO [%] the oxygen content in the surrounding gas (21% in air) and T_K [K] the temperature.

In practice, when a steel ladle with a new MgO-C lining is heated up, a decarburisation of about 1cm has been observed. After 3h, a temperature of 700°C is reached, and after 12h, 1,250°C, which is held for another 12h. Measurements of the atmosphere inside the ladle during heating up resulted in CO = 6 Vol. % O₂. The open porosity after decarburisation is $\varepsilon = 0.25$.

At a medium temperature of 1,200°C (1473 K), the oxidation coefficient from equation (3) is:

$$\alpha = 0.021 \text{ cm}^2/\text{h}$$

From equation (2) the oxidised depth is calculated for 24 hours as:

$$\Delta x = (2 \alpha \cdot t)^{0.5} = (2 \cdot 0.021 \cdot 24)^{0.5} = 1 \text{ cm}$$

This is in agreement with practice.

Corrosion

In many cases, in practice and in laboratory tests a slag line erosion is observed along the three-phase line slag/steel/refractory and can be explained by Marangoni convection. The refractory reacts with both the slag and steel. The dissolution of carbon into the liquid steel may be hindered by the oxide and, vice versa, the dissolution of the oxide into the slag may be hindered by the graphite. Nevertheless, about 1% carbon may be dissolved into the slag, as a consequence of which a local gradient of carbon and oxygen arises along the slag/steel phase boundary.

Figure 4 shows a schematic drawing of the corrosion zone due to Marangoni convection. The wetting conditions, gravity and the fluid flow are bending the slag/steel phase boundary downwards. The so-called three-phase boundary consists mainly of the two, two-phase boundaries refractory/slag and slag/steel, respectively. At the point σ_{II} the slag layer is very thin, the diffusion path short and the carbon concentration may be higher than at the point σ_I , far away from the refractory. For the oxygen content of the steel at the phase boundary, the opposite is valid.

Because oxygen dissolved in steel is very capillary-active a gradient of interfacial tension results. The fluid flow of the phase boundary steel/slag moves very fast in the direction shown, and on its way back it passes the refractory.

$$U_M = \frac{d\sigma}{dC} \cdot \frac{|\text{grad } C|}{\eta_{sl}} \cdot h \quad (4)$$

From this model, based on laboratory experiments the mass transfer coefficient β from the refractory into the slag has been calculated:

$$\beta = \left\{ D_{Sl} \left[\frac{200}{\eta_{sl} \cdot h} \left(1 - \frac{C_{[O]}^{II}}{C_{[O]}^I} \right) \right]^3 \cdot \frac{\rho_{sl}}{\eta_{sl}} \right\}^{1/6} \quad (5)$$

At 1,650°C the following numbers may be taken.

$$\frac{d\sigma}{dC} = - \frac{200}{C_{[O]}^I} = - 4 \cdot 10^4 \frac{\text{mN}}{\text{m}^2}$$

$$D_{Sl} = 10^{-7} \text{ cm}^2/\text{s} \text{ (diffusion coefficient in the slag)}$$

$$\rho_{Sl} = 2.7 \text{ g/cm}^3 \text{ (density of slag)}$$

$$\eta_{Sl} = 1 \text{ g/cm} \cdot \text{s} \text{ (viscosity of slag)}$$

$\eta_{St} = 0.03\text{g/cm} \cdot \text{s}$ (viscosity of steel)
 $= 5 \cdot 10^{-3} \text{ wt\%}$ (oxygen content in steel at point I)
 $C_{[O]}^I = 3.35 \cdot 10^{-3} \text{ wt\%}$ (oxygen content in steel at point II)
 $C_{[O]}^{II}$ point II)
 $h = 2\text{cm}$ (height of the corrosion zone)
 $\rho_R = 3.2\text{g/cm}^3$ (density of refractory).

Taking these values (equation 4) gives the velocity of the Marangoni convection $U_M = 2.2 \cdot 10^3 \text{cm/s}$ from which the mass transfer coefficient $\beta = 8.4 \cdot 10^{-4} \text{cm/s}$ results (equation 5). Now we can write down the corrosion rate of the refractory as :

$$V_{\text{corr}} = 360 \beta \cdot \frac{\rho_{Sl}}{\rho_R} \cdot (C_{\text{sat}} - C_O) \quad (6)$$

$$= 0.25 (C_{\text{sat}} - C_O) \text{ [mm/h]} \quad (7)$$

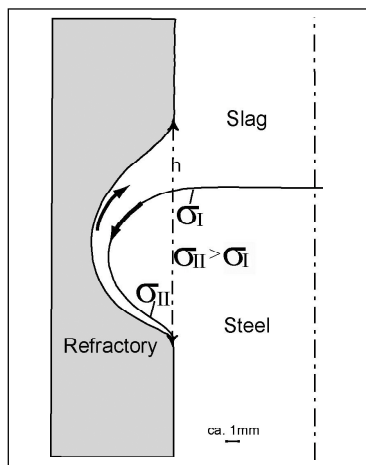
C_O is the concentration of that oxide in the slag, which determines the dissolution of the refractory at the beginning of the process and C_{sat} is its concentration if the slag is saturated. This may be MgO or Al_2O_3 and is determined by the phase of saturation like periclase, corundum, spinel, calcium aluminate, etc.

Equation 7 has been compared with laboratory experiments using a basic and an acid slag shown in Table 2.

The refractory contains 10wt% carbon and different amounts of Al_2O_3 and MgO . C_{sat} have been calculated using FactSage software. Figure 5 compiles all results: the lowest corrosion results from the combination of $\text{MgO} \cdot \text{C}$ lining plus Ca-S la g.

A practical example

A ladle is filled with free cutting steel containing 0.09%C and top-slag. The slag has the medium composition in wt.% (10 Al_2O_3 , 29 SiO_2 , 6 Fe_2O_3 ,



● Figure 4 Slag line erosion caused by Marangoni convection

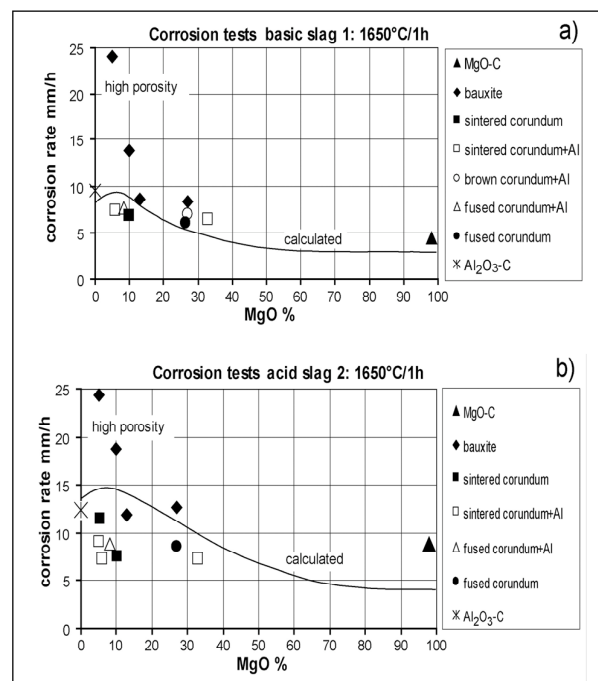
Chemical composition%	slag 1 basic	slag 2 acid
CaO	40	44
Al ₂ O ₃	37	5
SiO ₂	5	36
MgO	5	4
FeO	3	3
MnO	4	3
CaF ₂	6	5

● Table 2 Chemical compositions of the slags used for the corrosion tests

33 CaO, 5 MgO, 17 MnO). Its basicity is about 1 and according to FactSage at 1,650°C the saturation concentration of MgO is $C_{\text{sat}} = 17 \text{ wt\%}$. One batch takes about 1h to process. The observed corrosion along the slag line in that period is about $\Delta x = 2.7\text{--}4.1\text{mm}$ (mean 3.4mm/h).

For the calculation of the chemical corrosion rate we use equation 7 as a first approach:

$V_{\text{corr}} = 0.25 (17-5) = 3\text{mm/h}$ and is in agreement with practice. However, we also have to take into account that in practice erosion and abrasion occurs as well as chemical corrosion. Examples are tapping and stirring of the steel melt. In addition cleaning the ladle using machines may break off the solidified (basic) slag and the adhering refractory. Therefore the corrosion in practice should be higher than in laboratory tests, which have been the basis of equation 7.



● Figure 5 Relationship between corrosion rate and MgO content (ignited material) of the bricks and raw material base

Conclusions

The properties and corrosion of $\text{Al}_2\text{O}_3\text{-MgO-C}$ (AMC)-refractories containing 5–33% MgO and (approximately) 10%C, as well as $\text{Al}_2\text{O}_3\text{-C}$ (AC) and MgO-C (MC) have been examined. The changes in porosity, strength and dimension of the bricks after firing at different temperatures under reducing and oxidising conditions were examined. Owing to the formation of spinel at high temperature, a post-firing expansion of the AMC refractory is observed. This post-firing expansion becomes stronger with higher contents of MgO. Using bauxite as a basis, a shrinkage is observed after burning out of carbon.

The decarburisation of AMC refractories in air is controlled by the diffusion of oxygen in the open pores. A slag layer on the refractory surface has been found, both by laboratory tests and practical results, to be the best protection for preventing oxygen diffusion.

The metallurgical corrosion resistance of bauxite-based AMC refractories has been found to be poor in comparison to alumina-based ones. The slag line erosion along the three-phase line slag/steel/refractory is explained by Marangoni convection. A

computational model based on simple assumptions is in fairly good agreement with laboratory tests and makes it possible to compare those tests with practical results. Using the combination of a MgO-C lining and a CA-slag results in the lowest corrosion.

Thanks

The research project was accomplished at the DIFK Deutsches Institut für Feuerfest und Keramik GmbH for the 'Forschungsgemeinschaft Feuerfest e.V.', Bonn, in the context of the 'Industrielle Gemeinschaftsforschung' and from means of the Federal Minister of economics over the 'Arbeitsgemeinschaft industrieller Forschungsvereinigungen Otto von Guericke' e.V. (AiF) promoted under file reference 12629.

For fruitful discussions we thank Mrs. S. Bethlehem-Seidel, SAARSTAHL, Mr. K. G. Bain, CORUS and Dr. H. Jansen, REFRATECHNIK Steel. Mr. T. Deinet and Dr. R. Simmat (both DIFK) conducted some of the experiments, for which we thank them very much.

Jürgen Pötschke and Gerald Routschka are with DIFK Deutsches Institut für Feuerfest und Keramik GmbH, Bonn, Germany.