Carbon-containing Refractories with Antioxidants in Laboratory and Practical Application

Dedicated to Dr.-Ing. Peter Bartha on the occasion of his 75th birthday

H. Jansen

Antioxidants are common additives to carbon-containing refractories. They reinforce the carbon-bond by creation of new oxidic or non-oxidic bonds while reacting with refractory components and ambient oxygen. Strength is increased and porosity reduced, but elasticity and slag resistance as well as resistance towards thermal decomposition is lowered, particularly under vacuum conditions. Antioxidants can be recommended for applications with strong abrasion and erosion loads, e.g. in ladle impact pads. Problems with hydration of used Al-containing MgO-C bricks can be avoided by using Al-Mg alloys in distinct ratios. Apparently Al-additives cannot be recommended in slag zones of ladles with deep-vacuum treatment at high temperatures. Although boron containing additives are in industrial use to some extent, their benefit could not be verified in ladle slag line tests, most likely due to formation of low melting phases and subsequent slagging.

1 Introduction: general aspects of antioxidants

The development of MgO-C bricks for steelmaking applications was described first in 1979 [1]. Only a few years later also the addition of antioxidants to carbon-containing refractories was discussed in Japanese technical papers [2, 3]. Antioxidants are metallic or non-metallic powders that are added to carbon-containing refractories such as MgO-C, AMC- and Al_2O_3-C to improve their properties. Fig. 1 gives an overview about the system of antioxidants for carbon-containing refractories. Besides these antioxidants other materials of lesser importance like Fe-Si, TiB_2 and others are used. The most common antioxidant is aluminium (Al). The fine antioxidant-powder in the carbon-containing refractories reacts with both, the ambient oxygen and brick components like MgO or Al_2O_3 and C. Fig. 2 shows a microphoto of an MgO-C brick containing 2 % Al-powder after 1000 °C in a reducing CO-atmosphere. While still residual metallic Al-grains are visible another Al-grain has already reacted, leaving a hollow cavity that is surrounded by a thin seam of mainly Al_4C_3 and traces of MA-spinel. At 1500 °C treatment temperature the formation of MA-spinel is completed (Fig. 3).

2 Antioxidizing effect

The original approach to add antioxidants to carbon-containing refractories was to slow down the detrimental burnout of carbon by the antioxidants' preferred oxidation. Oxida-

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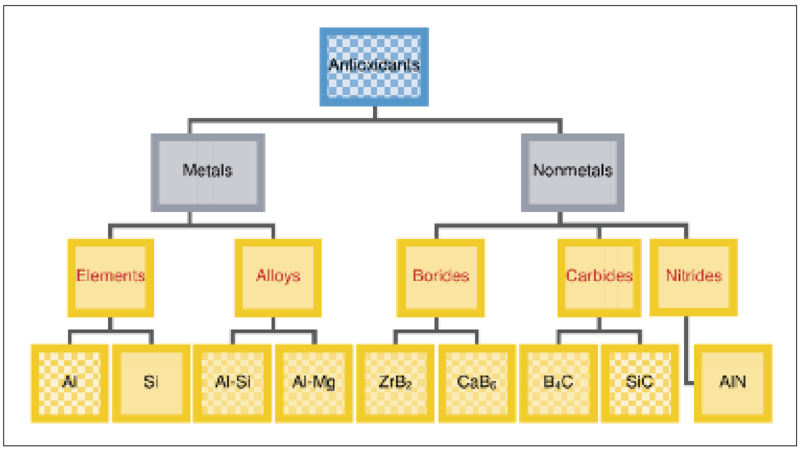

Fig. 1 System of antioxidants for carbon-containing refractories

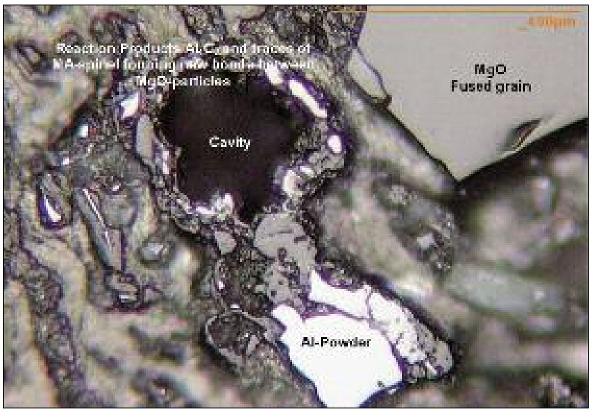

Fig. 2 Microphoto of an MgO-C brick containing 2 % Al-powder after 1000 °C in reducing atmosphere

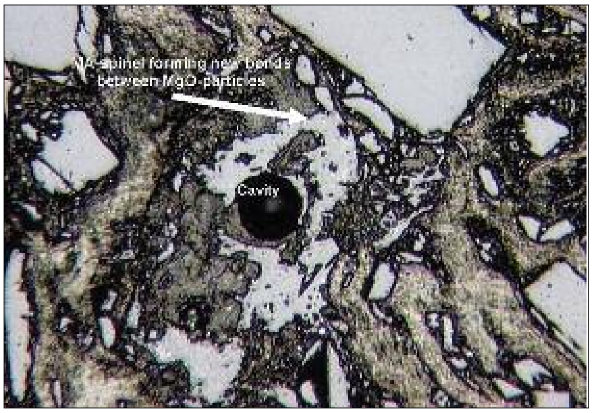

Fig. 3 Microphoto of an MgO-C brick containing 2 % Al-powder after 1500 °C in reducing atmosphere

tion of carbon-containing refractories is either due to direct oxygen contact at elevated temperatures (ambient air, process oxygen) or indirect by oxides like FeO and MnO in the slag that are reduced to metals and oxidise carbon to gaseous CO. The antioxidants' common property is a higher reactivity towards oxygen than carbon, thus, the intention was to let them work as an "oxygen trap". However, investigations have shown and practice proved that the literal "antioxidizing effect" of the common antioxidants, particularly Al-powder, is neglectable [4]. This seems to be reasonable because all kinds of antioxidants can only act once. After reacting with oxygen even the theoretical possibility to capture more oxygen is zero. In metallurgical practice there is normally oxygen and time in abundance to neutralise the relatively small amount (2–5 %) of antioxidants in C-containing bricks. A certain reduction of oxidation – at least in laboratory scale samples – is achieved by the clogging of open pores by the reaction products of the antioxidants with oxygen and refractory material.

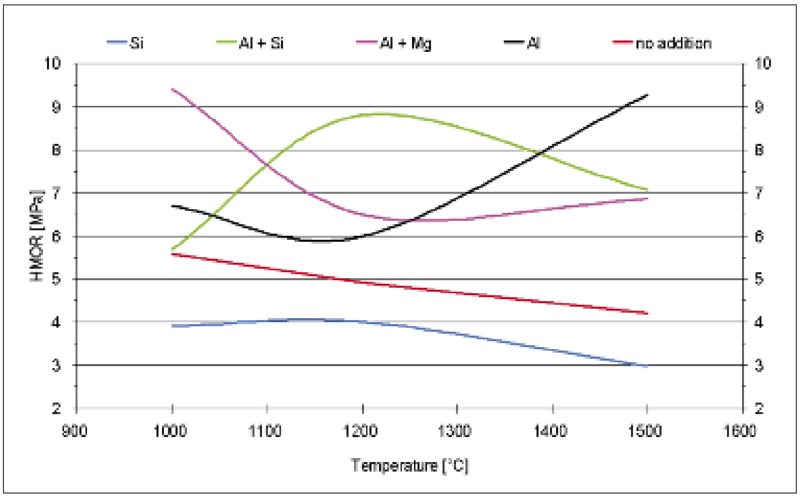

Fig. 4 Influence of metallic antioxidants on the HMOR of MgO-C bricks

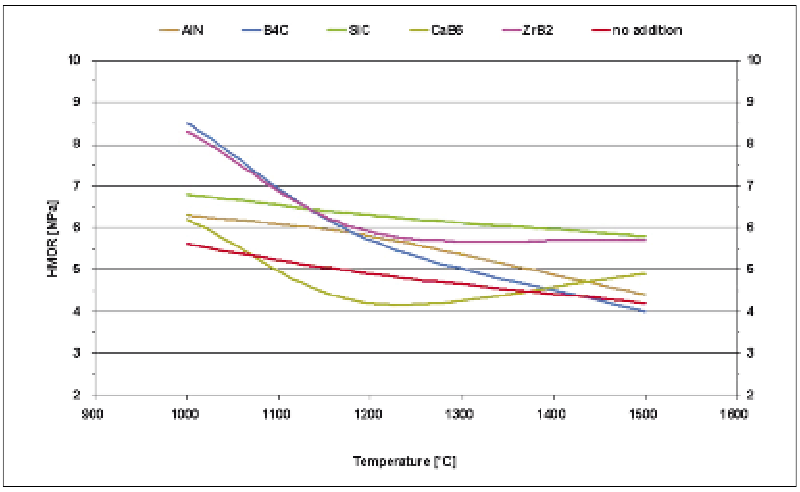

Fig. 5 Influence of non-metallic antioxidants on the HMOR of MgO-C bricks

3 Reinforcing effect

Another, very important and more beneficial effect of antioxidants is the creation of additional bonding in carbon-containing refractories [5]. Both, metallic and non-metallic additives form oxides, once their reaction with ambient oxygen is completed. In some cases intermediate reaction products like carbides are formed that decompose to oxides when temperature and oxygen concentration are high enough. The creation of additional bonding is mirrored by the hot modulus of rupture (HMOR) of MgO-C bricks (based on fused magnesia (FM) 97, resin-bonded, 10 % flaky graphite) at temperatures between 1000 °C and 1500 °C (metallic antioxidants in Fig. 4 and non-metallic antioxidants in Fig. 5). In both figures the reinforcing effect is obvious for most of the additives. Particularly the addition of metallic powders leads to a significant increase of hot strength in bricks, the addition of Al-powder even with increasing temperature. Low-melting phases like magnesia-borates are responsible for the negative impact of temperature on bricks with boron-containing additives (CaB_6, ZrB_2, B_4C). The addition of SiC does not result in a similar drop of strength as does the addition of Si. Possibly SiC does not create magnesia-silicates and calcia-magnesia-silicates so easily, which might be caused by the higher reactivity of molten or even gaseous Si in the brick.

4 Influence on thermomechanical properties

The reinforcement by additional bonding has an influence on the thermomechanical properties as well. Due to the rigid nature of the ceramic-like bond caused by antioxidants the *Young*'s modulus of most of MgO-C bricks with metallic antioxidants is higher than without addition, as can be seen in Fig. 6. It shows the development of Young's moduli as a function of pretreatment temperatures, but under ambient conditions. With the exception of Si-addition the metallic antioxidants lead to an increased level of Young's moduli, which on the other hand increases their brittleness. The impact on the refractoriness under load (RUL) and the time-dependant creep of MgO-C bricks is also influenced by the addition of antioxidants. Due to the generation of new linkages and, in the case of Al-addition, a volume increase by the reaction with oxygen and thus formation of MA-spinel the bricks tend to expand with increasing temperature and time. Fig. 7 shows a combined RUL/creep diagram of an MgO-C brick (based on FM 97, resin bond, 10 % flaky graphite) without and with 2 % Al-powder addition. It can be seen clearly that both, linear thermal expansion (RUL) and volume expansion during the creep test are higher in bricks with Al-addition. This higher thermal expansion leads to a general increase of stress in the bricks, once they are installed in a tight brick lining. Although strength of Al-containing bricks is higher the higher stress level might result in spalling and cracks.

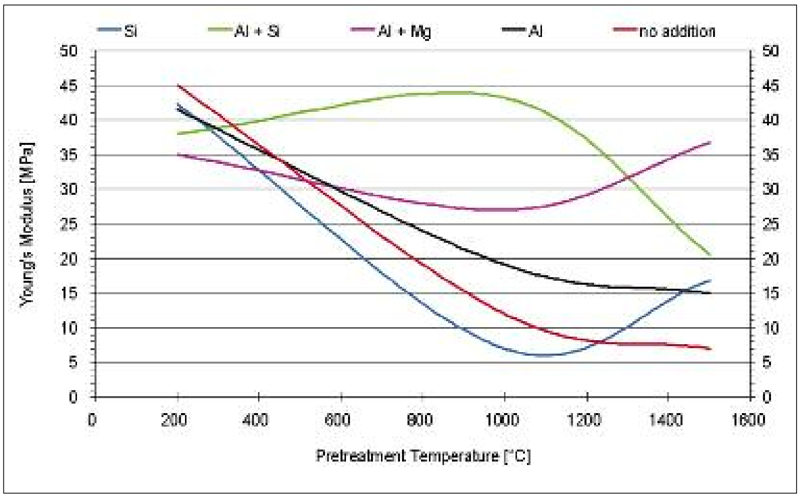

Fig. 6 **Influence of metallic antioxidants on the Young's modulus of MgO-C bricks, pretreated at different temperatures**

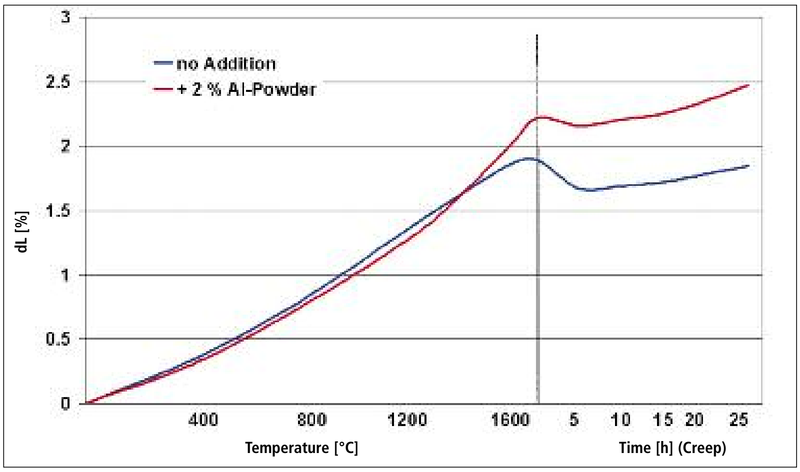

Fig. 7 **RUL and creep of MgO-C bricks with and without 2 % Al**

5 Sensitivity to humidity of MgO-C bricks with Al-addition

A well-known phenomenon is the sensitivity of used Al-containing refractories towards water. Al-powder leads to the formation of aluminum carbide Al_4C_3 up to a temperature of approx. >1250 °C when the reaction to MA-spinel and secondary carbon in a subsequent second oxidising reaction takes place:

(1) 1st reaction (~700 – ~1250 °C):
$3\ C + 4\ Al \rightarrow Al_4C_3$

(2) 2nd reaction (>1250 °C):
$Al_4C_3 + 2\ MgO + 3\ O_2 \rightarrow 2\ MgAl_2O_4 + 3\ C$

Traces of MA-spinel from this 2nd reaction can be found microscopically but not by means of XRD (detection limit here is typically ~2 %), beginning from 1000 °C. A general formation cannot be expected before 1250 °C. In a steel plant significant parts of an MgO-C brick lining are beyond the hot face and do not face temperatures exceeding 1250 °C. This is why quite a big portion of Al_4C_3 can be found in spent MgO-C linings as well as idling ladles, convertors and other furnaces if Al-powder was added to the bricks. The residues of the reaction of water and Al_4C_3, aluminium hydroxide $Al(OH)_3$ and methane CH_4, create cracks and even complete deterioration of a refractory lining because of the accompanied volume expansion, once the temperature drops beneath the dew point of water.

(3) $Al_4C_3 + 12\ H_2O \rightarrow 4\ Al(OH)_3 + 3\ CH_4$

The reuse of spent refractory linings has become an important source for MgO-C raw materials but residual Al_4C_3 has to be removed from the bricks by watering, initiating reaction (3) and subsequent drying to avoid problems in the manufacturing of new bricks.

Results of a systematic investigation of the destruction of antioxidant-containing

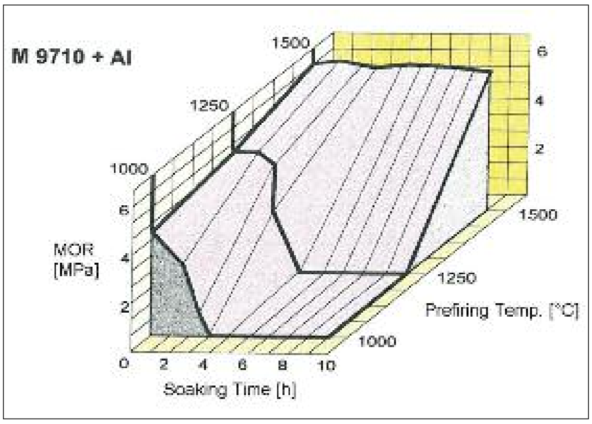

Fig. 8 Influence of humidity on the destruction of Al-containing MgO-C bricks

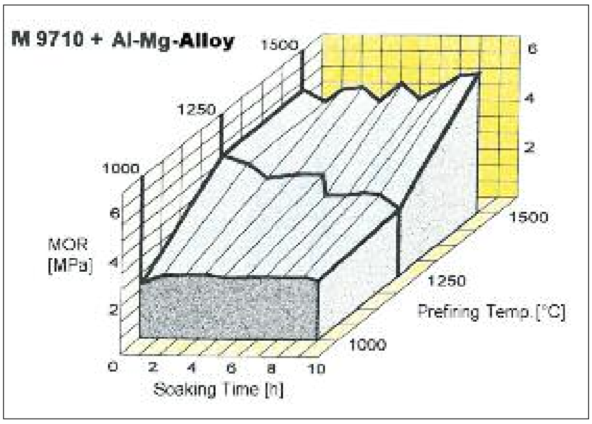

Fig. 9 Influence of humidity on the destruction of Al-Mg-Alloy-containing MgO-C bricks

MgO-C bricks by humidity are presented in Fig. 8 and 9. 10 samples (bars of 250 mm × 30 mm × 30 mm) of MgO-C (M 9710 = DBM 97 based, 10 % C, resin-bonded) with 2 % Al and 2 % of Al-Mg alloy respectively were prefired under reducing atmospheres at 1000 °C, 1250 °C or 1500 °C and subsequently soaked in a 100 % water-saturated atmosphere for up to 9 h at 45 °C. Every hour one sample was taken out for modulus of rupture (MOR) measurement. The brick with 2 % Al-addition did not show any strength anymore after 3 h soaking time and prefiring temperatures of 1000 °C or 1250 °C due to the deterioration by the reaction of Al_4C_3 with water. Only after firing at 1500 °C the bricks were not affected by the humidity anymore because Al_4C_3 has reacted to MA-spinel at this temperature. When replacing Al-powder by an Al-Mg-alloy in a distinct ratio a direct reaction to MA-spinel is maintained. MA-spinel is not sensible to water and humidity. Even samples pre-fired at 1000 °C do not show any deterioration by water at a soaking time as long as 9 h.

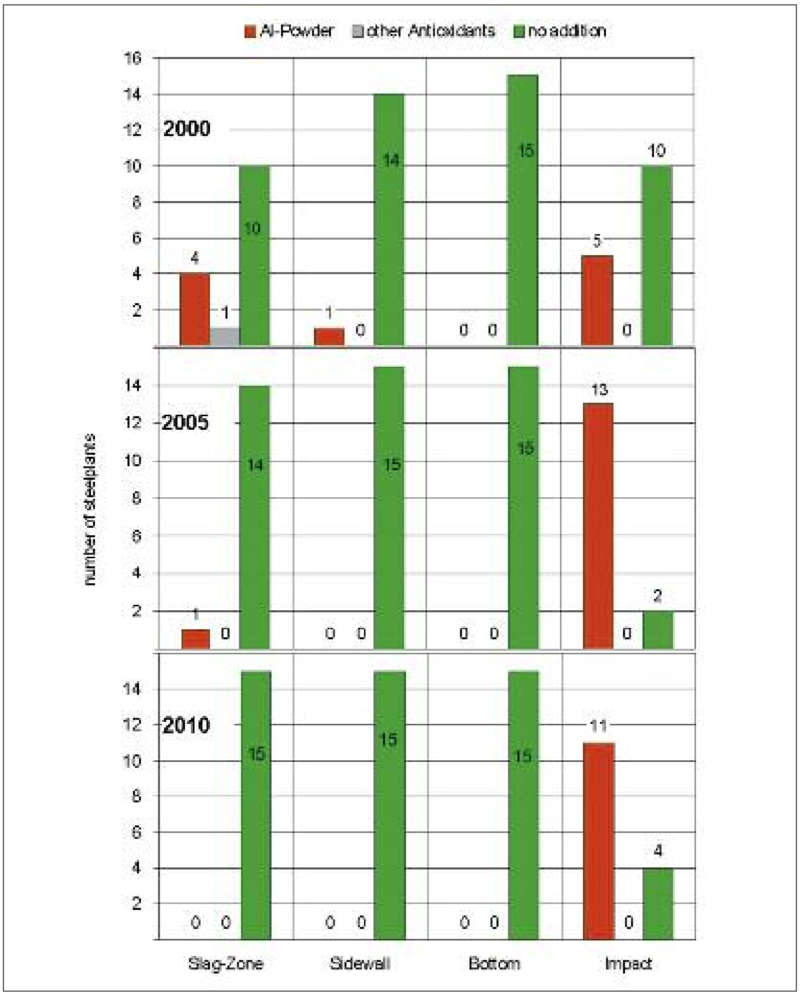

Fig. 10 Use of antioxidants in MgO-C bricks in 15 ladles of representative steel plants in Europe

6 Antioxidants in practical applications in steel ladles

There are different potential applications for carbon-containing refractories with antioxidants, e.g. in ladles, BOFs and EAFs. In this investigation the use in steel ladles shall be highlighted. The development of the use of antioxidants in MgO-C bricks in steel ladles in 15 representative steelplants in Europe according to the experience of *REFRATECHNIK Steel* is depicted in Fig. 10. The ladle lining is subdivided into 4 areas: slag-zone, sidewall, bottom and impact. Between 2000 and 2010 the number of steel plants using bricks with antioxidants have come down to 11 plants, which use them exclusively in the impact pads, mostly in BFA-based AMC-bricks with 5 % carbon and 7 % FM.

There is a broad variety of scientific papers dealing with antioxidants in carbon containing refractories and there are as many different judgements on their harm and benefit. In [6] it is stated that Al and its alloys do not lead to any improvement of performance of MgO-C bricks in steel ladle linings and Al, Si and boron-compounds such as B_4C and CaB_6 increase corrosion rates by formation of low-melting compounds. These antioxidants might also lead to unwanted pollution of steel with hard inclusions, like alumina and spinel or boron. The investigation comprised both, laboratory and field tests. In [7] the authors found superior properties of MgO-C bricks with magnesium-borate ($Mg_3B_2O_6$) compound that was determined to be present by characterisation studies on B_4C added specimens. Magnesium borate, which is in liquid state above 1360 °C, had an excellent effect on the oxidation resistance of the bricks by filling up the open pores and forming a protective layer on the surface. In [8] the author reports of detrimental low-temperature oxidation of carbon in MgO-C bricks because unmelted Al-powder is unable to protect graphite at temperatures below 700 °C. While the authors in [9] claim, that the use of antioxidants is useful for bricks in various areas of BOF linings the authors in [10] state that at high oxygen partial pressure and temperatures >1680 °C in BOFs the use of antioxidants is detrimental. Finally, in [11] the negative influence of additives on corrosion resistance and corroded microstructures of MgO-C refractories is described.

Fig. 11 shows the formation of a dense layer in a microphoto of a laboratory sample of a FM 98 + 10 % flaky graphite based MgO-C brick with an addition of 0,8 % B_4C and 2 % Al-powder after a thermal treatment of 1500 °C for 6 h under reducing atmosphere. Tab. 1 gives a comparison of properties of these bricks without (brick type 1) and with antioxidant addition (brick type 2) after coking at 1000 °C. The increase in hot strength (HMOR) and work of fracture (WOF) is impressive.

Fig. 12 shows the brick type 2 after only 46 heats service in a steel ladle slag line. Apparently, the boron content has caused a rapid dissolution of the coarse high grade MgO crystals and the detailed microphoto (Fig. 13) shows how this dissolution by Ca- and CS-slag components took place. The brick failed completely.

It is remarkable that apparently most of the positive judgements on the use of antioxidant in literature are based on results from laboratory scale samples, where superior oxidation resistance is found, often caused by boron-containing additives that create a sealing dense layer of high viscous melts on top of the refractories or clogging reactions that prevent oxygen to enter them. However, there is little evidence of these phenomena in real practice. It is likely that high viscous melted protection layers are simply washed away by powerfully agitated slags and melts at very high temperatures, which can hardly be simulated in laboratories. But, also a general statement about Al, the most commonly used antioxidant, becomes not perfectly clear from literature studies.

Apparently a general recommendation for the use of antioxidants cannot be given yet. Therefore it is interesting to find an approach to the determination of the benefits of antioxidants that is based on practical large scale trials in steel plants.

Tab. 1 Comparison of brick properties

	Brick Type 1 no Addition	Brick Type 2 + Al + B_4C
Young's modulus [GPa]	11,00	20,00
Open porosity [%]	9,00	7,80
CCS [MPa]	25,00	47,00
MOR [MPa]	3,50	7,70
HMOR [MPa]		
1000 °C	4,50	11,00
1200 °C	4,00	8,50
1500 °C	3,50	6,80
WOF [N/mm]		
1000 °C	75,00	340,00
1200 °C	70,00	320,00
1500 °C	65,00	150,00

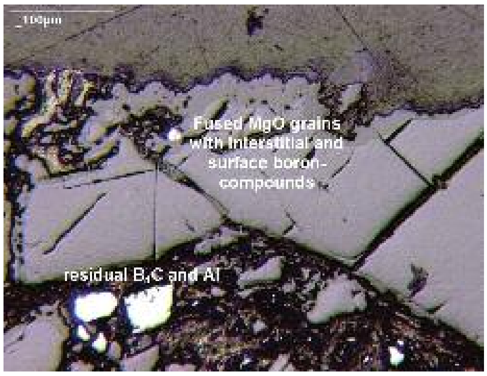

Fig. 11 Dense layer of an MgO-C brick with an addition of B_4C and Al-powder

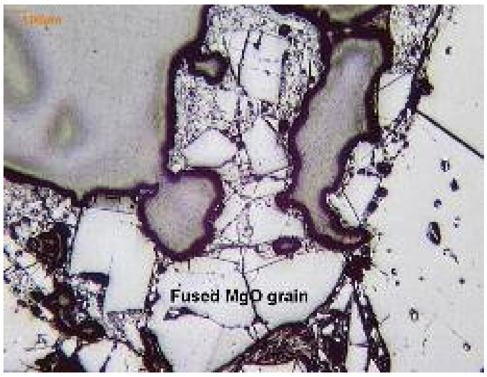

Fig. 12 Microphoto of brick type 2 after 46 heats service in a steel ladle slag line

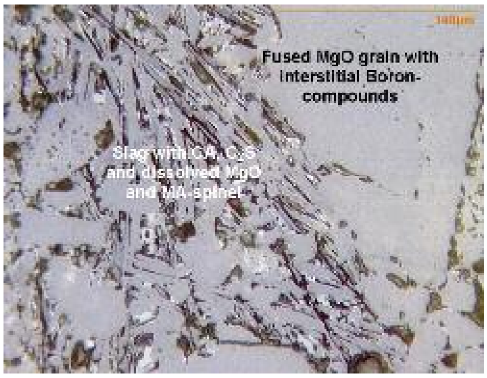

Fig. 13 Dissolution of boron-containing MgO into the slag

7 Steel-plant tests

Refractory wear in a ladle differs substantially dependent on the place or zone within the ladle. While the slag line is most dominantly affected by chemical corrosion, the impact pad suffers first of all from a combination of abrasion and some thermomechanical wear, as indicated by the shaded areas in the triangles of Fig. 14. In slag lines abrasion and erosion loads are of inferior importance. The right triangle shows the loads acting on the refractory in impact-pads where abrasion

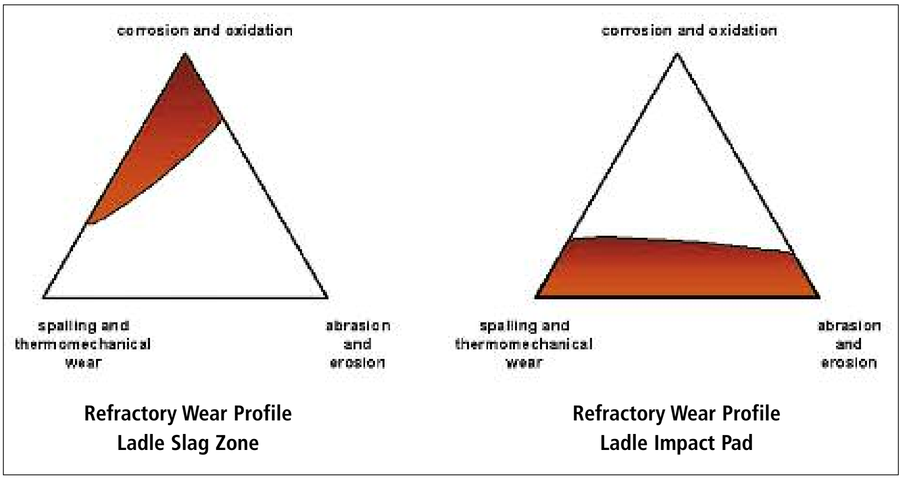

Fig. 14 Refractory wear in a ladle

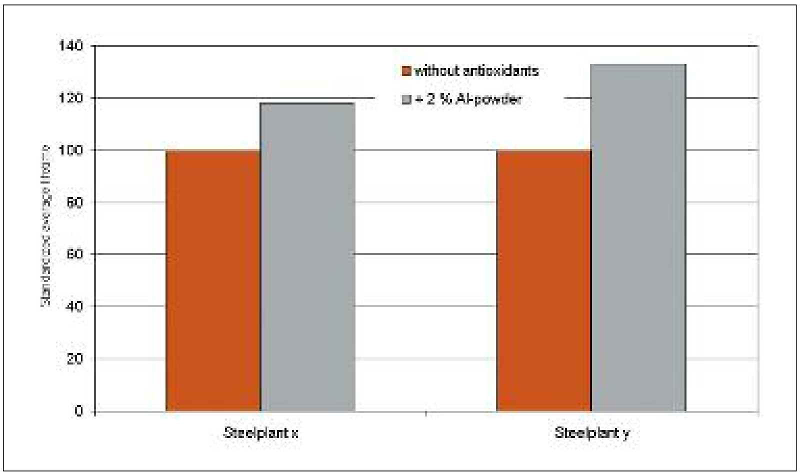

Fig. 15 Performance in ladle bottom impact pads; Al_2O_3-MgO-C brick, BFA-basis, 5 % C

Tab. 2 Average tapping temperature and deep vacuum treatment

	Average Tapping Temperature [°C]	Deep Vacuum Treatment [%]
Steel plant 1	1645	20
Steel plant 2	1735	75

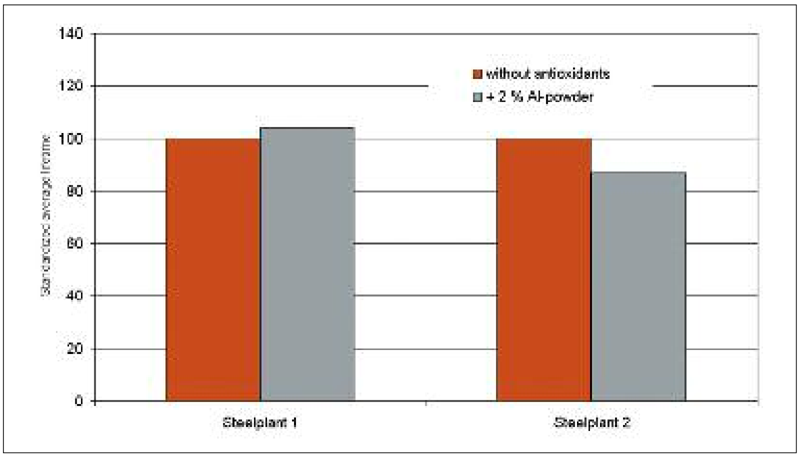

Fig. 16 Performance in ladle slag lines; MgO-C brick, 98 FM-basis, 15 % C

and erosion and thermomechanical loads are predominant while corrosion and oxidation loads are inferior.

The first series of trials' target was to evaluate the benefit of antioxidants in the only current standard application, the use in BFA based AMC-bricks for bottom impact pads of ladles. As stated already in Fig. 10 most customers use refractories with antioxidants in this area. Comparison trials in 2 steel plants x and y delivered an advantage of 18–33 % less wear when antioxidants were used (Fig. 15). Main load acting in this area is abrasion and the reinforcement and increase of strength as shown in Fig. 4 and 5 is likely to be responsible for this benefit.

The second series of tests were conducted in slag zones of two different BOF steel plants. The test comprised three linings each. The setups of these steel plants in terms of average tapping temperatures and deep vacuum treatment vary significantly. Tab. 2 shows the results of these trials. While the performance of MgO-C bricks with antioxidants in steel plant 1 is slightly better it is 13 % worse in steel plant 2 (Fig. 16). Apparently the reason for this has to be found in the different steelplant setups. The conditions in steel plant 2 are much harsher than in steel plant 1: higher temperatures and lower atmosphere pressure. The p/t-diagram from [12] shows, that the stability field of MgO + C is relatively small. MgO-C tends to decompose to gaseous phases at high temperatures. Particularly MgO becomes unstable with rising temperatures and sinking p_{O2} pressure. It was interesting to evaluate, how Al influences this stability at low oxygen pressure. Therefore two laboratory scale samples of MgO-C, based on FM 98 and 15 % graphite, precoked at 1000 °C for 6 h were investigated by means of thermogravimetry up to 1450 °C and under argon atmosphere (Fig. 17).

Astonishingly the decomposition of MgO-C bricks with 2 % Al-addition proceeds faster and stronger than without Al-addition. Al-containing bricks are apparently less stable in low O_2-pressure atmospheres or generally under vacuum conditions and at high temperatures. It is likely that the lower wear resistance and poorer performance of bricks with Al-addition under the severe conditions of steel plant 2 can be attributed to this stronger and faster weight loss. The decomposition of Al-containing phases leads to an impairment of the brick structure due to loss of spinel-bonds between MgO-grains and a rapid increase of open porosity. Instead of protecting the MgO-C brick Al promotes its decomposition under these conditions.

8 Conclusions

The conclusion of this investigation is that the addition of antioxidants to MgO-C bricks not necessarily results in a better performance. If the main wear loads on the refractories are abrasion and erosion or any other application that requires increased strength the addition of antioxidants as reinforcing element is suitable and beneficial. Boron containing additives may induce a higher sensitivity towards corrosion and drop of refractoriness in ladle slag-zones. In deep-vacuum applications under high temperatures the addition of Al leads to an accelerated decomposition of MgO-C bricks and thus lower wear resistance.

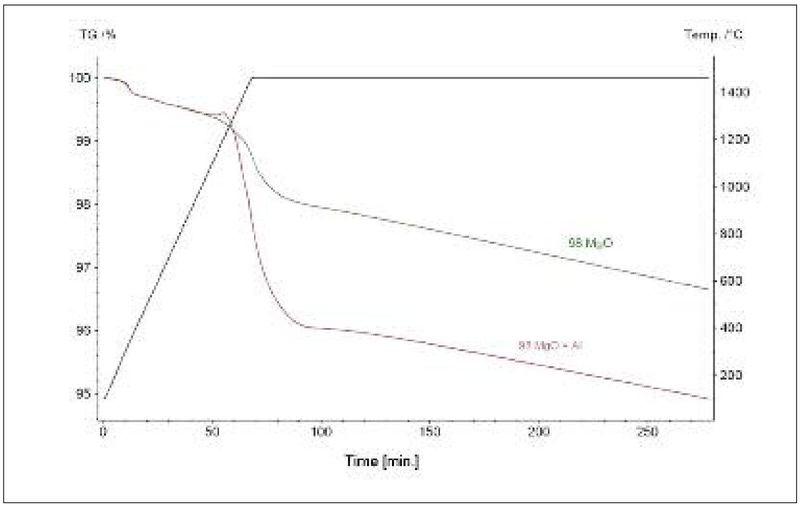

Fig. 17 Thermogravimetric mass loss of MgO-C bricks with and without Al-addition [13]

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