TESTING MAGNESIA-CARBON BRICKS FOR OXIDATION RESISTANCE

*Jana Bounziová[1)] *, Iveta Nagyová[1)] , Vincent Zajac[1)], Lucia Hrabčáková[1)] , Pavol Vadász[2)] , Rastislav Kamenský[3)]*
[1)] *U. S. Steel, Košice, s.r.o., USSE Research and Development, Košice, Slovakia*
[2)] *Technical University of Košice, Faculty of Metallurgy, Košice, Slovakia*
[3)] *RMS, a.s., Košice, Slovakia*

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*Corresponding author: *jbounziova@sk.uss.com Tel.: +421 55 673 0771, U. S. Steel, Košice, s.r.o, USSE Research and Development, Primary Process Technology Department, Vstupný areál U. S. Steel, Košice, 044 54 Košice, Slovakia*

Abstract
MgO-C based refractory materials are used in steel metallurgy to a large extent. Magnesia-carbon bricks are tested for basic physical-mechanical parameters in as supplied state, for carbon content, and chemical analysis of magnesium component. According to the type of their usage, they are subjected to tests at higher temperatures, carbonization firing, and after firing, the physical-mechanical parameters are determined at specified temperatures. One of the most tested properties of these materials is their resistance to oxidation. The methodology for such testing is not yet defined in ISO, EN and ASTM test procedures, therefore the methodology used in other countries is being applied. In conditions of U. S. Steel, Košice, s.r.o., the MgO-C bricks intended for the working lining of slag zones of steel ladles are tested by oxidation resistance test (oxidizing area procedure). The described test method was developed at U. S. Steel Research and Technology Center in Munhall and has been used for more than 15 years to evaluate various carbon containing bricks. Test specimens in the shape of a cube are heated in an oxidizing atmosphere to a temperature of 1482°C with holding time of 5 hours. After cutting of the test specimens, the percentage of oxidized area is calculated. This test is used for selecting the appropriate type of lining material for the working lining of slag zone of the steel ladle in the steelmaking secondary metallurgy process and for the building of database of different types of MgO-C bricks.

Keywords: MgO-C refractories, Oxidation, Oxidation resistance, Steel ladle (Teeming ladle)

1 Introduction

In the past, teeming ladles were used only as a container for transporting molten steel from the refining furnace to the casting site. However, in recent years, the used conditions have become much more severe with higher temperature steel and longer holding time, due to the increased availability and use of secondary refining and continuous casting. So to improve ladle linings, effort has been directed to development of both corrosion resistant refractories and labor-saving techniques and facilities [1]. MgO-C bricks have dominated the slag line of ladles for at least a decade as they possess superior slag penetration resistance and excellent thermal shock resistance at elevated temperature because of the non-wetting properties of carbon (graphite) with slag, high thermal conductivity, low thermal expansion and high toughness [2, 3].

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Oxidation of carbon was one of the main drawbacks of carbon containing refractories. The oxidation of carbon in MgO-C refractories happens in two ways (a) direct oxidation and (b) indirect oxidation. Directly, carbon and oxygen combine to form CO (gas) at ~1400°C. Indirectly, above 1500°C, carbon oxidizes through the reaction with MgO with the carbon to form Mg (gas) and CO (gas). The resulting Mg gas reaction oxidizes again and generates MgO which is called the secondary oxide phase or the dense layer [4-8]. In service, carbon interacting with aluminium forms Al_4C_3 greater than 750°C then greater than 1100°C Al_4C_3 forms Al_2O_3. Finally greater than 1400°C it forms $MgO.Al_2O_3$ spinel [9]. Oxidation takes place from the edges of the graphene layers, at the edges of crystals or where vacancies in exposed graphene layers reveal such edge atoms [10]. Carbon in MgO-C bricks inhibits slag from penetrating the bricks. On the other, the carbon may oxidize by oxygen: (a) in the liquid phase, (b) in the gas phase, (c) by MgO (MgO-C reaction) [11].

2 Experimental materials and method

2.1 Characteristics of MgO-C samples

Carbon-containing refractories are tested as received, after removal of volatile components, and, where appropriate, after removal of carbon [12]. The test procedures are given in ISO 10060:1993 [13]. The presented work shows the results of testing four types of MgO-C bricks from different manufacturers with different carbon content, type and grain size of magnesia, type of carbon bond, size and type of graphite, a type of antioxidants. Their basic physical and chemical properties are given in **Table 1, 2, 3**.

Table 1 Physical properties

Delivered properties					
Sample no.	**Bulk density [kg/m^3]**	**Porosity [%]**	**Cold crushing strength [MPa]**	**Cold modulus of rupture [MPa]**	**Carbon content [%]**
B64	2960	4,0	35	15	9,5
B53	3010	4,0	30	13	12
B66	3080	4,0	30	11,4	10
B65	3000	5,5	30	12	10
Properties after cooking					
Sample no.	**Bulk density [kg/m^3]**	**Porosity [%]**	**Cold crushing strength [MPa]**	**Cold modulus of rupture [MPa]**	**Carbon content [%]**
B64	2950	6	26	6	10
B53	2840	9	27	3,1	10,8
B66	2930	8	25	2,7	10,3
B65	2980	10	28	8	12

Table 2 Additional properties

Sample no.	**Type of binder**	**Type and amount of antioxidants**
B64	resin	3%Al +1%Si
B53	pitch	none
B66	resin	3%Al+1%Si
B65	pitch	none

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Table 3 Chemical properties

Chemical composition of magnesia					
Sample no.	**MgO [%]**	**Fe_2O_3 [%]**	**Al_2O_3 [%]**	**CaO [%]**	**SiO_2 [%]**
B64	98	0,6	0,2	0,9	0,2
B53	95,6	0,3	1,0	2,0	0,8
B66	83	0,7	0,9	1,4	1,7
B65	97	0,6	0,15	1,4	0,7

2.2 Oxidizing area procedure

Test for the resistance to oxidation (oxidizing area procedure) was performed on test specimens - cubes measuring 50x50x50mm. All four types of tested samples were heated simultaneously (at the same time) in the electric laboratory furnace with the air atmosphere at a rate of 5°C/1min. to a temperature of 1482°C with holding time of 5 hours at the maximum temperature. After firing, cooling and cutting the samples, the extent of the oxidized area was monitored macroscopically, comparing to the original un-oxidized area, and then the percentage of oxidized area was calculated.

Fig. 1 Oxidation resistance of B64 specimen

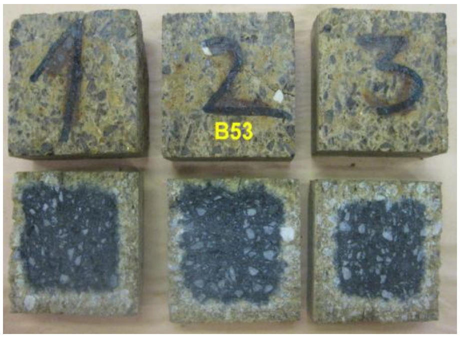

Fig. 2 Oxidation resistance of B53 specimen

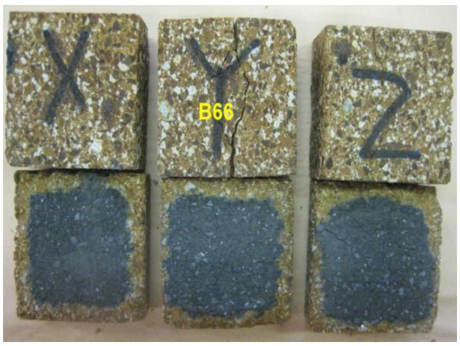

Fig. 3 Oxidation resistance of B66 specimen

Fig. 4 Oxidation resistance of B65 specimen

3 Results and discussion

To determine the oxidation degree of MgO-C samples, each sample was weighed; thickness of oxidized layer was measured before and after the firing, to determine the loss of mass, volume

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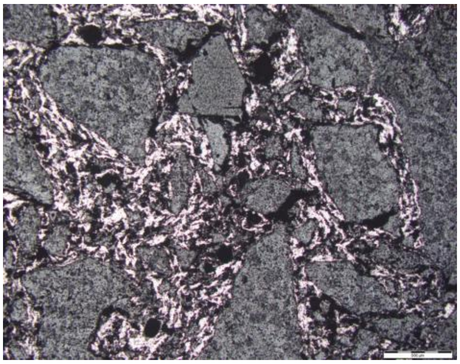
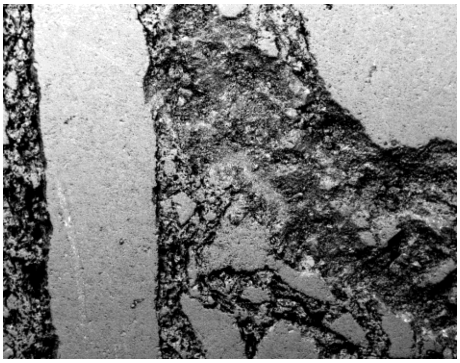
changes and size of un-oxidized area. By comparing the results, deviations were found between the different types of MgO-C bricks samples, **Table. 4**.

Table 4 Oxidizing area procedure evaluation

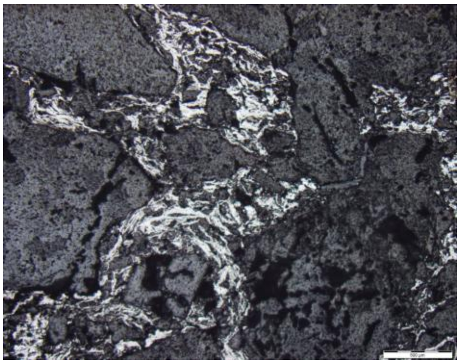
Sample no.	**Oxidizing thickness range [mm]**	**Oxidizing area [%]**	**Weight loss [%]**	**Volume changes [%]**
B64	2,5-11,1	20,87	- 4,25	0,56
B53	11,8-16,4	47,51	-7,93	-0,23
B66	7,7-14,1	35,96	-6,86	4,37
B65	11,6-15,7	46,74	-11,4	-0,12

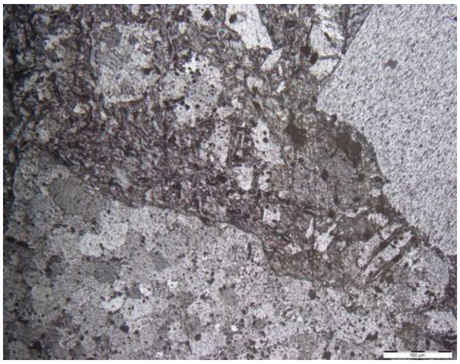
Figs. 5-12 show the microstructure of the tested samples before and after the oxidation test. Grains of magnesia, the pores and different types of carbon bonds are seen n the microstructures.





Figs. 5, 6 Microstructures of the studied MgO-C sample no. B64 before and after oxidizing procedure look in the light microscope





Figs. 7, 8 Microstructures of the studied MgO-C sample no. B53 before and after oxidizing procedure look in the light microscope

The presented results of the oxidation resistance tests show that the oxidized thickness range of samples ranged from 2,5 mm to 16,4 mm, oxidized area ranged from 20.87% to 47.51%, weight loss was from -4.25% to -11.4%, and volume changes from +4.37% to -0.23%. Sample B66 had volume increase of +4.37%, which also led to the formation of cracks. These deviations are

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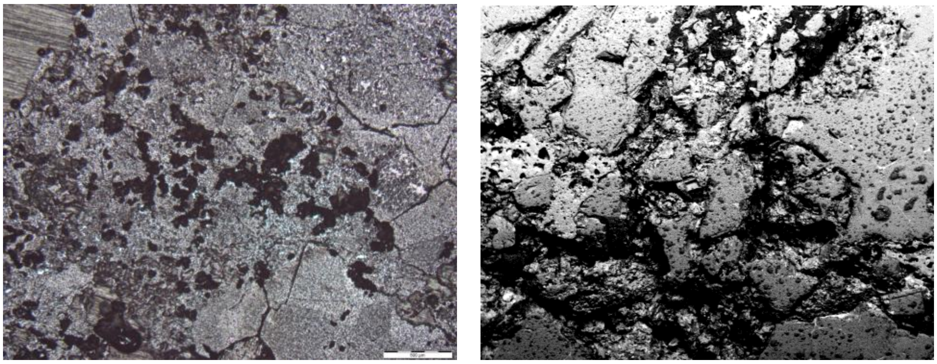
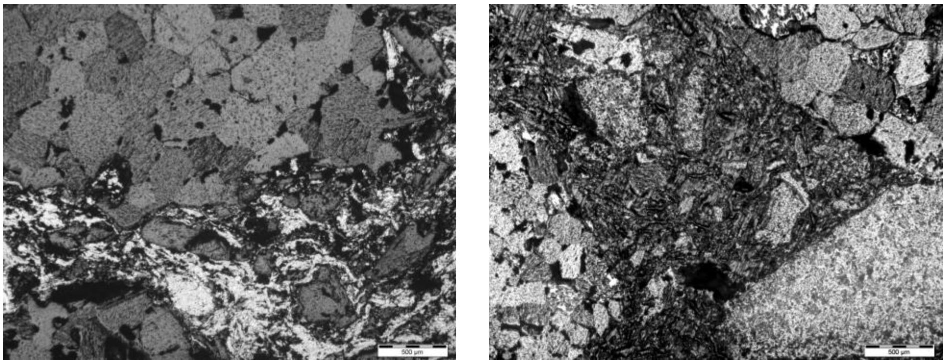
indicators of active carbon oxidation, the oxidation of antioxidants in the MgO-C products, and the escape of volatiles from the organic binders. Deviations in the result could be due to the difference in physical and chemical properties of the four types of bricks including amount of carbon, porosity, graphite purity, amount and type of binder and amount and type of antioxidants. The highest percentage of oxidized area was observed on samples with pitch bonded with higher porosity after carbonation. The least oxidized area was found on the samples bonded with a synthetic resin, made without additions of pitch (in any form) and with antioxidants.



Figs. 9, 10 Microstructures of the studied MgO-C sample no. B66 before and after oxidizing procedure look in the light microscope



Figs. 11, 12 Microstructures of the studied MgO-C sample no. B65 before and after oxidizing procedure look in the light microscope

Temperature, heating rate, nature of the carbon, presence of additives, etc. are some of the parameters pointed here to be of great importance in oxidation experiments [14].
Carbon and graphite oxidation is very detrimental because these material losses lead to porosity, the low specific gravity of carbon causes material loss to lead to higher porosity. The minimize the rate of carbon and graphite oxidation, new additives-antioxidants or oxygen inhibitors, have been successfully used. Among the many additives now available, the metallic aluminum-based alloys are the most commonly used, sometimes in conjunction with various nonmetals, such as silicon carbide and boron compounds.
These additives are used to delay carbon debonding and graphite oxidation. In addition, they often act as pore blockers, and many of them have a net positive effect on the mechanical strength of the refractories [15, 16].

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Whilst antioxidants do improve oxidation resistance they also have a deleterious effect on the ductility and corrosion resistance of the product. At the present time the use of antioxidants is far less although they are used in areas the ladle freeboard where bricks are above the metal line. In this place the contact of the brick with air for a long period of time tends to promote the oxidation of the carbon and the ladle can prematurely stop because two or three lines of bricks. Other situation that sometimes requires caution is in the case of preheating the ladle. There have been several examples where removing the antioxidants addition and reducing the carbon content has an advantageous effect on ladle performance. For a higher performance of the lining the operation condition must be evaluate the real needs for using metallic powder [17, 18]. However, the controlling mechanisms of the carbon oxidation are not yet fully understood, leading many authors to different conclusions [19-22].

4 Conclusion

In this research paper we have looked at the practice oxidizing area procedure which is performed in USSE Research and Development ceramic laboratory. This test method was adapted from a test method developed and used by U. S. Steel Research and Technology Center in Munhall, USA. The results of this procedure can help to find the effect on steel ladle performance. Laboratory results are being compared with the achieved operating results of steel ladles, and are used to select the best supplier of technical solution for steel ladle slag line in conditions of U. S. Steel, Košice, s.r.o..

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