CORROSION OF BASIC REFRACTORIES IN COPPER METALLURGY

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Abstract
Knowledge of corrosion processes on the melt – solid boundary is very important for life time of refractories and for refractory using design. The aim of this study was to realize and evaluate laboratory corrosion tests of three types basic refractories used in copper refining. Influence of the melts of $CuO-Na_2O.2SiO_2$ on the magnesia, magnesia-chromite and magnesia-carbon refractories was studied by crucible corrosion tests. The samples for the crucible corrosion test were made up from commercially manufactured refractories. The static crucible corrosion tests were carried out in laboratory electric resistive furnace at 1350 °C during 10 hours in air atmosphere. The results of tests were evaluated by macroscopic, microscopic and chemical analysis.

1 Introduction
Knowledge of corrosion processes on the melt – solid boundary is very important for life time of refractories and for refractory using design. This paper is aimed to experimental testing of three types basic refractories used in copper refining. Influence of the melts of $CuO-Na_2O.2SiO_2$ on the magnesia, magnesia-chromite and magnesia-carbon refractories was studied by crucible corrosion tests. Penetration of the melts into body of the refractories was observed. Results were evaluated by macroscopic, micrographic and chemical analyses [1 - 9].
The effort of these experiments was to describe interactions ongoing during the contact of basic refractories with the slag melt from the copper refining process. Perhaps the effort was also to demonstrate the potential uses of other types of basic refractories for usage in copper metallurgy. The substitutions for chromite-magnesia and magnesia-chromite refractories are being sought, which would have appropriate properties for copper pyrometallurgy as well as the worn-out lining which would not constitute a burden for environment [5 - 13]. Interactions of refractories containing Cr_2O_3 with the metallurgical melts may produce compounds containing hexavalent chromium, which, according to some literary sources, belongs to carcinogens [13 - 15], or is harmful to health [16-18].

2 Experimental part and methods
Experimental corrosion test programme was focused on the wear modeling of the lining in the process of pyrometallurgical copper refining in the flame furnace. Corrosion tests were

performed as crucible corrosion tests of the three types of commercially manufactured refractories [19]. Static corrosion test were performed by synthetic melt whose composition characterises the slag produced with pyrometallurgical refining and corresponds to the compound $Na_2O.2SiO_2$ from the steady-state phase diagram of the system $Na_2O-2SiO_2$ at the fusion point 874 °C [20].

The chemical analysis and the selected features of investigated refractories are presented in **Table 1**. Type A represents magnesia refractory, B – magnesia-chromite refractory and the sample C presents magnesia-carbon refractory. The crucibles for corrosion test were cut out of the refractories: sample A (74 x 76 x 76 mm), sample B (88 x 88 x 64 mm), sample C (82 x 82 x 84 mm). Subsequently, the hole was drilled in the samples, with dimensions$\varnothing$ 30 mm in diameter and 30 mm in height, and then these samples were put into the laboratory dryer for 24 hours/ 110 °C.

Table 1   Chemical composition and selected features of tested refractories

Components	Chemical analysis [wt. %]					
	Sample A		Sample B		Sample C	
	producer	verification	producer	verification	producer	verification
MgO	95	95,67	58	56,294	97	91,711
Fe_2O_3	1	1,34	11,5	10,15	0,6	1,4
Cr_2O_3	-	-	20	25,57	-	-
SiO_2	-	0,49	2,2	1,55	-	1,28
Al_2O_3	-	0,28	5	3,91	-	3,67
CaO	1,4	2,18	2	2,48	-	1,92
residual C	-	-	-	-	9,5	9,85
Physical properties	Sample A		Sample B		Sample C	
	producer	verification	producer	verification	producer	verification
Porosity π_a [%]	20	15,3	17	16,7	5	3,3
Bulk density ρ_b[kg.m^{-3}]	2885 (min. 2800)	2890	3200	3152	3035 (min. 2980)	3071

Synthetic slag system was made up from compounds SiO_2 (96,5 %) and Na_2CO_3 proportionately ($Na_2O-2SiO_2$) and CuO p.a.. The corrosive medium had the following composition: 25 g CuO, 4 g SiO_2 and 3.53 g Na_2CO_3, which represents saturated system of CuO in the melt $Na_2O.2SiO_2$. Corrosive medium was added to the prepared samples – ''crucible'', first CuO and subsequently the mixtures of chemicals SiO_2 and Na_2CO_3. The samples were put into the electric resistance furnace; they were heated to reach the temperature of the corrosion test 1350 °C with 10 hour maintenance in the open air. After the termination of the maintenance period, the samples were being freely cooled in the furnace.

3   Results

Crucible corrosion tests have been evaluated by the chemical and macroscopic analysis. The samples from the corrosion test were cut to width and the cut surface served for observation of

the infiltration depth of the corrosive medium to the body of the refractories and the chemical composition of the body was observed in the selected layers.

3.1 Macroscopic evaluation

Macrostructures after the corrosion test are documented in **Figs. 1 - 3**. The infiltration depth is statistically processed in **Table 2**.

Two to three infiltration zones were macroscopically observed at the cross-sections of the samples. The first zone, so-called reaction zone, occurs in the surface layer of refractory during the contact with the corrosive medium. The second zone represents the impregnated layer which is penetrated by the melt $CuO-Na_2O.2SiO_2$ and on macrostructure it is characterised by discoloration of the body. Then there is the third layer and this one represents the original body in case of magnesium and magnesia-chromite refractories and it is the external oxidised body in case of magnesia carbon refractories.

Table 2 The average infiltration depth of the corrosive medium to the samples [mm]

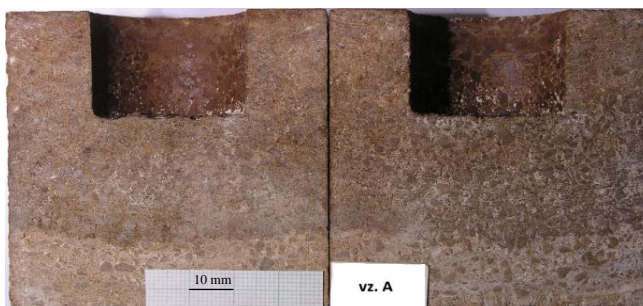| Sample	Zone 1		Zone 2		Zone 3	
	bottom	wall	bottom	wall	bottom	wall
A	2,1	0,8	8,2	17,0	16,6	-
B	3,8	4,1	15,9	11,4	6,8	4.6
C	3,2	2,1	35,7	9,4	1,4	8,9

Fig. 1 Macrostructure of the magnesia refractory (A) after the corrosion test with the melt of the system $CuO-Na_2O.2SiO_2$

Fig. 2 Macrostructure of magnesia-chromite refractory (B) after the corrosion test with the melt of the system $CuO-Na_2O.2SiO_2$

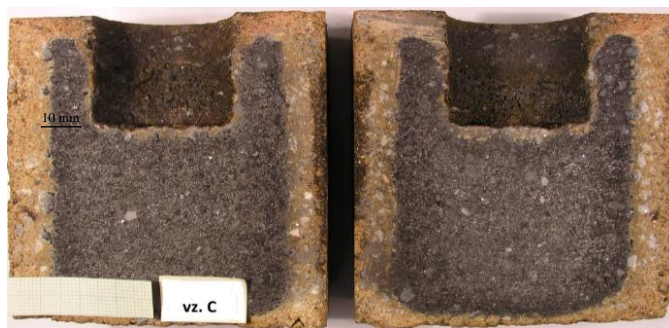**Fig. 3**   Macrostructure of magnesia-carbon refractory (C) after the corrosion test with the melt of the system CuO-Na$_2$O.2SiO$_2$

From the presented figures it is obvious that during the corrosion test the penetration of the melt CuO–Na$_2$O.2SiO$_2$ is complete, however the residual layer of the products from the mutual reaction of the slag and the body has been observed.

In the surface layer of the body, so-called reaction layer (zone 1), there is an increased concentration of oxides of copper and of reaction products between the body of the refractories and the corrosion melt. According to the visual assessment, the density of this layer is higher than the following body zone, its thickness is from 0,8 mm (sample A) to 4,1 mm (sample B) in the crucible walls, or at interval from 2,1 mm (sample A) to 3,8 mm (sample B) at the bottom of the crucible.

After macroscopic evaluation of the external surface of the samples (the crucible sides) after the crucible corrosion test it was found that during the corrosion test the corrosion melt penetrated into the external surface of the samples.

3.2 Chemical analysis

The infiltration depth of corrosive medium components was studied by the chemical analysis of the body at a distance of 5 mm (e.g. A-1), 20 mm (e.g. A-2) and 40 mm (e.g. A-3) from the crucible bottom (sample). For the element analysis, within an adequate distance the samples were drilled by the method AAS on the equipment PerkinElmer 3100. The infiltration of elements Cu, Na and Si was observed; the obtained results are presented in **Table 3**.

Table 3   The element analysis of the penetrated body after the corrosion test depending on the distance from the crucible bottom (5, 20 and 40 mm).

sample	Content of elements [wt. %]		
	Cu	**Si**	**Na**
A-1	5,53	0,80	0,41
A-2	4,03	0,41	0,12
A-3	0,063	0,32	0,18
B-1	4,53	0,64	0,26
B-2	1,33	0,99	0,12
B-3	0,33	1,26	0,31
C-1	0,39	0,78	0,01
C-2	0,26	0,85	0,09
C-3	0,32	1,10	0,095

4   Discussion

On the samples of the basic refractories (magnesia, magnesia-chromite and magnesia-carbon refractories) observations were made on the corrosion melt of the system $CuO-Na_2O.2SiO_2$ at 1350 °C/ 10 hours by the crucible corrosion test. The obtained results demonstrate the complete infiltration of the corrosion melts to the body of the basic refractories. In case of MgO-C refractory, during the contact with the oxidic slag a thin layer was formed at the crucible bottom and on the sides of crucible. During the corrosion application the new zone structure is being created in the body of the refractories. In the surface layer (thickness about 1 to 2 mm) there is the intensive penetration of the corrosive medium and also there are the chemical reactions with the refractory components (MgO, or $MgO-Cr_2O_3$) resulting in the formation of the relevant compounds. The next one is the infiltrated zone impregnated by the corrosion melt and the process of the chemical reactions is assumed to be the same as the one in the reaction zone. The last zone presents the least corrosive body where no significant visual changes of the body has been observed during the macroscopic evaluation of the samples.

The results of the chemical analysis of the corrosive samples proved the knowledge from the macroscopic observation. In the magnesia sample (sample A) and the magnesia-chromite sample (sample B) it was established that the surface layer (under the reaction zone) contains a maximum content of copper (5.53 wt.% or 4.53 wt.%) decreasing towards the sample surface to 0.063 wt.% or 0.33 wt.%. The concentration of silicon and sodium differs in the process. In magnesia refractory (sample A) there is a gradual decrease in the content of Si and Na in the body of the sample. In case of the magnesia-chromite refractory a contrary process in the content of Si and Na is possible to observe; their concentration decreases from the reaction surface towards the external surface. This difference in composition of the penetrated body is connected with the presence of the chromic ore in the sample B. The corrosion of magnesia-carbon refractory (sample C) occurred in a completely different way. The content of copper in the corrosive body has been considerably lower than in the samples A and B, while the change in the content of silicon demonstrated the similar process as the sample of the magnesia-carbon refractory (sample C). The biggest difference was found in the penetration of sodium into MgO-C refractory. The measured concentrations were approximately an order-rate lower than in MgO, or $MgO-Cr_2O_3$ refractories.

On the basis of the presented results of the corrosion tests it is obvious that the corrosion mechanism of the studied types of basic refractories by the melt of the system $CuO-Na_2O.2SiO_2$ takes place as various chemical reactions. The provided results confirm the presumptions about the mutual reactions between the components of the basic refractories (MgO and Cr_2O_3) as well as the presumptions about the change of the redox conditions during the corrosion of magnesia-carbon refractories.

5   Conclusion

In the presented contribution there is an assessment of the process of the corrosion wear of the basic refractories by the melt of the system $CuO-Na_2O.2SiO2$. Corrosion tests were performed as crucible corrosion tests at 1350 °C during the period of 10 hours. The corrosion process has been evaluated by macroscopic and chemical analyses. The obtained results indicate the significant difference in the corrosion wear of the magnesia, magnesia-chromite and magnesia-carbon refractories. To know the wear process of the studied systems it is inevitable to perform further evaluations of the corrosive body as well as to know the structure of the corrosion melt

depending on redox conditions. The given evaluation presents the primary results for comparison of the corrosion process and they may provide the basic knowledge for substitution of the chomite and magnesia-chromite refractories in copper metallurgy.

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