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BEHAVIOR OF REFRACTORIES IN INTERACTION WITH METALLURGICAL SLAG

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ABSTRACT

The aim of this paper is to present the studies concerning behavior of the refractory to metallurgical slag corrosion. The corrosion resistance at high temperatures using the static method on samples containing chamotte or alumina were performed. The corrosion degree of refractory plastic mass was established by corrosion determination, and the corrosion rate and macroscopic image analysis measurements. The analysis of samples subjected to macroscopic measurements showed a better behavior in terms of corrosion resistance for alumina samples.

KEYWORDS: refractory plastic mass, cast iron, slag, chemical corrosion

1. Introduction

The most solicited parts in direct contact with the cast iron and metallurgical slag are the tap hole of the furnace and the cast iron gutters for the transportation of the cast iron ladles. The maintenance and correct operation of the tap hole cast iron have a great importance for the normal operation of the furnace in complete safety. It is necessary that the amount of plastic used to seal, the outlet provide, besides a good seal, a wear protective of carbon mass of the crucible and the tap hole. A measure for assessing the refractory plastic mass behavior during utilisation is the chemical corrosion resistance. A mass with a high chemical corrosion resistance protects the surrounding area but also provides a corresponding flow to technology.

Corrosion resistance, in this case, is considered the property of refractory products that do not degrade under the chemical action of cast iron and slag. The corrosion intensity of refractory lining depends on the chemical nature of the refractory material and of the corrosive material that reacts with the first. The temperature has an important role in enhances of the corrosion process.

The chemical etching of the refractory by the cast iron or steel occurs after a solid-liquid reaction, quite slow and less important than the reaction of the refractory material with slag. For this reason, the studies are directed, particularly, to the system slag - refractory material. There are many studies on the chemical corrosion of refractories. In the following part will be presented a few examples of the corrosion processes, referring to the refractories Al_2O_3-SiC-C systems.

1.1. A review of the corrosion mechanism study

The study of refractory etching by slag is one of particular importance [1]. The refractory resistance could be weakened by the dissolving action in liquid slag. The slag etching on refractories in contact can occur in two ways:

- corrosion - refractory wear and tear caused by the chemical etching of slag;
- erosion - caused by mechanical action, namely detachment and involvement of the slag material by the slag refractory material [1].

The slag and metal infiltration in the refractory grains, the mechanical erosion caused by moving liquid slag and the slag chemical etching, all that contributes to the loss of the refractory masonry [2].

The chemical corrosion can be defined, as it is known [3] that refractory wear by mass loss, ie the thickness of refractories exposed as a result of chemical etching by a corrosive liquid. The refractory and the liquid will react at the interface, reaching chemical equilibrium in the contact area between the refractory and corrosive liquid.

With the chemical reactions during corrosion, physical changes occur that could accelerate the corrosion process. The corrosion is the refractory wear by the loss of thickness and mass of the exposed refractory due to chemical etching by the melt, in a process where refractory and melt react, chemically balanced in the contact zone between the refractory and the melt. This is a key point because the corrosion reaction continue until it reaches a steady state. For the corrosion analysis and to anticipate the chemical strategies to reduce the corrosion and wear rate, some authors [3] propose phase equilibrium diagrams. In this context, there are two possible approaches: the first is to see the corrosion as a chemical and physical process without a detailed application of equilibrium phase diagrams, called "phenomenological approach" and the second approach involves using information from the phenomenological approach in phase equilibrium diagrams. This last option is necessary for a full understanding of refractory corrosion [3].

Juergen Pötschke and Thomas Deinet think that the refractories in contact with molten slag and steel show a wide variation of behavior in terms of corrosion resistance. The corrosion is based on the Marangoni convection.

References provide details on this topic [4]. The diffusion process and the controlled chemical reactions between the three phases - slag, refractory and steel - lead to a concentration gradient affecting the interfacial free energy of steel and slag, minimization of them.

This causes a strong flow transmitted by convection from the boundary between phases, which causes a significant reduction and improvement layer diffusion and mass transfer. A model was developed to predict the corrosion rate. This paper presents a contribution to understanding the experiments and their quantitative expression. As a first approximation, the corrosion rate in mm/h can be estimated as the difference between the refractory and the slag saturated concentration and the initial composition, regardless of the slag type and the steel composition. These studies can develop depending on the slag composition of steel and steel mills specific conditions [5]. Local corrosion was studied on alumina-graphite refractory interface and slag by immersion tests and direct observation technique using high temperature X-ray. Combining these investigations with microscopic studies, a mechanism for local corrosion was developed.

The mechanism is based on the cyclic dissolution of alumina and graphite in slag, respectively molten metal phases. It was found that during the dissolution of refractory with alumina slag film, movement induced Marangoni effect and the evolution of gas bubbles can accelerate the dissolution process [6]. William Smothers and A.R. Cooper studied the situations when there is mutual penetration of two interacting phases (refractory material and liquid slag) beyond the border pan, in the adjacent plan [9]. They have revealed that the dissolution of the solid phase in a liquid phase (slag in the present situation), decreases the rate of diffusion through the liquid phase to exceed the solubility limit in oxide components of the refractory material.

The corrosion occurs due to heterogeneous chemical reactions between liquid phases (slags and other melts) and refractories. Reaction products can exist in one of the following situations: moving, in general, in the slag or melting, to form new compounds, to diffuse into the surface lining or refractory lining [9].

2. Materials and methods

The corrosion resistance study at high temperatures using the static method (STAS 5193/1-83) on a set of samples containing alumina or chamotte were analyzed. To evaluate the corrosion degree of refractory plastic mass, the corrosion coefficient and the corrosion rate, macroscopic image analysis measurements of samples were made.

Two types of refractory masses, noted A and B were subjected to analysis.

The proportion of raw materials, the chemical – oxide composition and physico-mechanical properties of the samples are presented in Tables 1 and 2.

Table 1. *Raw materials composition*

Material used	**Material quantity [%]**	
	A	**B**
Sand	25.0	-
Fire clay	15.0	-
Alumina	-	39.5
Reactive alumina	-	0.5
Clay	30.0	30.0
Coke breeze	10.0	10.0
Graphite	10.0	10.0
Silicon carbide	10.0	10.0
Phosphoric acid	27.65	27.65
Novolac	2.9	2.9
Hexamethylen tetramine	0.9	0.9
Tehnocell	1.0	1.0
Meraklon	0.5	0.5
Ceramic fiber	-	1.0

In Tables 3 and 4 are presented the variation limits of the chemical composition for blast furnace slag and cast iron analyzed.

Table 2*. Chemical and oxide composition, physical and mechanical properties*

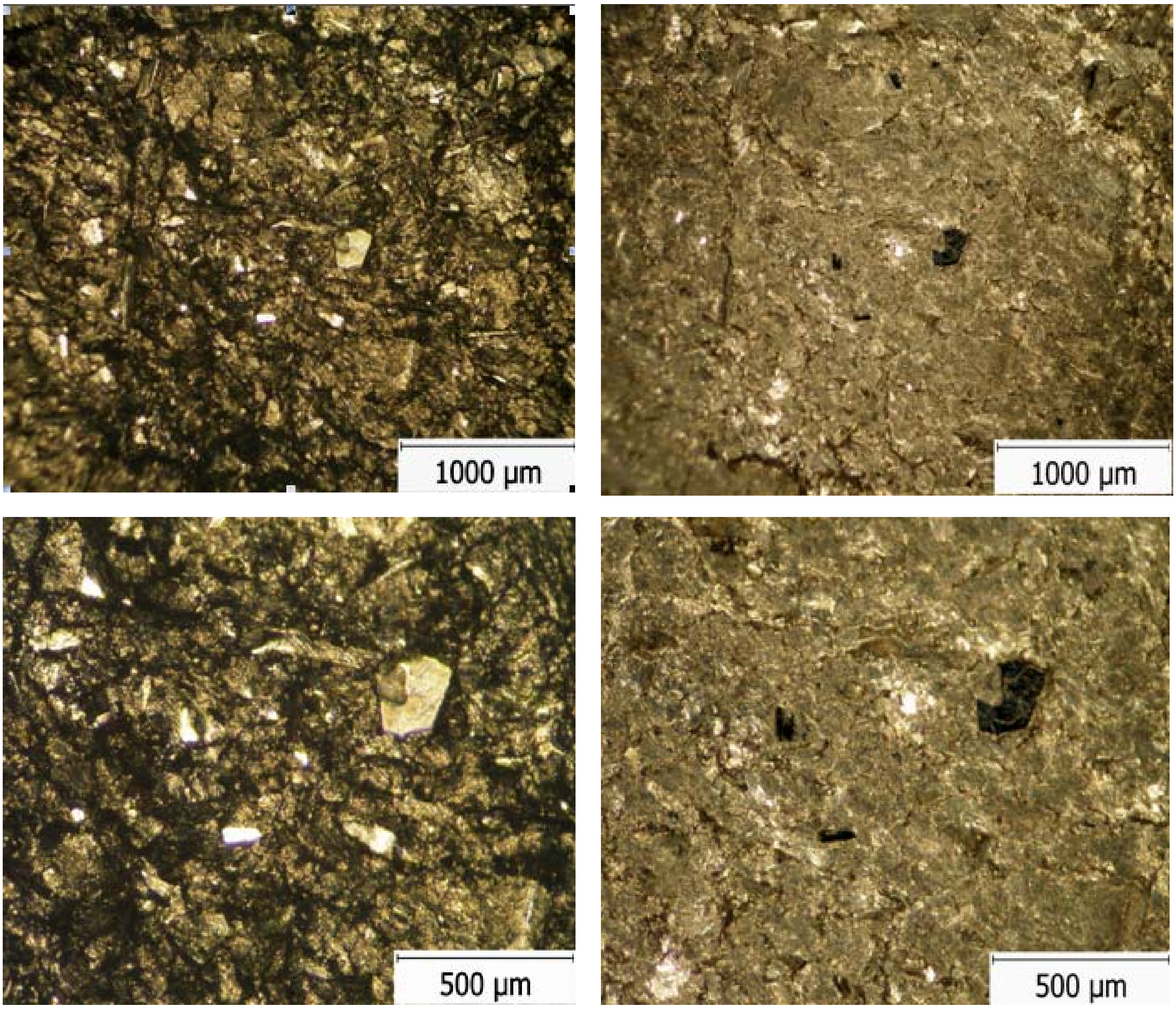
Experimental masses	**Composition**					**Physical and mechanical properties**		
	SiO_2	**Al_2O_3**	**SiC**	**C**	**Fe_2O_3**	**Apparent density**	**Apparent porosity**	**Compressive strength**
	[%]					[g/cm^3]	[%]	[N/mm^2]
A	48.28	17.22	9.30	17.41	1.26	2.03	28	12
B	19.50	47.95	9.30	17.41	0.86	2.36	20	16

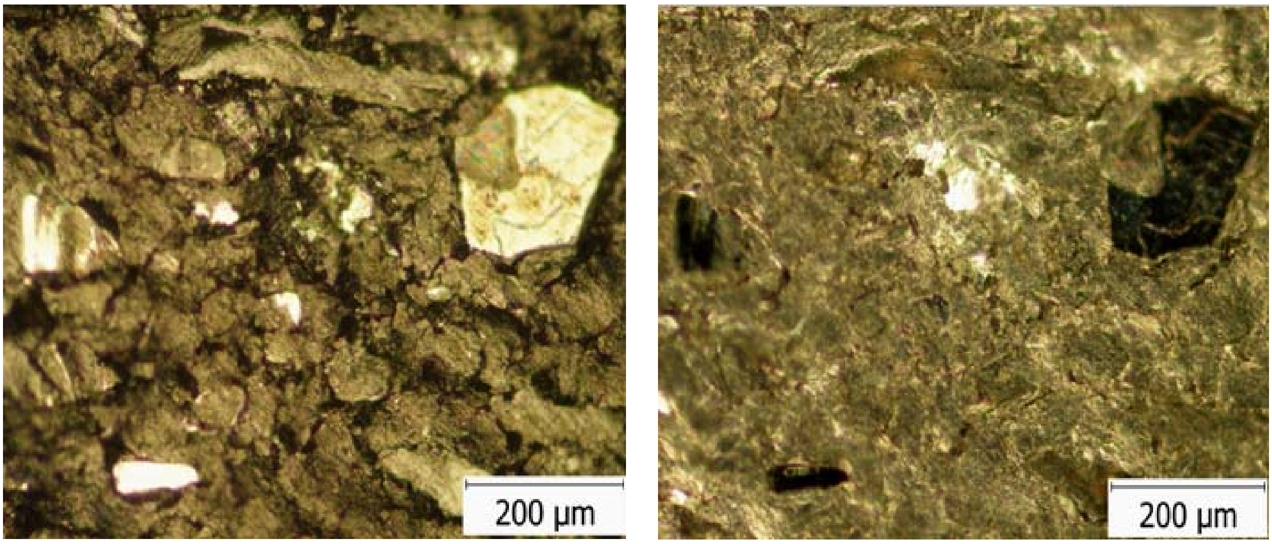
Table 3. *Chemical composition of blast furnace slag, [%]*

CaO	**SiO_2**	**Al_2O_3**	**MgO**	**MnO**	**FeO**
43 ÷ 44	34.1 ÷ 35	12.5 ÷ 13.5	5.86 ÷ 6.26	0.66 ÷ 1.49	0.54 ÷ 0.66

Table 4. *Chemical composition of cast iron, [%]*

C	**Mn**	**Si**	**S**	**P**
3.90	0.4 ÷ 0.7	0.4 ÷ 0.7	> 0.003	0.08÷ 0.10





a b

Fig. 1. *Optical micrographs of sample A for polished surface in bright field (a) and dark field (b) at various magnifications*

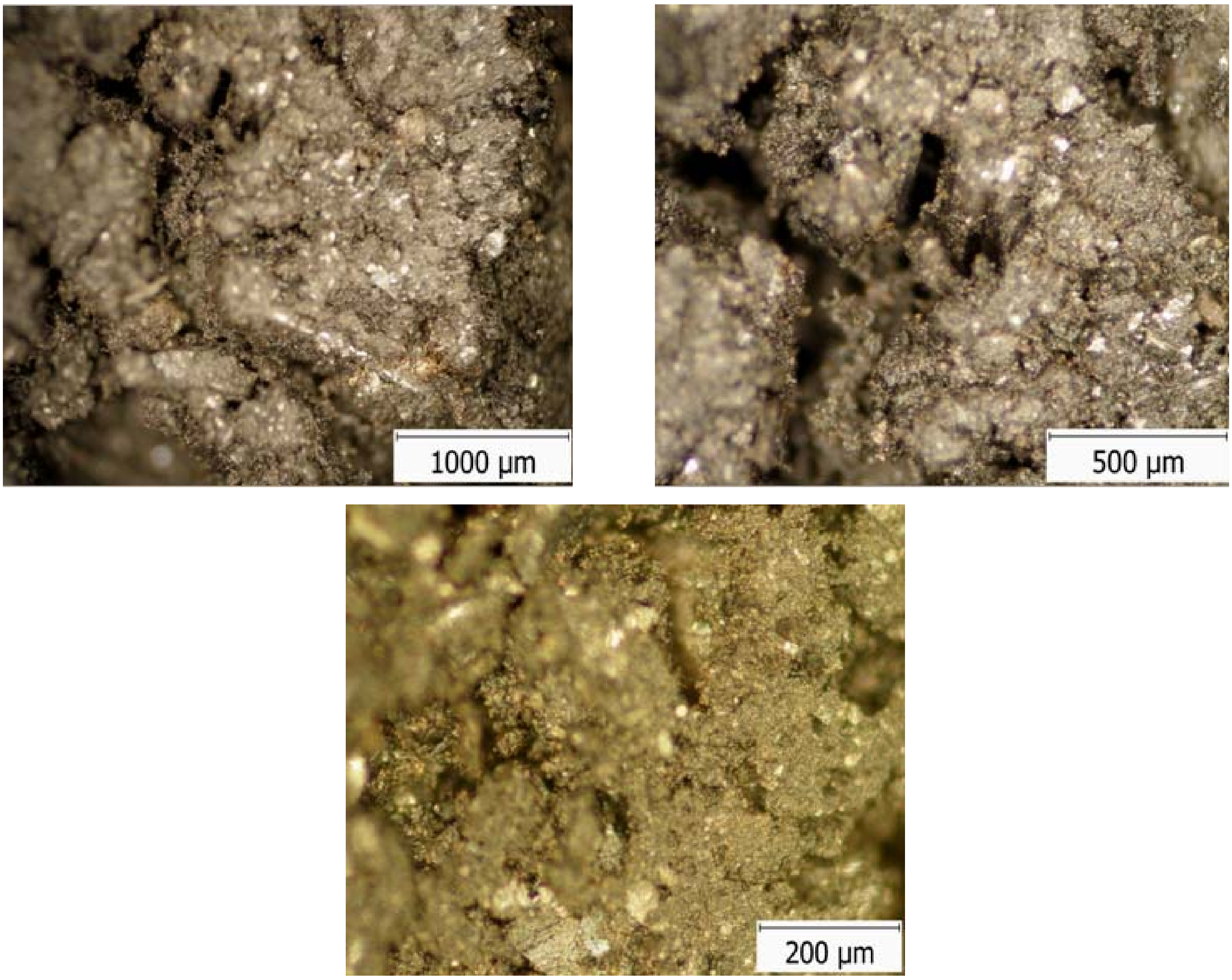
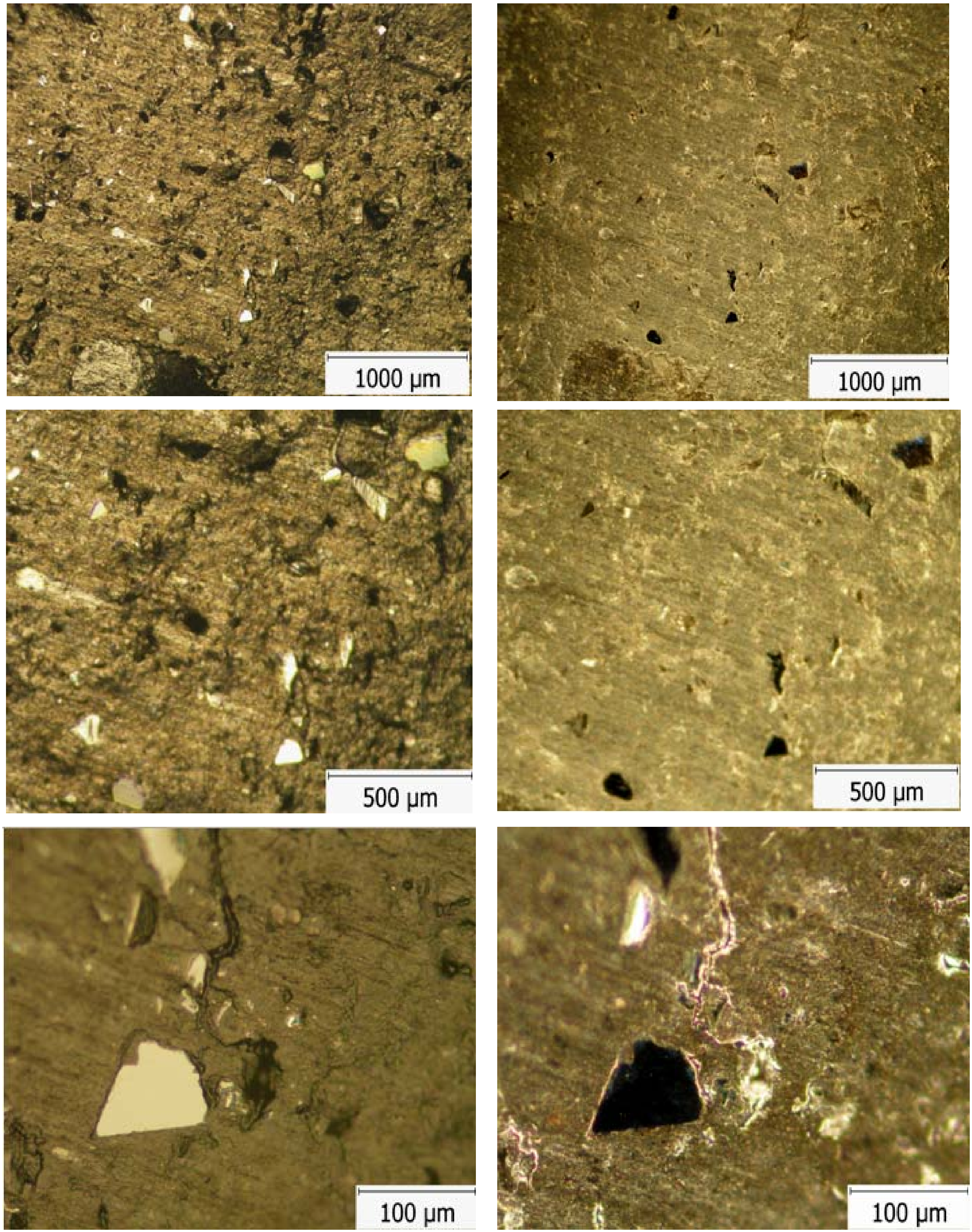


Fig. 2. *The optical micrographs of sample A for breaking surface in dark field at various magnifications*



a b

Fig. 3. *The optical micrographs of sample B for polished surface in bright field (a) and dark field (b) at various magnifications*

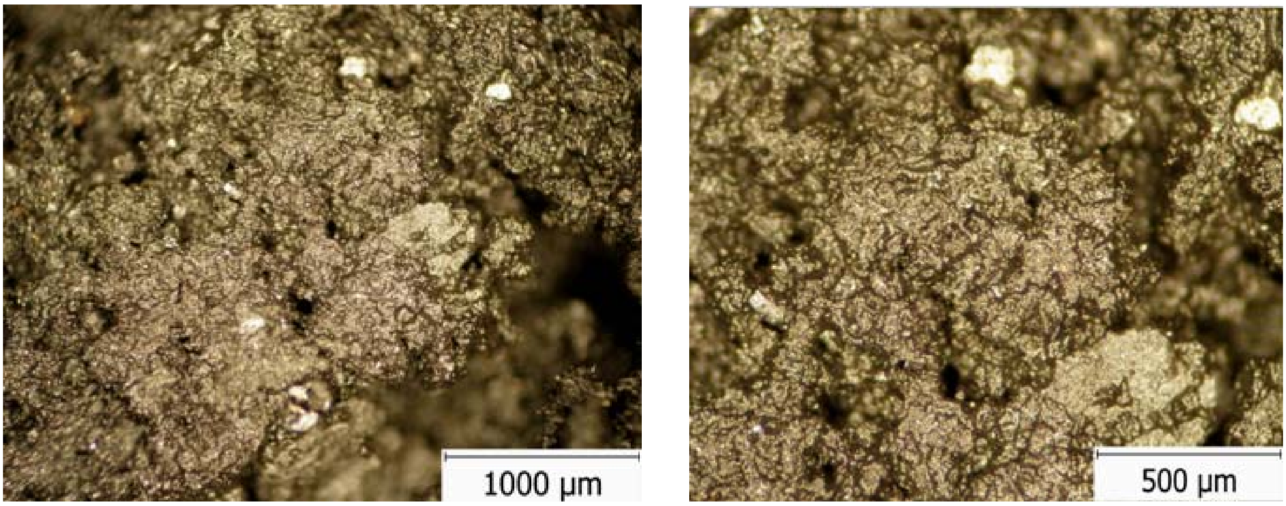


***Fig. 4.** Optical micrographs of sample B for broken surface in dark field at various magnifications*

The two refractory materials, noted A and B, were analyzed using optical microscopy (Figures 1-4).

The metallographic analyzed were conducted at the Faculty of Metallurgy and Materials Science and Environment, “Dunarea de Jos” University of Galati, with an Olympus BX51M metallographic microscope image analysis are briefly presented.

In Figures 5, 6, 7, 8 the specimens appearance after the corrosion measurements are presented.

Fig. 5.** Fire-clay containing sample, subjected to the action of iron **(A1)

Fig. 6.** Alumina -containing sample, subjected to the action of iron **(B2)

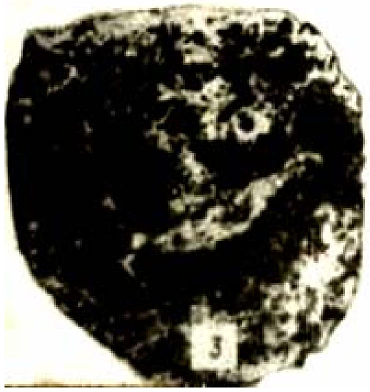


Fig. 7.** Fire-clay containing sample, subjected to the action of slag **(A3)

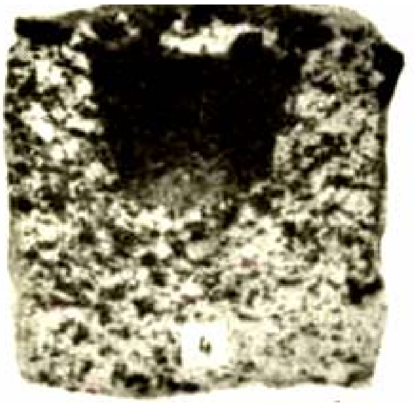


Fig. 8.** Alumina -containing sample, subjected to the action of slag **(B4)

Table 5. *Texture description of samples*

Sample	Basic materials	Homogeneity	Compactness	Grain size	Grain distribution
A	Chamotte, quarz, silicon carbide	homogeneous	porous	coarse	iregular
B	bauxite, quartz, silicon carbide	homogeneous	compact	fine	uniform

The four sets of samples were tested, two corresponding to mass composition A and two corresponding to mass composition B. Corrosion measurements are presented in Table 6.

Table 6. *Corrosion measurements for analyzed samples*

Sample	The main component	Corrosive factor
A1	chamotte	iron
B2	alumina	iron
A3	chamotte	slag
B4	alumina	slag

3. Results and discussion

The corrosion degree of refractory plastic mass was identified by determining:

1) corrosion coefficient, I [%];
2) corrosion rate, V_c [mm/s].
3) macroscopic image analysis;

The resulting values from the determinations are presented in Tables 7 and 8. In Figures 5, 6, 7, 8 in samples with cast iron (A1 and B2) it was found that samples having the chamotte refractory as aggregate were deformed, while those which had used high purity alumina remained undistorted (Figures 5, 6).

Table 7. *Corrosion coefficient of analyzed samples*

Sample	Initial surface, S_o	Final surface, S_f	Final diameter, D_{if}	Coefficient α	Initial volume, V_o	Final volume, V_f	Corrosion coefficient, I
	[mm^2]		[mm]		[mm^3]		[%]
A1	600	704	34	1.20	14130.00	30294.72	214.40
B2	600	651	32	1.20	14130.00	28297.68	200.27
A3	600	1092	44	1.30	14130.00	50227.44	355.47
B4	600	651	32	1.20	14130.00	28297.68	200.27

Table 8. *Corrosion rate of analyzed samples*

Sample	Initial radius, R_o	Final radius, R_f	Time keeping, T_c	Corrosion rate, V_c
	[mm]		[s]	[mm/s]
A1	15	17	7200	27.78×10^{-3}
B2	15	16	7200	13.89×10^{-3}
A3	15	22	7200	97.22×10^{-3}
B4	15	16	7200	13.89×10^{-3}

In the structure of alumina samples (Figs. 6 and 8) two zones can be distinguished: one impregnated with slag and an area unchanged. The impregnated area, with thickness up to 1 mm grain consists of slightly glazed with iron and silicon carbide crystals unchanged diffused in glazed mass, mixed with metal droplets. The unimpregnated area consists of large portions (about 2 mm diameter) of glassy appearance and black crystals with sharp angles of silicon carbide. Samples with chamotte, after slag etching resistance (Figs. 5 and 7) were deformed, if the sample containing slag, there are three areas (Fig. 5):

- *the working area*, with up to 6 mm thickness is coated with slag;

- *the least modified area* of about 1.2 mm thickness is brighter than working area, but mass was melted and compacted;
- *the unchanged area* is loose, opaque and fragile.

The sample containing alumina is instead much less etched by slag (Fig. 8). The silicon carbide refractory mass does not change during heat treatment.

4. Conclusions

Following corrosion measurements and the corrosion degree of the refractory plastics mass, it was found that:

- ⇨ the action of cast iron on the refractory material is less intense than the action of the slag. Replacing the chamotte in the mass composition with alumina increased the corrosion resistance of the refractory mass at slag corrosion.
- ⇨ the alumina sample (noted B) resulted in a smaller corrosion coefficient and the corrosion rate is lower than that of the chamotte sample (noted A).
- ⇨ the analysis of samples subjected to macroscopic measurements showed a better behavior in terms of corrosion resistance for alumina samples.
- ⇨ the test results for corrosion are related to chemical and mineralogical composition, texture and compactness, sample B having a homogeneous structure with uniform grain distribution and more compact than sample A, having strengths higher corrosion than sample A;
- ⇨ the alumina sample (noted B) is better in terms of chemical stability, the resulting lower corrosion coefficient values and the corrosion rate being lower than the chamotte sample (noted A). This conclusion is confirmed by the macrostructural analysis performed in the fracture surface.

It can be appreciated that in set B, the amount of alumina particles is higher, they are finely dispersed and are physical barriers to crack propagation.

This led to the dispersion hardening phase samples (a significant increase in compressive strength) and on the other hand they have blocked sample degradation by delaying the formations of a network of intercommunicant cracks.

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