

## STUDYING FURNACE REFRACTORY LINING PROPERTIES WITH COPPER MATTE SMELTING

Received – Primljeno: 2019-07-15

Accepted – Prihvaćeno: 2019-09-10

Preliminary Note – Prethodno priopćenje

Today the most common copper matte smelting process is smelting in reverberatory furnaces. The problem is that due to the depletion of ore reserves, the poorer ore is involved in the processing. If in 2007, according to the data of the Kazakhmys Corporation LLP, the average copper content in ore was 1,24 %, in 2018 this indicator has already decreased to 0,91 % [1-4].

*Key words:* chromite ores, magnesite, strength, porosity, structure

### INTRODUCTION

Changing the composition of copper ore and, therefore, copper concentrate towards its depletion leads to changing the composition and quantity of matte and slag formed during smelting. According to [5-8] in the 90-s of the last century the content of sulfur in the matte of the Balkhashtsvetmet JSC was 26,8 %; at the moment this figure has increased to 29,3 %. The zinc content in the slag is 0 % and 0,6 %, respectively. The amount of slag increased from 1,1 t/t of copper to 1,3 t/t of copper.

It is obvious that changing the composition and increasing the amount of slag affects adversely the durability of the furnace lining during matte smelting. The composition of slag affects its viscosity: slag with a high content of FeO is low-melting, it has low viscosity, it easily flows into the pores of the lining and causes its destruction.

In recent years, due to changing the composition of raw materials, the composition of slag during matte smelting has changed in the direction of increasing the FeO content, which contributes to further decreasing slag viscosity, which, in turn, contributes to greater destruction of the lining.

According to the technical specifications (ST DGP 38911750-001-2019).

At present for the furnace walls lining with matte smelting, there is used magnesite-chromium brick of the following composition: 25 – 30 % chromite, 65 – 70 % magnesite, 1,2 - 1,5 % sulfite-alcohol stillage as a binder. Partial replacement or repair of the lining occurs on average after 5 - 6 heats; the main reason for the lining or its individual sections failure is chemical interaction of the slag and the matte components that leads to corroding the surface and leaking the melt into the

pores, and, as a result, to the complete destruction of the masonry.

The objective of this study is to develop a refractory for the furnace lining with copper matte smelting that possesses increased resistance owing to adjusting the parameters of porosity.

Present day refractory magnesite-chromium products have open porosity in the range of 10 - 15 %. Reducing the value of porosity below these limits seems inappropriate, because decreasing porosity will lead to increasing density and, consequently, the mass of the product. Therefore, the solution of the problem must be approached on the other hand: not to reduce the proportion of porosity in general but to reduce the proportion of open porosity, i.e. the proportion of pores available for melt flowing.

The analysis of studies [9-15] dealing with the relationship of strength and porosity shows that with increasing the number and the radius of pores, the body strength decreases. In addition, the pore size distribution greatly affects the refractory strength: the more monotonous the nature of the pore size distribution, the higher the probability of increasing the body strength.

Summarizing these provisions, it can be stated that the most optimal porous structure for the refractory in terms of strength and resistance to melt flowing will be the structure with the maximum possible proportion of closed porosity, and the pore size distribution should be fairly uniform. Increasing total porosity above 10 – 15 % in this case does not make sense, because it will lead to strength reducing; decreasing the proportion of porosity, as noted above, will lead to increasing the mass of the product.

In this study there was used the following mixture: poor chromites of the Sarsai deposit 35 %, magnesite from the Buranov deposit 60,5 % (both from Kazakhstan), sulfite-alcohol stillage as a binder 2 %, water 2,5 %. The composition of the basic components is given in Table 1.

A. Z. Issagulov, M. K. Ibatov, Sv. S. Kvon, V. Yu. Kulikov, Chsherbakova Ye. P. (e-mail: sherbakova\_1984@mail.ru, KSTU), Karaganda State Technical University, Karaganda, Kazakhstan.

Table 1 The composition of the charge basic components

Sample	Chromite	Sintered magnesite
Content / %		
MgO	24,2	46,2
SiO <sub>2</sub>	2,8	10,5
Fe <sub>2</sub> O <sub>3</sub>	22,3	1,1
Al <sub>2</sub> O <sub>3</sub>	16,3	1,1
CaO	2,4	2,6
Cr <sub>2</sub> O <sub>3</sub>	29,3	-
FeO	5,1	-

The formation of the porous structure is affected by several main factors: the fractional composition of the charge; pressing pressure; the firing temperature and time; the amount and composition of the liquid phase formed during sintering [5].

The classic mode of pressing magnesite-chromite refractories is pressing pressure in the range from 80 to 130 MPa, and pressing is carried out at constant pressure. The calcination temperature is 1 600 °C ... 1 700 °C within 20-30 hours. During the calcination process the moisture of the charge is removed; as a result of interaction of chromite and oxides of silicon, magnesium and aluminum, compounds of a number of olivine with a high melting point are formed, which determines the refractory properties of the product.

It is known that in order to reduce the product porosity it is necessary to combine the coarse and fine grinding fractions [6]. This combination of large and small fractions allows filling the voids that are formed by a large fraction and thereby reduce the charge mass fractional void volume that later on forms porosity.

In this study, the following fractional composition was used. Chromite ore was crushed to the particle size of 150 microns, magnesite pitch to the fraction of 50 microns. Next, the components were mixed in the above proportions, samples were pressed from the prepared mixture, and pressing pressure varied throughout the process. The pressure variation during pressing is due to the following circumstance. Studying the relationship between changing porosity and the value of externally applied pressure [5, 6] has shown that the applied external pressure has a different effect on the process of changing porosity at different stages of pressing.

At the initial stage external pressure contributes to the reducing porosity and developing high speed shrinkage due to the «healing» of small pores and void volume; at this, the average pore size varies slightly.

At the next stages of the process external pressure does not practically affect the change in total porosity but contributes to the pores coalescence and their closure, while the average pore size somewhat increases according to the law:

$$R \approx \tau^{1/3}, \quad (1)$$

where R is the pore average size;  
 $\tau$  is the time.

Thus, the pore size distribution depends on external pressure: the number of small pores decreases with in-

creasing pressure and is accompanied by significant porosity reducing, at the second stage pressure has a smaller effect on the reduction of the total pore volume but it contributes to the coalescence process and their partial closure.

## EXPERIMENTAL STUDIES

### Equipment and tools

As noted above, the optimal structure for the refractory lining will be a porous structure with evenly distributed closed pores, and the pore size range should not be very large.

Based on the above, we proposed the following graph of pressure changes: high pressure at the initial stages of pressing, which contributes to the speed of shrinkage and reducing porosity; pressure reducing at the second stage contributes to the process of forming closed porosity, reducing energy consumption and reducing wear of hydraulic presses (Figure 1).

The graph of pressure changing is shown in Figure 1.

Then the samples were dried and placed in a kiln for firing. The firing temperature also varied throughout the process (Figure 2).

Gradual changing the heating temperature contributes to reducing the risk of thermal stress development

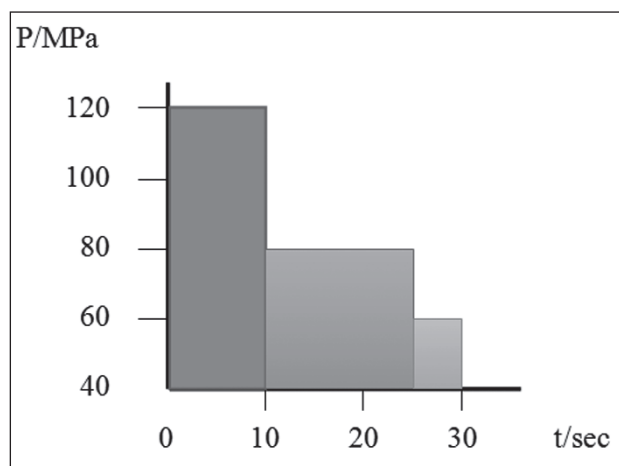


Figure 1 Graph of pressing pressure changing

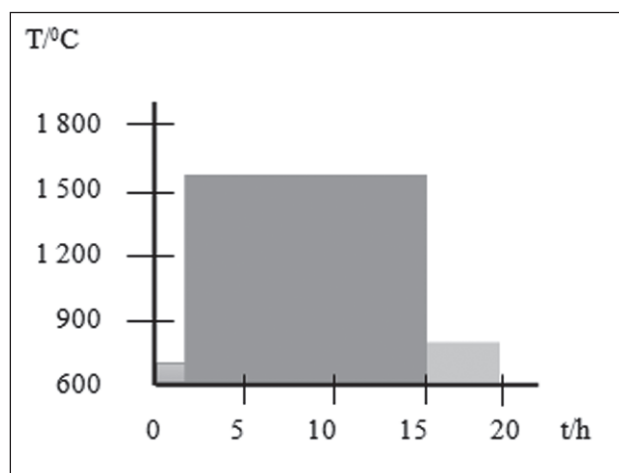


Figure 2 Graph of the firing temperature changing

and structure stabilization. Reducing the firing time according to equation (1) reduces the recrystallization time of the pores, as a result of which the average size should decrease.

After firing and complete cooling the porous structure of the test samples was studied. At the first stage the total porosity of the samples was determined by the pycnometric method, at the second stage the open porosity was determined by the mercury porometry method using the Pascal400 system, which allowed obtaining complete information of the porous structure nature.

## Discussion of the results

The results of the studies are summarized in Table 2. For comparison, samples of the currently used lining of the furnace at the Balkhashtsvetmet JSC (reference sample) were used.

Table 2 Results of testing porosity

Sample number	1	2
Sample	reference	prototype
Total porosity / %	14	13,5
Open porosity / %	12	6
Average size of open pores / $\mu\text{m}$	17,3	0,36

From the data in the Table it can be seen that with the same total porosity, in the reference sample the percentage of open porosity is almost two times higher than in the prototype. In addition, the reference sample is characterized by a large average pore size and a non-uniform pore size distribution function (Figure 3a).

The prototype has lower open porosity, it is characterized by a more uniform pattern of pore size distribution (Figure 3b) and has a smaller average pore radius. Decreasing the average size of open pores is sharper than expected according to equation (1), this fact can be explained by the formation of a liquid phase during firing that was not taken into account. The different nature of the porous structure of the prototype suggests that it will have higher resistance to slag flowing into the pores and, therefore, all other things being equal, a longer service life.

To determine resistance against slag flowing, the following tests were performed. In the samples there was bored a hole with the diameter of 15 mm and the depth of 35 mm. The crushed slag was poured into the hole after smelting on matte, the samples were placed in the kiln at the temperature of 1 600 °C and held within 4 hours. After complete cooling the samples were cut along the hole and the size of the column of flown slag was measured at  $\times 50$  magnification (Figure 4).

In addition to the depth of penetration, the temperature resistance of the prototype was also determined by the method of immersion. The prototype and the reference sample were immersed in the copper matte melt at the temperature of 1 500 °C and held within 15 minutes. After complete cooling to the room temperature the sample was again immersed in the melt and held.

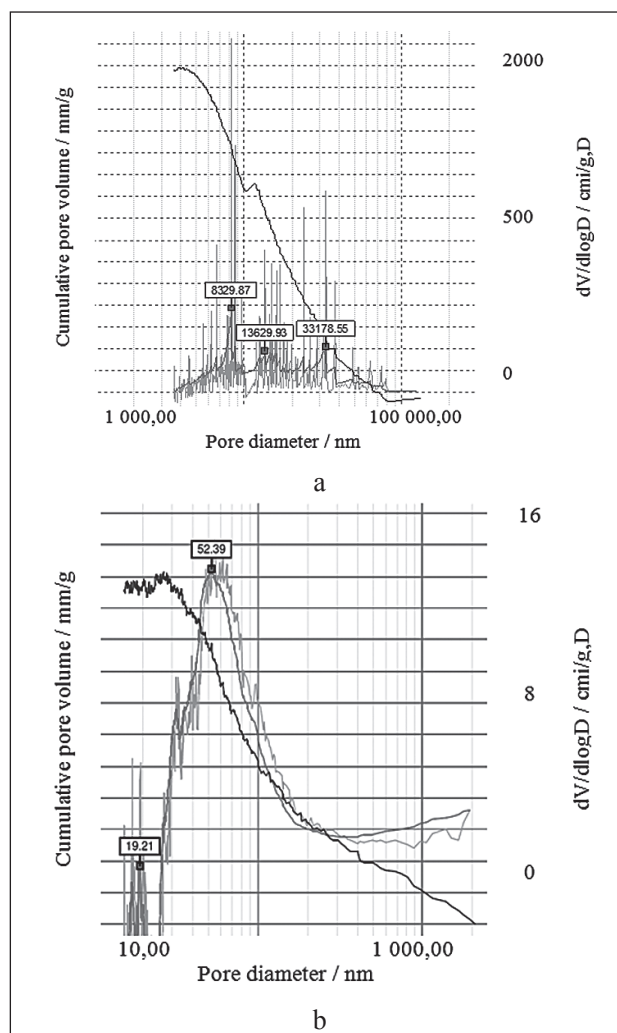


Figure 3 Samples porograms: a – reference sample; b – prototype

The end of the test was the sample destruction. The test results are shown in Table 3.

The test results show that the prototype had a higher degree of resistance to slag penetration and increased

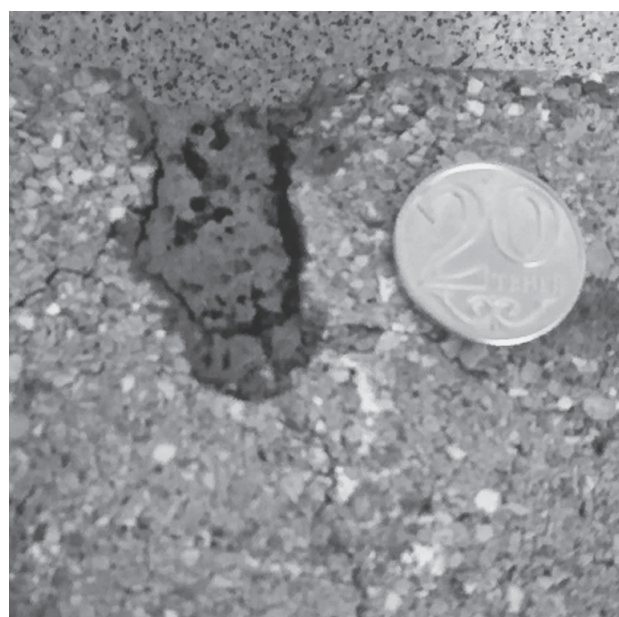


Figure 4 Example of slag flowing in the Prototype – 50x

Table 3 Results of testing for slag resistance and heat resistance

Sample number	1	2
Depth of penetration / mm	35	27
Number of immersions	12	8
Compressive strength / MPa	23,3	20,5

heat resistance. This fact can be explained only by the nature of changing porosity in the prototype. A smaller percentage of open porosity and decreasing the average size of open pores contribute to the improvement of slag resistance, more uniform distribution of pores contributes to increasing heat resistance since the level of stress in the refractory decreases.

## CONCLUSION

Thus, the pressing of chrome magnesite using poor chromite ores according to the proposed pressing and firing mode, contributes to forming a product with reduced open porosity, a smaller average open pore size and more uniform distribution of pore size. This nature of the porous structure provides higher operational properties of the lining with copper matte smelting.

## REFERENCES

- [1] <http://www.kazakhmys.kz/ru/news/id/120/> Official site of the Kazakhmys LLP
- [2] [http://metallcheckiy-portal.ru/news/2012/6/22/kazaxmis\\_na\\_mednom\\_golodanii](http://metallcheckiy-portal.ru/news/2012/6/22/kazaxmis_na_mednom_golodanii)
- [3] Kremer R., Lutz R. Improving the quality of shaped refractory products due to modern pressing technology. *Refractories and Technical Ceramics*, 4(2007), 31-35.
- [4] Issagulov, A.Z., Kvon, Sv.S., Kulikov, V.Y. Studying microstructure of heat resistant steel deoxidized by barium ferrosilicon. *Metalurgija*, 55(2016)3, 388-390.
- [5] Geguzin Ya.E. *Sintering Physics*. M.: Nauka, 1984. 312 p.
- [6] Lutz R. Two-layer refractory products obtained by automatic pressing of two different materials in one working cycle. *Refractories and Technical Ceramics*, 3 (2007), 33-36.
- [7] Zouaoui, H.; Bouaziz, J. Performance enhancement of the ceramic products by adding the sand, chamotte and waste-brick to a porous clay from Bir Mcherga (Tunisia) // *Applied clay science*, 143(2017)7, 430-436.
- [8] Karklit, A.K.; Kondakova, S.V.; Mel'nikova, G.G. Service of chamotte articles in furnaces for melting aluminum // *Refractories and industrial ceramics*, 39(1998)5-6, 183-185.
- [9] Bednarova, L.; Liberko, I. Benchmarking application in firms for production of chamotte bricks // *Acta montanistica Slovaca*, 13(2008)4, 502-510.
- [10] Kulikov, V.Y., Issagulov, A.Z., Kvon, S.S., Sidorina, Y.A. Studying the effect of boron on heat-resistance properties of Ni-Cr alloys. *Metalurgija*, 56(2017)3-4, 409-411.
- [11] Kvon, S.S., Kulikov, V.Y., Filippova, T.S., Omarova, A.E. Using high-chromium iron as material for production of the equipping components of mine shafts. *Metalurgija*, 55(2016)2, 206-208.
- [12] Ibrahim, S.I.; Ali, N.M.; Abood, T.W. Improving The Thermal and Physical Properties of Fire Clay Refractory Bricks by Added Magnesia // *Conference on Technologies and Materials for Renewable Energy, Environment and Sustainability (TMREES): Beirut, Lebanon: Feb 01-03, 1968(2018)*, 030025.
- [13] Nematzadeh, M.; Baradaran-Nasiri, A. Residual Properties of Concrete Containing Recycled Refractory Brick Aggregate at Elevated Temperatures // *Journal of materials in civil engineering*, 30(2018)1, 126-131.
- [14] Artir, R; Gunay, V; Bekisoglu, B. The effect of fused magnesia addition on the properties of chamotte refractorie // 8th Conference of the European-Ceramic-Society: Istanbul, Turkey, Jun 29-Jul 03, 264-268(2003)III, 1807-1810.
- [15] Kvon, S.S., Kulikov, V.Y., Issagulov, A.Z., Dostayeva, A.M., Kovalyova, T.V. Studying structure and properties of shaped ingots obtained in various conditions of crystallization. *Metalurgija*, 57(2018)4, 313-316.

**Note:** The responsible for England language is Nataliya Drag, Karaganda Kazakhstan