Electrofused Magnesio-Chromite: Complex refractory material

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INTRODUCTION

Refractory materials are used to create an inner cover for furnaces in pyrometallurgical industries (lining) as copper, lead, steel, nickel and so on. Without them, the operation with furnaces would be impossible (ANFRE, 2010). Depending on the industrial process and its requests, refractory materials are made of different elements in order to match them to the aggressive environment of the molten bath inside the furnace (Fig. 1).

One century ago, silica based refractories were used for copper making industry. In this case, the refractory performance (defined as tons of copper per tons of refractory used) was critically low because of the chemical effect of silica incorporation to iron slags, resulting in fayalite. In the 1910´s, magnesia based refractories began to be used and the life campaign of the furnaces was drastically increased, multiplied by many times (Southwick, 2008). In the 1960´s, chromium was included in the refractory making, and an additional increase in the performance was noticed.

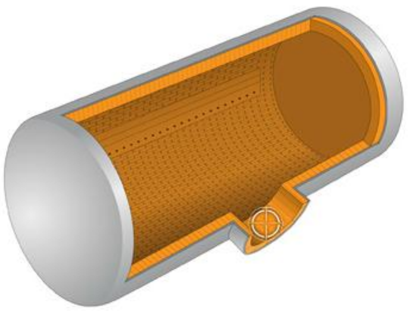

fig 1. Converter drawing (Open inside view). Courtesy of AMR refractories.

To go further, in recent decades new refractory making methods has been developed in order to increase the inner union of the raw materials in the refractory making process: direct bonded, rebounded or fused grain among others. Nowadays, magnesio-chromite refractory type as mixture of different raw materials is widely used in the lining of furnaces to produce copper from ore and/or scrap via pyrometallurgical processes (ANFRE, 2010). The aim of this work is to study the nature of the electrofused magnesio-chromite.

REFRACTORY MAKING

Refractories are made of the following materials: chromite from ore, magnesia, and electrofused magnesio-chromite as well as electrofused magnesia. On the one hand, many of those raw materials come from mine and from manufacturing processes like electrofusion in order to purify them and increase their refractory properties. On this way, it is possible to go further regarding availability (ANFRE, 2010).

Due to the degradation of refractory lining, it is necessary to reline periodically the refractory in furnaces. The most damaged areas are located in regions of the furnace where slag is in direct contact with refractory bricks. Additionally, movement of the slag and copper bath produces an effect of thermo-mechanical erosion (Slovikovskii & Gulyaeva, 2014; Petkov, 2007). All improvements in refractory industry have been focused to reduce this damage.

The standard fabrication process for refractory consists in (ANFRE, 2010):

1.- Reduction of size of the raw materials and classification.
2.- Mixing of the raw materials according to the requirements.
3.- Making the bricks by pressing (2000-2500 tn/cm^2).
4.- Heating treatment up to 1800ºC. At this temperature, raw materials grains are directly bonded to the internal structure of the brick. In some cases, a second step is carried out getting re-bonded bricks.

ELECTROFUSED MAGNESIO-CHROMITE

One of the high quality raw materials for refractory making is the electrofused magnesio-chromite due to its high resistance to chemical attack (Taschler, 2004).

This material comes from a previous making process where refined magnesia (calcined caustic magnesia) and chromite from ore are crushed, mixed and finally heated up to 2500ºC using electric power. At this temperature the mixture is fused getting a homogeneous molten system. Finally, it is cold down and crushed (ANFRE, 2010).

ANALITICAL METHODS

For this study, samples of electrofused magnesio-chromite were collected (Fig. 2).

fig 2. Electrofused Magnesio-Chromite as raw material for industrial refractory making.

Those samples were cut using a diamond saw, and polished with diamond suspensions (without presence

palabras clave: Refractario, Cobre, Magnesio—Cromita, Electrofundida. | key words: Refractory, Copper, Magnesio-Chromite, Electrofused.

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of water in order to avoid MgO degradation). They were covered with evaporated carbon in order to provide them with a conductive layer for analysis using Scanning Electron Microscopy and energy dispersive X-ray microanalysis (SEM-EDS). A carbon evaporator EMITECH K250X was used for this cover.

Additionally, liquidus and equilibrium temperature as well as phase distribution have been calculated through thermochemical computation using Fact Sage ® for thermochemical computation (Gheribi et al, 2011; Gheribi et al 2012). The equilibrium phase association for Mg-Cr electrofused materials is the result of a Gibbs energy minimization procedure.

ImageJ 1.50i software has been used to calculate characteristic textural parameters, as the particle distribution and the partial area covered by them.

RESULTS

Electrofused magnesio-chromite is a mixture of chromite crystals inside a slag's glass mainly composed of MgO as is shown in Fig. 3 and table 1.

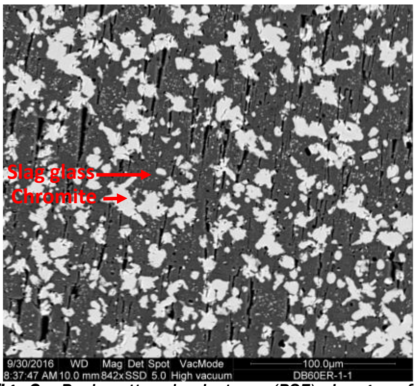

fig 3. Backscattered electron (BSE) image of electrofused magnesio-chromite. In white=chromite; in dark=slag glass.

Wt%	Electrof. MgCr	Chromite	Slag glass
O	34.55	35.2	38.94
Mg	45.81	14.17	61.06
Cr	12.96	38.58	
Fe	4.8	6.43	
Al	1.88	5.63	

Table 1. EDS corresponding to Fig. 3: analysis of the whole image and each phase separately (chromite and slag glass).

Electrofused microstructure matches with a specific crystallization state in which crystals of chromite have crystallized in equilibrium with melted magnesium rich slag (Table 1). The composition of the melted slag corresponds to that of a liquidus for the Mg-Cr electrofused system with iron and aluminum (Table 1).

Equilibrium temperature estimation:

Using both BSE images (Fig. 3) and ImageJ software, it has been calculated the number of chromite particles, the total area which corresponds to those particles and finally the percentage of area with respect to the total:

-Number of particles: 1219
-Total area for particles: 0.023 mm²
-%Area for particles: 32.3% (slag 67.7%).

As these data correspond to surface analysis, it is necessary to approximate them to 3D reality by stereological calculations.

Using the area for all chromite particles and the number of them, the average radius for particles was obtained (0.025 mm). On the other hand, it is possible to obtain the radius of the equivalent sphere for our system from the area studied in the BSE image.

If we take a slide from this sphere just in the diameter region, the area obtained is the number of particles of our initial studied BSE image. So multiple slides can be determined from the center to the perimeter and based on that, the equivalent number of particles contained in each one according to the area of them. The thickness of each slide is the average diameter of chromite particles (0.025x2).

Summing up all the particles of the slides we obtained the total amount of chromite particles (22439) which correspond to 0.3361 g (density=4.37 g/cm³ from Fact Sage ®). So the volume of the slag glass can be calculated as the difference between the total volume minus the chromite volume and using the density 3.58 g/cm³ (from Fact Sage ®) the mass for slag glass obtained is 3.4784 g. So the mass percentage of each phase is: chromite 8.8%wt and slag glass 91.2%wt.

Fact Sage ® was used to determine the equilibrium temperature via thermodynamic calculations applied to analytical data of electrofused magnesio-chromite from table 1 and the mass percentage of each phase previously calculated. It was necessary to calculate the mass distribution for both phases (chromite and slag glass) at different temperatures and identify the one which matched with the real mass distribution above mentioned.

Following this calculation scheme it was possible to estimate the liquidus temperature (1730.4 °C) and the equilibrium temperature (1625 °C) for the coexistence between chromite (ss) and melted slag. The equilibrium compositions of chromite and liquid-slag are shown in Table 2.

	Chromite	Slag Glass
O	33,70	37,89
Mg	12,76	46,71
Cr	50,94	8,67
Fe	1,10	4,92
Al	1,50	1,82

Table 2. Analysis at equilibrium temperature for the studied system using Fact Sage.

CONCLUSIONS

The microstructure for the electrofused magnesio-chromite corresponds to a hypereutectic microstructure and it is equilibrated to 1625ºC.

ACKNOWLEDGMENTS

We thank Atlantic Copper S.L.U. for the funding of this research work and AMR Refractories for getting samples.

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