A NEW GENERATION OF CHROME FREE REFRACTORIES FOR COPPER PRODUCTION

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ABSTRACT

Magnesia-chromite refractories are the essential refractories for copper making since several years. High stability against various environments and a high corrosion resistance are key properties for the application as wear lining in copper production furnaces. Weak points are their heavy infiltration during copper making with process melts like matte or copper, poor thermomechanical resistance, high risk of spalling, a high density of the material, corrosion by fayalitic slag and also the environmental aspect of chromite based refractories. Based on these weak points the present work introduces a new family of refractory materials that combine an effective infiltration barrier with a very good corrosion resistance and thermomechanical resistance. Furthermore, they have a lower density than magnesia-chromite bricks. Several industrial trials have proved the high potential of this new refractory material family.

Keywords: chrome free refractories, basic refractories, copper

INTRODUCTION (STATE OF THE ART)

Copper metallurgy is very complex and divided into various process steps (concentration, smelting and refining). Typically, sulfidic copper ores (0.5-2.0 wt.-% Cu) are used as raw material. By the aid of flotation of finely ground and milled ore a concentrate is produced (20-30 wt.% Cu). The concentrate is then being smelted into a matte (50-70 wt.-% Cu) in e.g. submerged nozzle smelters or flash smelters [1,2]. Afterwards the matte is refined in an e.g. Peirce-Smith converter (Fig. 1) to blister copper (99 wt.-% Cu). The second refining step starts with blister copper in an anode furnace to generate anode copper (99.5 wt.-%) to be casted into copper anodes [2].

Based on the Peirce-Smith converter process some typical process steps will be outlined. The sulfidic matte mainly consists of copper, iron and sulphur. In the first step the iron as FeS has to be separated from the matte by the aid of oxygen from the blowing air and by the aid of SiO_2 which is added as quartz sand. The reaction products are Fe_2SiO_4 (fayalite slag) and SO_2 according equation 1. The target Fe-content of the matte is below 1 wt.-% [2].

$$2\ FeS\ (l) + 3\ O_2\ (g) + SiO_2\ (s) \rightarrow Fe_2SiO_4\ (l) + 2\ SO_2\ (g) + heat \quad (1)$$

The process starts with charging matte from e.g. flash furnace and quartz sand for slag formation while air is blown into the converter through the tuyeres. When the conent of Fe in the slag reaches a maximum, the slag is tapped and fresh matte is being charged. Depending on the Fe-content of the matte and converter operation conditions this step is repeated several times. So, the furnace has different positions for filling, blowing and tapping. If the Fe-content in the matte reaches its target value, the air blowing rate is increased to separate copper and sulphur. This second step is called copper blowing. By blowing air or oxygen enriched air into the Cu-S matte the copper sulphide is oxidised to Cu and SO_2 according equation 2. A significant oxidation of copper just starts if the S-content in the melt is below 0.02 wt.-%. [2]. The product of the Peirce-Smith converter process is called blister copper.

$$Cu_2S\ (l) + O_2\ (g) \rightarrow 2\ Cu\ (l) + SO_2\ (g) + heat \quad (2)$$

The atmosphere in the converter is highly oxidizing and rich in SO_2. The slag is rich in fayalite and depending on the process stages rich in SiO_2. Partially, in special sections of the converter high contents of CuO/Cu_2O can be found. The process temperature is typically about 1250 °C.

Matte and slag both have a very low viscosity and can easily infiltrate porous refractory brick material.

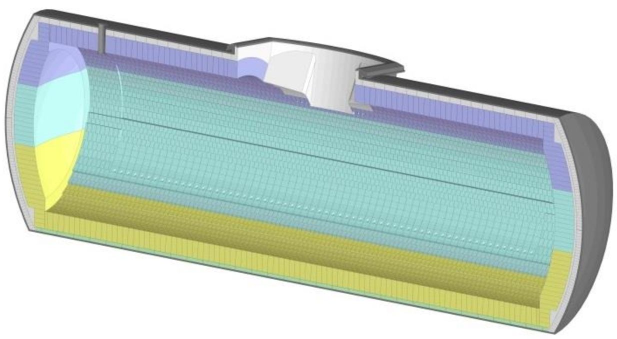

Fig. 1: Peirce-Smith copper converter

Nowadays, the state-of-the-art lining of all furnaces for the copper metallurgy is magnesia-chromite and/or magnesia bricks. The wear normally is a combination of chemical, thermal and mechanical factors. The acidic slag (fayalite, SiO_2) can corrode the basic brick material. Typically, chromite has a higher corrosion resistance than magnesia [1,3]. Due to its low viscosity it can infiltrate and degenerate the brick structure [1,3]. Also the low viscous matte and metallic copper can easily infiltrate the brick. Another often observed corrosion mechanism is sulphur attack on the magnesia under formation of magnesium-sulphate $MgSO_4$ which leads to a total decomposition of the magnesia grains. The sulphur penetrates the brick and on the cold face of the brick (T<1050 °C) the reaction takes place, combined with crack formation and spalling [1,3]. Besides these main factors also Cu-O-bursting, hydration of the magnesia and redox-reactions mainly of the iron oxide can occur always connected with structural decomposition. The infiltration of metallic copper, matte and/or slag is always changing the brick properties like thermal conductivity or brick flexibility [1,3].

Another important aspect of copper and matte infiltration into the brick structure is also a loss of valuable material for the copper producer in the residual bricks which have to be recycled in the process. Strong thermal cycling is also leading to strong crack formation [4].

The strong oxidizing atmosphere results in a decomposition of fayalite into magnetite and SiO_2, martitisation of magnetite, as well as cuprite-tenorite formation in the copper infiltrated brick structure [4]. The attacking acidic fayalite slag leads to the formation of low melting magnesium-silicates as well as magnesio-wustite formation [1,3,4].

These weak points are the main drawbacks of these high duty refractory materials. Due to their wide range of different grades and properties magnesia-chromite bricks are essential for furnaces of the copper metallurgy. The possibility of using different raw material grades and different firing conditions this brick family offers a wide range of properties. The high erosion resistance, refractoriness, corrosion resistance and resistance to changing redox conditions make them highly compatible to the copper metallurgy [3]. Environmental aspects of magnesia-chromite refractories are also subject of various discussions.

The focus of the present work is to provide a new generation of chrome free basic refractories for the copper metallurgy. The different conditions in the furnaces require a variety of customized materials. Looking at the Peirce-Smith converter for example three main zones of different conditions can be identified. The first area is the gas zone which is mainly exposed to temperature, process atmosphere and portions of slag splashes. The second area is the tuyere zone which is in direct contact with matte, slag and atmosphere and is exposed to high thermal shocks and erosive turbulent bath flow. The third area is the bath area which is mainly in contact with matte and slag.
The new chrome free refractories are all based on basic raw materials and provide an inherent infiltration barrier combined with low gas permeability. Furthermore, all of them contain matrix reinforcements. The main raw material selection for each zone faces the special demands of these zones.

PROPERTIES OF CUPRUMAX BRICKS

Table 1 shows the properties of the three different brick grades for each zone named brick A, B and C. Table 1 gives also an overview about the main raw materials, additives and bonding type of the bricks. Table 2 compares the chemical compositions of the bricks. Figure 2 compares the sectional cuts of the three different bricks. This current state of the brick development is the result of intensive laboratory trials and field trials including post mortem studies of used bricks. The brick properties are more or less within the range of typical magnesia-chromite refractories but have the benefit of relatively low open porosities. The bulk density is also lower than that of magnesia-chromite refractories. The thermal shock resistance is relatively high and fits to the demands of the process.

Tab. 1: Physical and Mechanical Properties of the new bricks

	A	***B***	***C***
Zone	gas area	tuyere area	bath area
main raw material	sintered magnesia	fused magnesia	olivine
additives	SiC	graphite, metallic antioxidants	graphite, metallic antioxidants
Bonding	ceramic	carbon	carbon
bulk density [g/cm3]	2.86	3.09	2.73
open porosity [%]	16.1	9.4	14.3
CCS [MPa]	68.0	52.0	64.9
CMOR [MPa]	3.6	7.5	10.1

Tab. 2: Chemical composition of the new bricks

[wt.-%]	***A***	***B***	***C***
SiO_2	13.07	1.42	21.89
SiC	4.89		
Al_2O_3	0.13	3.09	3.15
Fe_2O_3	0.36	0.45	5.05
CaO	1.09	0.79	0.39
MgO	85.07	87.58	62.39
C		6.50	6.50

By the aid of static and dynamic corrosion tests in the laboratory the suitability of the materials for the process were tested previously. Laboratory trials including corrosion tests with process melts give a first indication towards a possible suitability for the application.

The final qualification test however, has to be a field test in practice because all accomplished laboratory tests do not reveal practical conditions like e.g. changing atmospheres, slag compositions and interactions between all parameters.

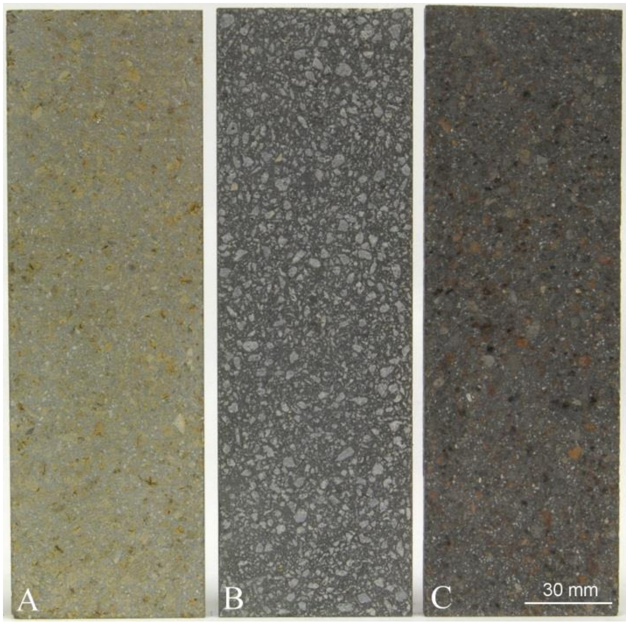

Fig. 2: Sectional cuts of the three different bricks A, B and C

FIELD TRIALS

All of the three introduced materials were tested in different Peirce-Smith converters in appropriate zones. Figure 3 shows a test field of brick B in the tuyere area after a typical service time. After the test it can be seen that the wear rate is comparable to that of the surrounding magnesia-chromite bricks. The test has shown the suitability of brick type B application in the tuyere zone.

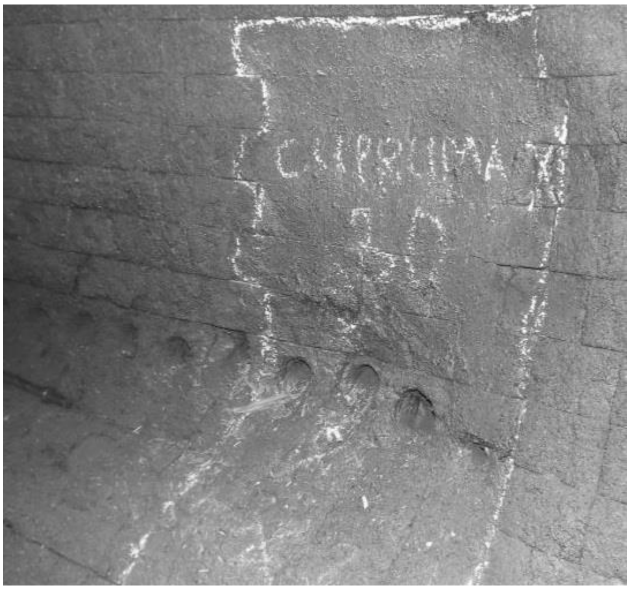
Fig. 3: Test field of brick type B in the tuyere area of a Peirce-Smith converter after a typical service time.

Figure 4 shows the condition of three test fields in a Peirce-Smith converter after a typical service time. The three brick types A, B and C were installed in the different zones according the description in Table 1. The test has proven the suitability of these new brick types for the process.

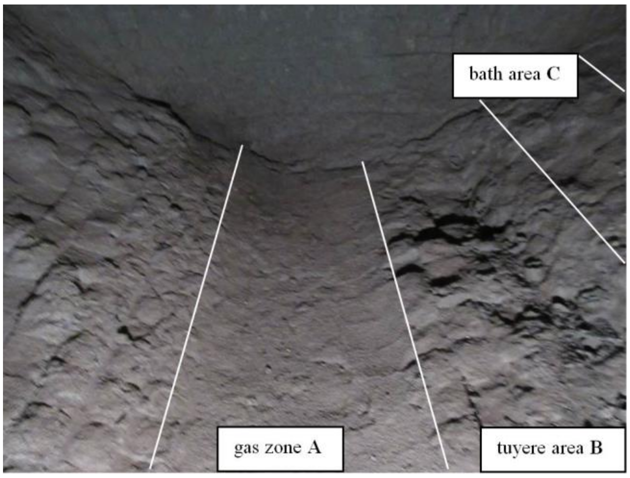

Fig. 4: Test field of brick type A, B and C in the gas area, tuyere area and bath area of a Peirce-Smith converter after a typical service time. The test fields are marked in the figure.

The conducted field trials in different zones of different Peirce-Smith converters have shown the necessity of a zoning into the before mentioned zones. Figure 5 show these zones.

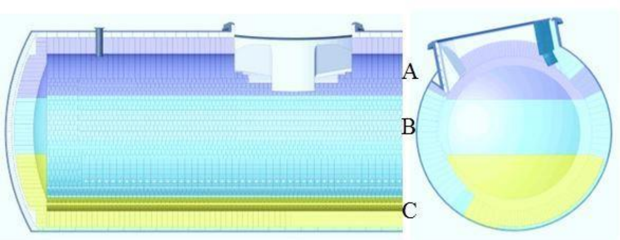

Fig. 5: Possible zoning of a Peirce-Smith converter for the new chrome free refractory material family (A-gas zone, B-tuyere zone, C-bath zone)

CORROSION RESISTANCE

Exemplary, a post mortem analysis of a brick type C sample of the bath area is shown. The sample had residual brick thickness of 350 mm and was cut for transport reasons. The brick sample shows only a layer of adherent slag but is free of infiltration. The brick structure is typical and unaffected. The marked zone in Figure 6 was observed at first by the aid of µXRF (Bruker Tornado M4). The element mapping in Figure 7 shows a semi-quantitative distribution of the most important elements like copper, iron, magnesium, silicon and sulphur. The mapping shows a sharp separation of slag and brick material without any diffusion or infiltration.

Fig. 6: Sectional cut of type C brick from bath area after test (see Fig. 5)

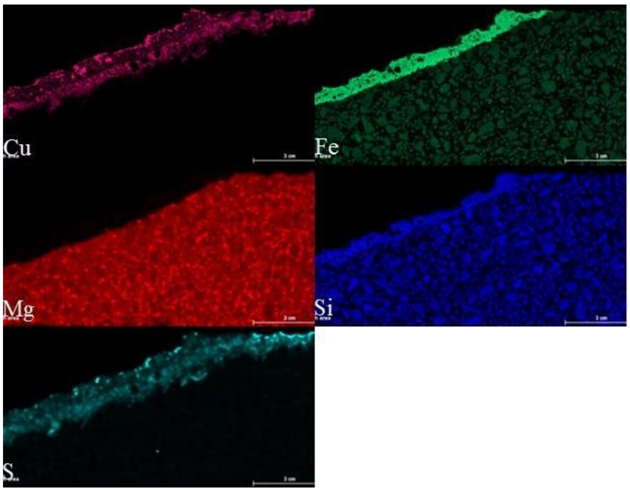

Fig. 7: Element mapping of the slag-brick interface of bath area brick C.

A polished section of the slag-brick interface was prepared for detailed analyses. Figure 8 shows the microstructure with a focus on the magnesia corrosion. The slag consists of magnetite, fayalite and traces of metallic copper and matte. The brick structure is free of infiltrations.

Fig 8: Microstructural overview of brick C from Fig. 6 with a detail of the magnesia corrosion at the hot face.

Figure 9 shows a more detailed micrograph of the magnesia corrosion from a scanning electron microscope. The sample was observed by the aid of wavelength dispersive X-ray diffraction. The marks in figure 9 show the position of the WDX analysis.

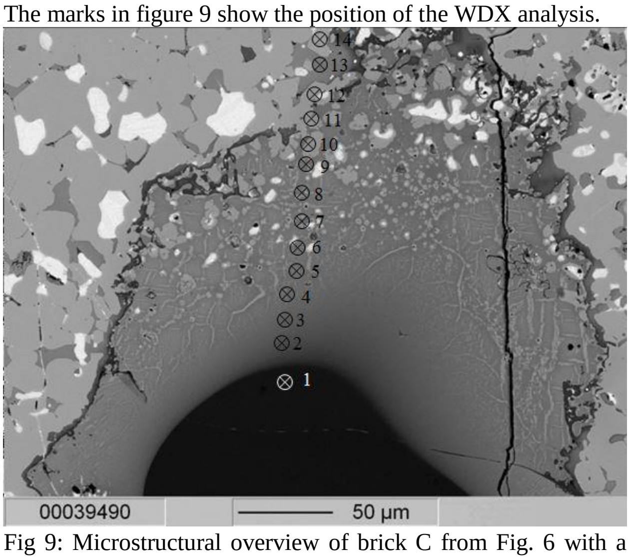

Fig 9: Microstructural overview of brick C from Fig. 6 with a detail of the magnesia corrosion at the hot face.

Table 3 gives the summary of the WDX analysis marked in figure 9. It can be seen that the magnesia has formed a solid solution of magnesia-wustite and the concentration of FeO is following a gradient towards the hot face. In direct contact with the magnesia an iron-rich olivine can be seen. The mechanism is based on the interaction between fayalite slag and magnesia by diffusion of FeO into the magnesia and MgO into the fayalite.

Tab. 3: Summary of WDX analysis in figure 9

No.	*mineral formula*
1	periclase/wustite $(Mg_{0.99}Fe_{0.01})O$
2	periclase/wustite $(Mg_{0.79}Fe_{0.20})O$
3	periclase/wustite $(Mg_{0.70}Fe_{0.30})O$
4	periclase/wustite $(Mg_{0.60}Fe_{0.39})O$
5	periclase/wustite $(Mg_{0.54}Fe_{0.45})O$
6	periclase/wustite $(Mg_{0.44}Fe_{0.54})O$
7	periclase/wustite $(Mg_{0.48}Fe_{0.51})O$
8	periclase/wustite $(Mg_{0.13}Fe_{0.83})O$
9	periclase/wustite $(Mg_{0.48}Fe_{0.51})O$
10	periclase/wustite $(Mg_{0.12}Fe_{0.83})O$
11	periclase/wustite $(Mg_{0.12}Fe_{0.84})O$
12	periclase/wustite $(Mg_{0.09}Fe_{0.85})O$
13	olivine $(Mg_{0.30}Fe_{1.68})SiO_4$
14	magnetite $(Mg_{0.03}Fe_{0.97})(Al_{0.07}Fe_{1.90})O_4$

Figure 10 shows the microstructure with a focus on the olivine corrosion.

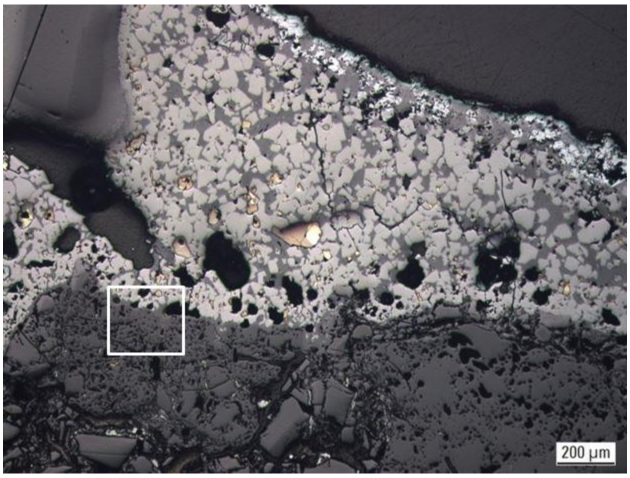

Fig 10: Microstructural overview of brick C from Fig. 6 with a detail of the olivine corrosion at the hot face.

Figure 11 shows a more detailed micrograph of the olivine corrosion including the position of the WDX analysis points.

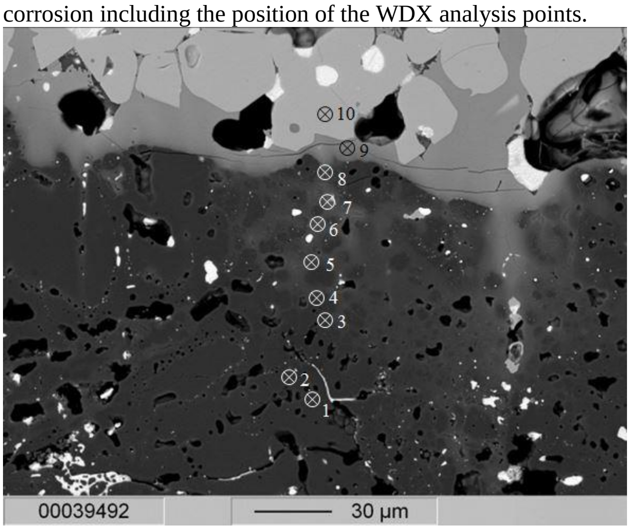

Fig 11: Microstructural overview of brick C from Fig. 10 with a detail of the olivine corrosion at the hot face.

Table 4 gives the summary of the WDX analysis marked in figure 11. It can be seen that the forsteritic olivine raw material and the fayalite slag have formed a solid solution following a gradient.

Tab. 4: Summary of WDX analysis in figure 11

No.	*mineral formula*
1	olivine $(Mg_{1.90}Fe_{0.12})Si_{0.98}O_4$
2	olivine $(Mg_{1.91}Fe_{0.11})Si_{0.99}O_4$
3	olivine $(Mg_{1.88}Fe_{0.14})Si_{0.98}O_4$
4	olivine $(Mg_{1.88}Fe_{0.13})Si_{0.99}O_4$
5	olivine $(Mg_{1.90}Fe_{0.12})Si_{0.99}O_4$
6	olivine $(Mg_{1.59}Fe_{0.37})SiO_4$
7	olivine $(Mg_{1.40}Fe_{0.54})SiO_4$
8	olivine $(Mg_{1.66}Fe_{0.30})SiO_4$
9	olivine $(Mg_{0.54}Fe_{1.40})SiO_4$
10	magnetite $(Mg_{0.03}Fe_{0.98})(Al_{0.06}Fe_{1.90})O_4$

CONCLUSION

The field trials have proven the suitability of the new generation of chrome free basic refractories for the copper metallurgy. The new bricks show a similar wear rate compared to magnesia-chromite bricks but have an infiltration barrier. These bricks have a lower bulk density than magnesia-chromite bricks while having a lower open porosity. The wear mechanism is different from that of magnesia-chromite bricks. The olivine formation between slag-fayalite and brick-forsterite in the reaction zone is forming a semi-frozen layer at the interface. The wear rate of the magnesia is depending on the primary crystal size that is selected according the demands in the zones of the furnace. The resistance towards sulphur attack is dominantly improved by the low gas permeability.

The environmental aspect is given by the absence of chromite.

Similar to the numerous modifications of magnesia-chromite bricks also the new brick types have to be customized according the demands of the processes and zones in the furnaces.

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