The impact of work environment on chemical and phase composition changes of magnesia-spinel refractories used as refractory lining in secondary metallurgy device

J Szczerba¹, D Madej¹, Z Czapka²

¹AGH University of Science and Technology, Faculty of Materials Science and Ceramics
al. A. Mickiewicza 30,
30-059 Krakow, Poland
²Zakłady Magnezytowe „Ropczyce” S. A.

E-mail: jszczerba@agh.edu.pl, dmadej@agh.edu.pl

Abstract. The study of magnesia-chrome refractories corrosion by liquid steel and the liquid calcium-silicate based slag was carried out in the environment in RH degasser. The microstructures of the as-delivered and tested samples were researched by SEM-EDS methods. Our experiment produced the following results: 1. the initial spinel phase, Mg(Cr,Al,Fe)₂O₄ solid-solution of magnesia-chrome brick was transformed into Fe and Mn-rich spinel phase (Mg,Mn)(Cr,Fe)₂O₄ solid-solution, 2. the new phase formed in the corroded brick were (Mn,Mg)O and (Ca,Mg,Mn)SiO₄ solid solutions.

1. Introduction

Today, secondary metallurgical units that may allow to the improvements in the steel quality in the ladle include: RH (Ruhrstahl Heraeus), RD-OTB (Recirculation Degasser with Oxygen Top Blowing), VOD (Vacuum Oxygen Degassing), VAD (Vacuum Arc Degassing), HALT (Heating Advanced Ladle Treatment) and CAS-OB (Composition Adjustment by Argon Sealed Bubbling with Oxygen Blowing) [1].

The Ruhrstahl Heraeus (RH) degasser is the most widely used vacuum decarburization unit in secondary steel making processes besides Vacuum Oxygen Decarburization (VOD) and Argon Oxygen Decarburization (AOD) technologies [2]. Vacuum degassing of steel is intended for improve mechanical properties by reducing the dissolved harmful gases content (H₂, O₂, N₂), decarburization and improving the purity of the steel. The RH circulation degassing process is one of the many healing methods used to the steel vacuum degassing processes. The RH process is carried out in a refractory-lined vessel, equipped with two tubes (snorkels) which are immersed in a molten steel bath and then the circulation of liquid steel through the vacuum chamber takes place [3].

Traditionally, snorkels of RH degasser are lined with re-bonded magnesia-chrome bricks while directly bonded magnesia-chrome bricks and semi-rebonded magnesia-chrome bricks are preferred in lower wear regions. Generally magnesia-chrome refractories are used the sector of ferrous metallurgy because of their good thermal stability and high temperature performance. Generally, the lifetime of a magchrome refractory lining can be defined by the number of steel treatments to failure. Both, in the RH-snorkels and in the lower of parts of the RH installations, having the most difficult temperature and chemical, mechanical, and
physical conditions of work, the intensive flow of steel occurs. Hence, the major destructive
factors are: erosion by the molten flowing steel, corrosion of refractories by iron oxides,
corrosion process of refractories connected with the infiltration of the calcium silicate phases,
the relatively high temperature which significantly increases corrosion and erosion of
refractory lining, the rapid temperature changes result from the periodic vacuum degassing
and vacuum reducing conditions. Generally, the refractory RH-snorkel linings lifetime ranges
between 50 and 200 steel treatments [3].

2. Experimental procedure
The basic procedure of this experiment included the following steps: (1) the preparation of
magnesia chrome bricks under industrial conditions, (2) the corrosion test which consisted in
the exposure of refractory lining to the RH snorkel for vacuum steel degassing conditions, (3)
the post mortem studies of magnesia chrome refractories.

The corroded samples were sectioned perpendicular to the interface. A typical
ceramographic grinding and polishing procedures then were used, after which all samples
were carbon-coated and observed under scanning electron microscope (SEM) and analyzed by
energy dispersive spectroscopy (EDS) detector. The ultra high definition NOVA NANO SEM
200 was used for this purpose.

The specimens of the as-delivered magnesia-chromite material (starting material) were also
characterized by SEM/EDS techniques.

2.1 Presentation of the refractory materials
The industrial refractories tested in this study were composed of fused grain magnesia-
chrome spinel (co-clinker), magnesia clinker and chrome ore. Figs. 1a-c show examples of
such microstructure. Fig. 1a shows the backscattered electron SEM image of mixed refractory
silicate and direct bonded magnesia chrome brick.

Direct-bond refers to direct attachment of the magnesia to the spinel phase without an
interrupting film of silicate. As it can be seen in this picture the magnesia-chrome fused grain
is bonded to the surrounding a chromium and magnesium-rich matrix. SEM backscattered
electron image showing the periclase phase (dark grey) in a direct-bonded magnesia-chrome
refractory brick (Fig. 1b). Elemental SEM-EDS analysis indicated that the composition of
spinel phase (the light spots) included Mg, Al, Cr and Fe elements (Table 1 – spot 1) whereas
the composition of magnesia phase (the dark spots) included Mg, Cr and Fe elements (Table 1
– spot 2). In the first case, it was found that the magnesium chromite (picrochromite)
MgCr$_2$O$_4$ with substitution of Al and Fe occurred in the refractory material. Secondary spinel-
type magnesium chromium oxides with substitution of Al and Fe can be expressed by a
general formula Mg(Cr,Al,Fe)$_2$O$_4$. In the second case, it was found that the composition of Cr
and Fe-rich periclase phase occurred in the refractory brick. It may indicate the presence of
Cr-Fe-rich inclusions in magnesium oxide and can be expressed by formula Mg(Fe,Cr)$_2$O$_4$.

Fig. 1c shows that the silicate bond forms a film surrounding the grains in the fine-grained
matrix. Quantitative EDS point analysis showed the presence of the artificial calcium and
magnesium silicate – monticellite, CaMgSiO$_4$; $T_d$ – 1490°C with admixtures of Cr and Fe
elements (Fig. 1c – spot 1).
Fig. 1 (a, b, c). SEM micrographs of as-delivered magnesia-chrome refractory brick. (Fig. 1b – Spot 1 and 2) EDS analysis: 1 – Mg(Cr,Al,Fe)$_2$O$_4$, 2 – Mg(Fe,Cr)$_2$O$_4$; (Fig. 1c – Spot 1) EDS analysis: 1 – CaMgSiO$_4$.

Table 1. Elemental analysis (% weight) of as-delivered magnesia-chrome refractories by SEM/EDS (Figs. 1b and 1c).

| Spot       | Element [wt. %] |
|------------|-----------------|
|            | O   | Mg | Al  | Cr  | Fe  | Ca  | Si  |
| 1 (Fig. 1b)| 42.8 | 13.7 | 5.9 | 33.0 | 4.6 | -   | -   |
| 2 (Fig. 1b)| 40.4 | 54.0 | -   | 2.8  | 2.8 | -   | -   |
| 1 (Fig. 1c)| 42.3 | 20.2 | -   | 1.7  | 1.1 | 18.9| 15.8|

2.2 Corrosion test
The chemical corrosion of magnesia-chrome refractories proceeded in the snorkel of a RH degasser for vacuum degassing of steel during 24 RH processes. The factors influencing the corrosion of refractories are: molten steel, slag, inclusions included, mainly Fe, Mn, Ca and Si.
elements. The reaction mechanism in magnesia-chrome refractories exposed to corrosion factors that influence the wear of the refractory lining of the snorkel for RH degasser progress through a combination of chemical attack and microstructural changes. The major destructive factors were: erosion by the molten flowing steel, corrosion of magnesia-chrome refractories by iron oxides, the infiltration of the liquid calcium-silicate based slag into refractory bricks and the rapid temperature changes result from the periodic vacuum degassing and vacuum reducing conditions. The temperature of the molten steel during vacuum degassing reached at least 1600°C.

3. Results and discussion
The SEM/EDS observation of corroded magnesia-chrome brick revealed the presence of the sharp-edged grains of secondary magnesia-chrome spinel enriched in Fe and Mn elements and more impoverished in Mg, Al and Cr elements (Fig. 2 – spot 1). As can be seen in the Fig. 2 direct bond exist between the periclase MgO and the secondary spinel \((\text{Mg,Mn})(\text{Cr,Al,Fe})_2\text{O}_4\) (Fig. 2 – spot 3).

![Fig. 2. SEM micrographs of reaction zone of corroded magnesia-chrome refractories. (Spots 1, 2 and 3) EDS analysis: 1 – (Mg,Mn)(Cr,Al,Fe)\(_2\)O\(_4\) solid solution, 2 – (Ca,Mg,Mn)SiO\(_4\) solid solution, 3 – MgO grain with inclusions of (Mg,Mn)(Cr,Al,Fe)\(_2\)O\(_4\).](image)

Moreover, the initial silicate phase (monticellite, CaMgSiO\(_4\)) was saturated with manganese due to diffusion of manganese ions (Fig. 2 – spot 2). This resulted in changes to chemical composition of monticellite phase. Hence, isomorphous manganese-rich solid solutions with mutual substitution of divalent cations was formed. This solid solution series with the olivine structure is the compositional range between end-member minerals such as kirschsteinite, CaFeSiO\(_4\) (T\(_{mp}\) – 1208°C), glaucochroite, CaMnSiO\(_4\) (T\(_{mp}\) – 1240°C), monticellite, CaMgSiO\(_4\) (T\(_{dp}\) – 1490°C) and tephroite, Mn\(_2\)SiO\(_4\) (T\(_{mp}\) – 1345°C). The presence of the Mn\(^{2+}\) cations in an isomorphous series caused substantial lowering of the melting point of the initial silicate bonding phase in matrix (monticellite).
Table 2. Elemental analysis (% weight) of corroded magnesia-chrome refractories by SEM/EDS (Fig. 2).

| Spot | Element [wt. %] | O  | Mg | Al | Cr | Mn | Fe | Si | P  | Ca |
|------|----------------|----|----|----|----|----|----|----|----|----|
| 1    |                | 37.1 | 6.6 | 3.0 | 13.6 | 13.6 | 26.1 | -  | -  | -  |
| 2    |                | 42.5 | 12.7 | -  | -  | 8.4  | 16.4 | 0.3 | 19.7 | |
| 3    |                | 34.9 | 16.0 | 0.8 | 4.1  | 17.0 | 27.2 | -  | -  | -  |

Results of the EDS point scan analysis shows that the regions 1 and 3 (Fig. 3 – spots 1 and 3) contain of magnesium, manganese, and iron, see Table 3. According to the binary phase diagram, the continuous solid solution exists between MgO and MnO oxides (Fig. 4). According to Kamenetskaya [4] the calculated liquidus from the regular-solution model (Fig. 4 – liquidus curve 3) is appreciably higher than the calculated one from an ideal-solution model in Ref. [5] (Fig. 4 – liquidus curves 1 and 2). In Ref. [5], the calculated solidus is in good agreement with the experimentally obtained solidus. Also, through EDS analysis, it could be seen a strong presence of iron in point 1 of the Figure 3, see Table 3. There was phase segregation that led to magnesioferrite, MgFe$_2$O$_4$ formation in the MnO-MgO solid solution.

Table 3. Elemental analysis (% weight) of corroded magnesia-chrome refractories by SEM/EDS (Fig. 3).

| Point | Element [wt. %] | O  | Mg | Mn | Fe | Si | Ca | Cr |
|-------|----------------|----|----|----|----|----|----|----|
| 1     |                | 36.1 | 29.8 | 26.5 | 7.6  | -  | -  | -  |
| 2     |                | 42.5 | 11.8 | 9.1  | -  | 16.3 | 20.3 | -  |
| 3     |                | 36.2 | 28.6 | 25.8 | 9.4  | -  | -  | -  |
| 4     |                | 37.4 | 7.5  | 15.0 | 29.1 | -  | -  | 11.0 |
4. Conclusions

Results of the corrosion of magnesia-chrome refractories tested under industrial conditions were reported. During the corrosion process in the snorkels of RH degasser, the initial spinel phase, Mg(Cr,Al,Fe)$_2$O$_4$ solid-solution of magnesia-chrome brick was enriched in Fe and Mn elements and more impoverished in Mg, Al and Cr elements. The initial periclase grains were also enriched in Mn and Fe elements. The studies indicated that MnO-MgO solid-solution formation took place by the diffusion of Mn$^{2+}$ ions into MgO lattices. Moreover, magnesioferrite, MgFe$_2$O$_4$ inclusions in (Mn,Mg)O solid-solution were detected. The silicate-bond (monticellite phase, CaMgSiO$_4$) was saturated with Mn$^{2+}$ ions. From those data, the (Ca,Mg,Mn)SiO$_4$ solid solution formation was concluded to cause substantial lowering of the melting point.

Acknowledgements

This work is supported by the grant no UDA-POIG.04.04.00-18-010/09-00 of the Polish Government.

References

[1] Buhr A 1993 Refractories for steel secondary metallurgy CN-Refractories 6 3 pp 19-30
[2] Van Ende M-A, Kim Y-M, Cho M-K, Choi J and Jung I-H A 2011 A kinetic model for the Ruhrstahl Heraeus (RH) degassing process Metallurgical and Materials Transactions B 42B pp 477-489
[3] Czapka Z, Śliwa A 2011 Ceramic Materials 63 3 pp 631-641
[4] Kamenetskaya D S, Riskiev T T, Revzin B L and Ni L M 1985 Izv. Akad. Nauk SSSR, Neorg. Mater., 21 3 pp 422-425; Inorg. Mater. (Engl. Transl.), 21 3 pp 356-359
[5] Schenck H, Frohberg M G and Nuenninghoff R 1964 Arch. Eisenhuttenwes. 35 4 pp 269-277
[6] ACerS-NIST, Phase Equilibria Diagrams, CD-ROM Database Version 3.1 – Fig. No. 09238