The influence of slag basicity and composition on ConArc magnesia-carbon refractories during the blowing phase

by A. Muller*

Paper written on project work carried out in partial fulfilment of B.Eng Metallurgical Engineering

Synopsis

The magnesia-carbon refractories used in the ConArc process experience severe wear as a result of the varying slag composition during the blowing phase. This work determines the basicity range in which minimum as well as maximum refractory wear was experienced by the magnesia-carbon refractories during service. In order to determine an optimum slag composition, the crucible test in an induction furnace was used. The magnesia-carbon refractory bricks were cut into cylindrical crucibles to which a synthetic slag in the form of pellets was added. The basicity (B_2) of the slag was varied from 0.5 to 3. Tests were done at 1 600°C for one hour. Apart from the crucible test in an induction furnace, visual inspection and SEM analysis were also done to investigate the corrosion mechanism. FACTSage® predictions about the interaction between refractories and slag were also done. These predictions were compared to the actual results attained. It was found that the extent of corrosion by slag attack decreases as the basicity increases. The most severe corrosion of the MgO-C refractories occurred at a basicity of 0.5 whereas the optimum basicity is above 2.0. SEM analysis indicated severe slag attack at the lower basicities with no visible refractory-slag interaction at higher basicities. The FACTSage® predictions supported most of the actual findings.

Keywords

Magnesia-carbon, ConArc, blowing phase, slag resistance, induction furnace, crucibles.

Introduction

Magnesia-carbon refractories are mostly used to line vessels in the steelmaking industry, specifically the electric arc furnace, basic oxygen furnace and steel refining ladles. Magnesia-carbon refractories are also used to line the ConArc furnace, which is a combination of the electric arc furnace and basic oxygen furnace.

MgO-C refractories are used in the ConArc process due to their superior corrosion resistance and thermal spalling resistance. MgO-C refractory bricks of different thicknesses and quality are used in the different regions of the ConArc furnaces based on the wear experienced by the refractory lining in each region[1]. In the regions experiencing more wear, MgO-C refractories with a higher carbon content, higher density and higher purity of raw materials are typically used[1]. The refractory lining is thus installed in such a way that the minimum amount of refractory lining is left in all the places in the furnace after a specific time in service[1].

The failure of the MgO-C refractories leads to failure of the refractory linings of the ConArc furnace vessels. If the refractory linings of the furnace vessels are not replaced within time, it leads to enormous losses in production time, production equipment and sometimes in the product itself.

Manufactures take great care to optimize the mechanical, physical or thermal properties of the refractory materials. Failure of the refractories usually occurs as a result of either mechanical wear or chemical wear. Chemical corrosion occurs mainly due to the oxidation of carbon and the dissolution of magnesia grains by the slag. It is important to optimize operating conditions in a process in order to extend the lifetime of refractory materials.

Experimental

The MgO-C refractory bricks were cut into cylindrical crucibles which were placed inside the induction coil. The crucibles had an outer diameter (D_o) of 46 mm and an inside diameter (D_i) of 20 mm. All crucibles were of the same height. The dimensions of the crucibles are shown in Figure 1.

Synthetic slags consisting of CaO, FeO, MgO and SiO_2 were used in the experiments. The FeO and MgO contents were fixed at 25 weight % and 10 weight % respectively. The weight percentages of CaO and SiO_2, as shown in Table I, were calculated by varying the basicity (B_2) value between 0.5 and 3 in increments of 0.5. B_2 is calculated as shown in Equation [1][2].

---

* Department of Materials Science and Metallurgical Engineering, University of Pretoria, South Africa.

© The Southern African Institute of Mining and Metallurgy, 2011. SA ISSN 0038–223X/3.00 + 0.00. Paper received Mar. 2011; revised paper received Mar. 2011.

Table I

Weight % of each species at a given B_2 value

B_2	Weight %				Mass (g)			
	MgO	FeO	SiO_2	CaO	MgO	FeO	SiO_2	CaO
0.5	10.00	25.00	43.33	21.67	0.5	1.25	2.17	1.43
1.0	10.00	25.00	32.50	32.50	0.5	1.25	1.62	1.62
1.5	10.00	25.00	26.00	39.00	0.5	1.25	1.30	1.95
2.0	10.00	25.00	21.67	43.33	0.5	1.25	1.08	2.17
2.5	10.00	25.00	18.57	46.43	0.5	1.25	0.93	2.32
3.0	10.00	25.00	16.25	48.75	0.5	1.25	0.81	2.44

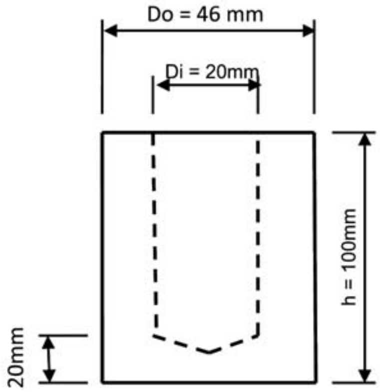

Figure 1—Dimensions of the cylindrical MgO-C refractory crucibles

Powdered slag samples of 5 g in size were prepared at each respective B_2 value. The powdered specimens were ground in an ethanol-based medium in the micronizing mill in order to ensure that it was homogenous. The micronized specimens were pressed into 5 g pellets by means of a hydraulic press.

$$B_2 = \frac{\text{CaO wt\%}}{\text{SiO}_2\text{wt\%}} \quad [1]$$

The 5 g slag pellet was then placed inside the refractory crucible. Furthermore 2.5 g of 99.97% pure iron pieces and 0.125 g of carbon powder was also added to the crucible. This ensured carbon saturation of the iron. The amount of slag was carefully monitored in order to prevent a too high slag level and possible burn-through of the thermocouple.

The MgO-C refractory crucible was placed inside a graphite crucible. The graphite crucible, which was very conductive, aided in heating the less conductive MgO-C refractory crucible. The MgO-C and graphite crucibles were placed at the centre of the induction coil ensuring evenly distributed heating. This whole arrangement was placed inside a well insulated stainless steel vessel. The stainless steel vessel was sealed off with an o-ring whereafter argon was blown into it for five minutes before starting with the test. The argon was also blown into the vessel for the duration of the test.

The MgO-C refractory was heated to 1 600°C and kept constant at this temperature for one hour. An Ameritherm Inc. 801-9106 solid state induction heating power source was used to power the induction coil. On completion of the test, the arrangement was allowed to cool to room temperature before the argon supply was disconnected and the vessel opened.

The MgO-C refractory crucibles were sectioned vertically along their diameter with a diamond blade. Reference points were selected along the diameter (length) of the cavity of the sectioned crucibles. The reference points were 5 mm apart with the first reference point being 5 mm from the top of the crucible. The change in the original diameter at each of these reference points was measured. The change in the original diameter was then used to calculate a change in the total volume of the cavity. It was assumed that the change in the original diameter of the cavity remained the same over a length of 5 mm. The total volume change of the cavity due to slag attack was calculated and expressed as a wear rate.

Apart from the visual evaluation of the amount of corrosion, samples taken from the sectioned crucibles were analysed with a scanning electron microscope. This allowed for the microstructure of the MgO-C refractories to be investigated. In addition, it provided insight regarding the wear mechanism and the degree of slag penetration experienced by the MgO-C refractory bricks.

FACTSage®

The software package, FACTSage®, was used to make thermodynamic predictions about the phenomenon of wear as a result of slag attack. The expected phases were predicted using 'Equilib', which is a module in FACTSage®.

The corrosion of MgO-C refractory bricks by a model slag was studied. The MgO-C refractory brick composition was simplified by ignoring all species present in less than one percent except for SiO_2. The simplified brick composition is given in Table II.

All possible proportions of the MgO-C refractory brick and the model slag were investigated by the reaction extent <A>.The temperature and pressure were kept constant at 1600°C and 1 atm respectively during all calculations.

The reaction extent <A> can be calculated as shown in Equation [2].

$$< A > = \frac{R}{S+R} \quad [2]$$

<*A*> is the reaction extent, *R* is the refractory and *S* is the slag.

When <*A*> is equal to zero, there is a 100% slag.

Results and discussion

Visual inspection

From Figure 2 it is seen that the wear rate, experienced by the MgO-C refractories, decreases as the basicity (B_2) increases.

Table II

Simplified MgO-C refractory brick composition for FACTSage® calculations

Species	Actual composition (%)	Simplified composition (%)
Residual C	10	9.76
MgO	96.5	88.45
FeO	0.2	-
Fe_2O_3	0.7	-
CaO	1.8	1.65
SiO_2	0.8	0.73
Total %	**110**	**100**

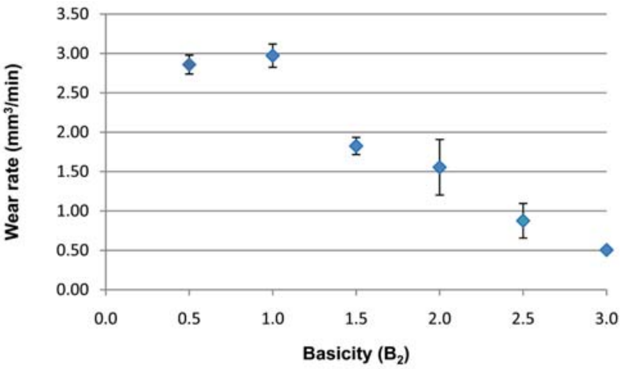

Figure 2—The average wear rate (mm^3/min) at a varying basicity (B2)

The wear rate at a basicity (B_2) of 1 is slightly higher than the wear rate at the basicity of 0.5. The error bars at these two basicities, however, overlap. The most severe corrosion experienced by the MgO-C refractories thus occurs at a basicity of 0.5 whereas the optimum operating basicity is at a B_2 value of 3.

Scanning electron microscopy

Basicity: 0.5

Figure 3 shows the MgO-C refractory microstructure after slag interaction. The slag attacked the matrix surrounding the MgO grains but did, however, not attack the MgO grains. This is due to the short reaction time of only one hour.

At the refractory/ slag interface crystals formed. These crystals are a solid solution of forsterite (Mg_2SiO_4) and olivine (Ca_2SiO_4). A slightly lighter phase, monticellite ($MgCaSiO_4$), surrounds the crystals. This phase is richer in MgO than the crystals. A $(Ca,Mg)Al_2SiO_6$ compound in turn surrounds the monticellite. The aluminium present in this solid solution most likely came from the MgO-C refractory brick matrix which was dissolved by the silica rich slag. The slag phase which penetrated the matrix of the refractory brick is also monticellite.

The $CaO-MgO-FeO-SiO_2$ isothermal projection at 1 600°C[3] suggests that two phases namely Fe(l) and a liquid slag phase will be present at 1 600°C. The monticellite that surrounds the MgO grains in Figure 3 is thus expected to have formed from the liquid slag phase upon cooling. The Fe(l) is present as a result of the reduction of FeO by carbon or graphite, which occurred during the experiments as discussed earlier.

Basicity: 1.0

The microstructure of the MgO-C refractory material after refractory/slag interaction, at a B_2 value of 1, is shown in Figure 4. A thick slag layer is present. Slag attack of the matrix but not of the MgO grains can be seen. The absence of slag attack on the MgO grains is due to the reaction time of only one hour.

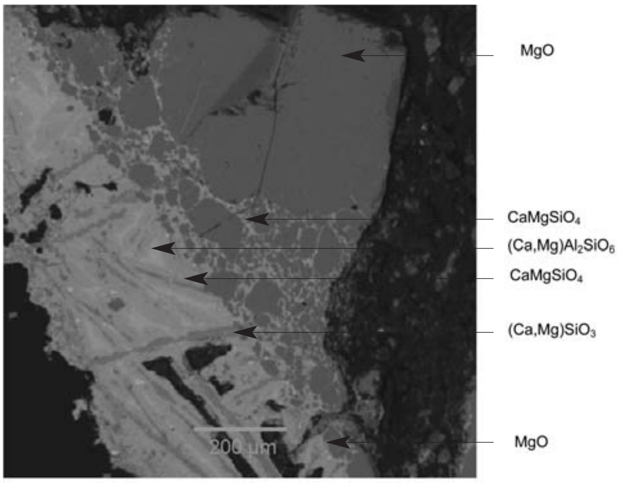

Figure 3—Backscatter electron image of the microstructure of the MgO-C refractory material after attack by slag with a basicity (B_2) of 0.5

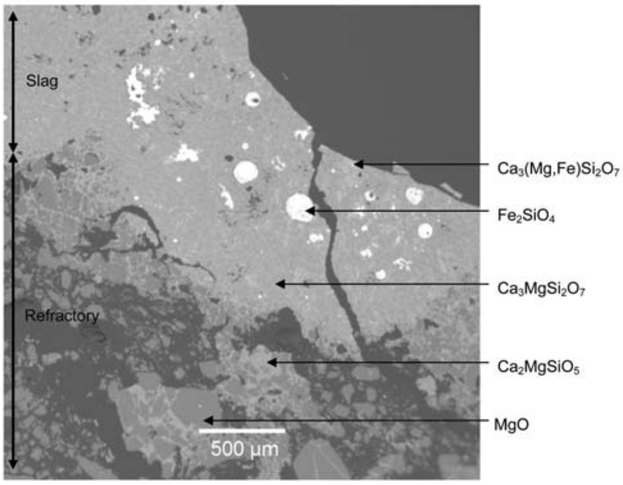

Figure 4—Backscatter electron image of the microstructure of the MgO-C refractory material after attack by slag with a basicity (B_2) of 1.0

The slag layer adjacent to the MgO-C matrix is merwinite based ($Ca_3MgSi_2O_8$). A small amount of Al_2O_3 is in solid solution with the merwinite. The Al_2O_3 came from the Al_2O_3 present as an impurity in the brick matrix, which was dissolved by the slag. Large fayalite (Fe_2SiO_4) inclusions are present in the slag layer indicating that conditions during testing were neither oxidizing nor reducing. The slag layer, surrounding the MgO grains in the refractory brick matrix, is melilite based (Ca_2MgSiO_5) and is less rich in CaO than merwinite.

The CaO-MgO-FeO-SiO_2 isothermal projection at 1 600°C[3] suggests that a single liquid phase will be present at 1 600°C. The merwinite based phase that surrounds the MgO grains in Figure 3 is expected to have formed from the liquid slag phase upon cooling. The other phases present also formed from the slag phase upon cooling.

Melilite has a higher lime content when compared to monticellite, which was the slag phase that penetrated the MgO-C brick matrix at a B_2 value of 0.5. It is suggested that the wear rate experienced by MgO-C refractories can be decreased by saturating the slag with lime[4]. It is therefore expected that more severe wear will be experienced by the MgO-C refractory brick at the lower basicity.

Basicity: 1.5

The microstructure of the MgO-C refractory material after the crucible test in the induction furnace, at a B_2 value of 1.5, is illustrated in Figure 5. No slag layer or slag penetration of the matrix could be seen in this sample. A dense MgO layer is, however, present adjacent to where the refractory-slag interface is expected to have been.

It is expected that a dense MgO layer will form during attack of the MgO-C refractory by slag[5]. The atmosphere becomes more reducing as one moves further away from the refractory-slag interface into the brick matrix. As the atmosphere in the brick matrix is reducing, MgO is reduced to Mg (g). The Mg (g) diffuses towards the slag layer where conditions are more oxidizing[5]. Upon reaching the slag layer, the Mg(g) is reoxidized to form a dense MgO layer[4,5].

Slag penetration of the brick matrix could not be distinguished as the dense MgO layer prevented the attack thereof on the matrix. One does, however, expect to see a slag layer adjacent to the dense MgO layer. The absence of the slag layer may be as a result of spalling causing the slag layer to detach itself from the MgO layer upon cooling.

Impurities are present along the grain boundaries of the MgO grains in Figure 5. These impurities are Ca_2SiO_4 and are common of sintered MgO_6.

Basicity: 2.0

The microstructure of the MgO-C refractory material, after attack by slag with a basicity (B_2) of 2.0, is illustrated in Figure 6. No slag layer is present and no penetration of the brick matrix by slag is visible.

The absence of the slag layer may be due to spalling which resulted in the slag layer detaching itself from the MgO-C refractory interface upon cooling. Spalling does, however, not explain the absence of slag penetration.

As previously mentioned, the extent of wear, due to slag attack, experienced by the MgO-C refractory bricks will decrease as the slag becomes more saturated in lime (CaO)[4]. The CaO content at a B_2 value of 2 therefore seems to be sufficient to limit slag attack to such an extent that no or limited corrosion of the MgO-C refractory occurs.

Similar results were found at basicities of 2.5 and 3.0.

FACTSage®

The FACTSage® system was optimized by selecting solid solution databases of all the solids which are expected to form. In order to ensure that optimization was done accurately, all the phases which may form in the CaO-MgO-FeO-SiO_2 system were selected. The possible immiscibility of liquid phases was also considered. The CaO-MgO-FeO-SiO_2 represents the model slag.

The number of solid and gaseous species as well as the solutions selected for the solution database for the optimized FACTSage® system is shown in Table III.

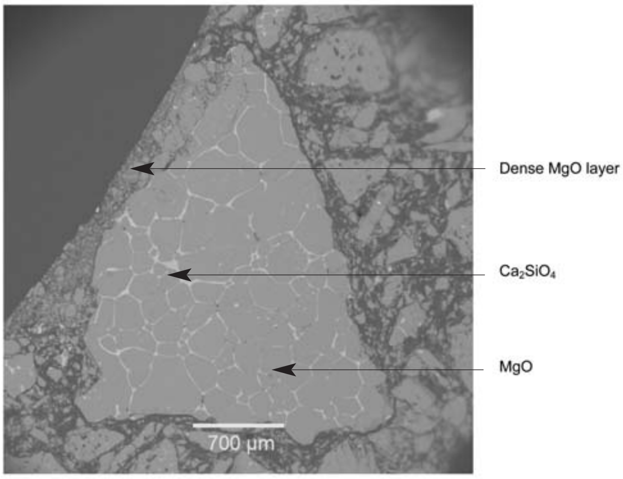

Figure 5—Backscatter electron image of the microstructure of the MgO-C refractory material after attack by slag with a basicity (B_2) of 1.5

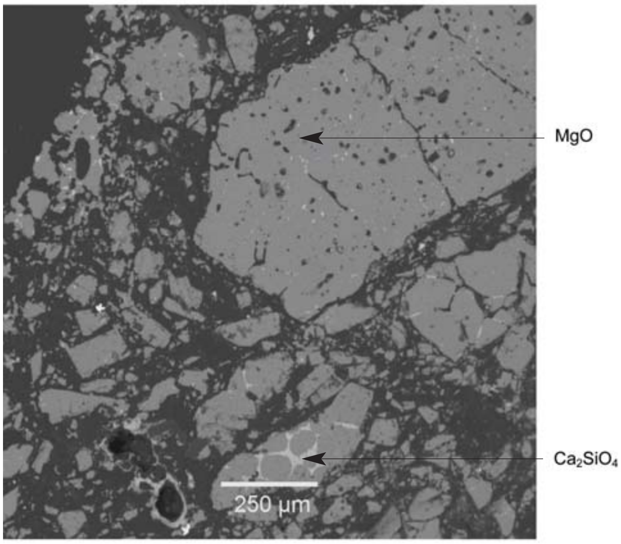

Figure 6—Backscatter electron image of the microstructure of the MgO-C refractory material after attack by slag with a basicity (B_2) of 2.0

Table III

Number of solids and gases and the solutions involved in the FACTSage® calculations

Gases	3
Solids	120
Solutions	FToxid_SLAGA FToxid_SPINA FToxid_cPyr FToxid_OlivA FToxid_Mel_ FToxid_LcPy FToxid_WOLLA

The reaction extent at different basicities for the MgO-C refractory bricks is shown in Figure 7. FACTSage® predicts that there will be almost no wear of the MgO-C refractory brick when it is in contact with slags in the basicity (B_2) range of 2.0 to 3.0. There will, however, be wear of the MgO-C refractory bricks when they are in contact with slags at lower B_2 values.

Above a reaction extent <A> of approximately 0.2 no slag phase forms at basicities of 2.0, 2.5 and 3.0. There is, however, slag formation at basicities of 0.5, 1.0 and 1.5 up to a reaction extent <A> equal to 1.

When the formation of solid species and compounds were investigated, it was found that no solid is formed in the case of the lower three basicities (0.5, 1.0 and 1.5). A solid solution of Ca_2SiO_4 (olivine) and $CaMgSiO_4$ (monticellite), however, forms in the case of the three higher basicity values (2.0, 2.5 and 3.0). The mass of the solid solution of olivine and monticellite formed as the reaction extent <A> changes is shown in Figure 8.

The point of formation of the maximum mass of the solid solution of olivine and monticellite at every basicity, corresponds to the reaction extent <A> at which there will be no more slag formation for the MgO-C refractory brick. It therefore appears that the formation of olivine is the mechanism that protects the MgO-C refractory bricks from wear as a result of slag attack.

Conclusion

FACTSage® predicts wear of the MgO-C refractory bricks when they are in contact with slags with basicities of 0.5, 1.0 and 1.5. FACTSage® further predicts almost no wear of the MgO-C refractory material when it is in contact with slags with basicities (B_2) of 2.0, 2.5 and 3.0. No slag interaction is visible in the backscatter electron images at basicities of 2.0, 2.5 and 3.0. It can thus be concluded that the prediction made by FACTSage® about slag formation is accurate.

FACTSage® predicts the formation of a solid solution of Ca_2SiO_4 (olivine) and $CaMgSiO_4$ (monticellite) at the refractory-slag interface, for slags with a B_2 value of 2.0, 2.5 and 3.0. The olivine type solid solution protects the MgO-C refractory bricks form wear by slag attack. No slag interaction is visible in the backscatter electron images at basicities of 2.0, 2.5 and 3.0. At present the predictions about the formation of the solid solution of olivine and monticellite can thus not be verified.

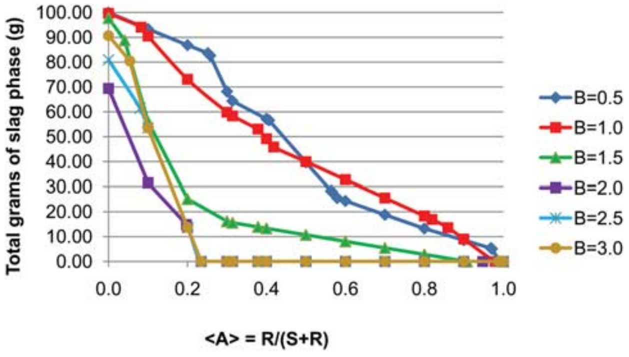

Figure 7—The mass of slag formed as a function of the reaction extent <A>

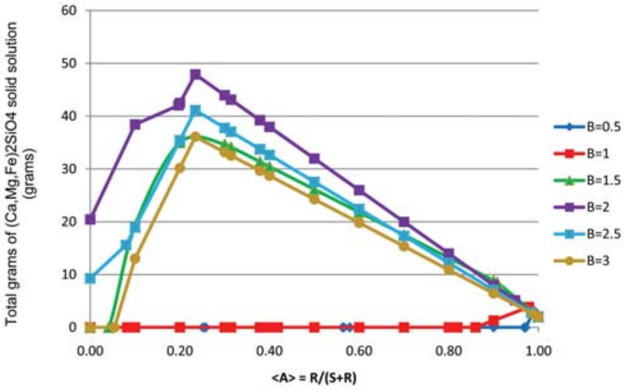

Figure 8—The mass of olivine (Ca_2SiO_4) and monticellite ($CaMgSiO_4$) formed as function of the reaction extent <A>

From the microstructures attained from SEM-EDS, the calculated wear rate and the predictions performed by FACTSage®, it can be concluded that the most severe corrosion of the MgO-C refractories occurs at a basicity of 0.5, which is the most acidic slag in the ConArc process. Furthermore, an optimum operating basicity exists at a basicity of 2.0 and higher.

References

1. Craven, R.F., Lankford, W.T., McGannon, H.E. and Samways, N.L. *The Making, Shaping and Treating of Steel*, Herbick & Held, United States of America, 1985.

2. Fruehan, R.J. and Turkdogan, E.T. *The Making, Shaping and Treating of Steel*, Eleventh edition, Steel Making and Refining Volume, Pittsburgh, 1998.

3. Kowalski, M., Neuschutz, D. and Spencer, P.J. *Slag atlas*, Chapter 3: Phase diagrams, Second edition, Verein Deutscher Eisenhuttenleute, 2008.

4. Tada, H. *Refractories Handbook*, 1.4. Carbon Containing Refractories, The Technical Association of Refractories, Japan, 1998.

5. Lee, W.E. and Zhang, S. Influence of additives on corrosion resistance and corroded microstructure of MgO-C refractories, *Journal of European Ceramic Society*, vol. 21, 2001, pp. 2393–2405.

6. De Aza, A.H., De Aza, S., Ortega, P., Pena, P. and Valle, F.J. Analytical characterisation of a Magnesia-Graphite Refractory, *Journal of the American Ceramic Society*, vol. 89, no. 5, 2006a, pp. 1704–1708.

◆