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Direct mineralogical composition of a MgO-C refractory material obtained by Rietveld methodology

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Abstract

Magnesia-graphite refractory materials are used in large quantities in the steelmaking process. The chemical characterization of this type of refractories is an arduous task that requires a rigorous set of laboratory tests and analyses. In the present paper, proper characterization of magnesia-graphite refractories has been approached by X-ray powder diffraction combined with Rietveld methodology. The quantitative phase analysis of a MgO-graphite refractory has been 68.3 wt% of MgO, 8.1 wt% of graphite, 13.5 wt% of Al_2O_3, 4.4 wt% of SiC, 0.6 wt% of Si, 1.2 wt% of Al, 1.5 wt% of $AlPO_4$ and 2.4 wt% of silicone. These results have been checked and validated with those obtained by other analysis procedures used to determine the crystalline and non-crystalline phases present in these materials.

Keywords: Refractories; MgO-C refractories; X-ray methods; Rietveld; Analysis

1. Introduction

Magnesia-graphite materials are an established refractory for the steel industry.[1] The excellent properties of various forms of carbon in refractories have been well known among industry experts for a long time. In the 1980s significant amounts of these materials were used in Japan,[2–7] but it was later on in the United States where products were developed and launched in response to demand arising from new processes in the metallurgical industry and advances in refractory technology.[8]

Magnesia-graphite refractories are characterised by excellent corrosion resistance due to their low wettability by fluid slag and metal; high resistance to thermal shock as a result of the graphite content that increases the thermal conductivity and reduces the thermal expansion; and good mechanical strength at high temperatures. The ease of oxidation by air, water or carbon dioxide at high temperatures is one of the main drawbacks of these materials. Therefore, they are commonly used in reducing atmospheres.

Originally, these materials were constituted by periclase (MgO), graphite (C) and aluminium (Al),[9,10] but in recent years, magnesia-carbon materials have been the subject of several projects aimed at improving their mechanical, thermal and chemical properties and reducing hazardous emissions during fabrication as well as during steel processing. Nowadays the anti-oxidation role of the aluminium is being enhanced by the addition of silicon (Si) or even, silicon carbide (SiC).[11,12] The composition of high-duty magnesia-carbon bricks has been improved in recent years, essentially in terms of the binders used.[1] Currently, the addition of some polysiloxane (silicone) as a binder is usual.[13]

Proper mineralogical characterization of a magnesia-graphite material is vital for its quality control and to understand its final performance. This is an arduous problem that requires a rigorous set of laboratory tests and analyses since C, Si and Al elements coexist with SiC (non-oxide inorganic phase) jointly with organic phases (polyxiloxanes), oxide phases (MgO, Al_2O_3), berlinite ($AlPO_4$), some additives and

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impurities. So, magnesia-graphite refractories must be considered as very complex materials.

In the scientific bibliography there is lack of information about a methodology to obtain a magnesia-graphite full-material chemical analysis. However, there are numerous papers that report the single analysis of each one of the components.[14–27] In a previous work the authors have developed a methodology that makes possible a whole analysis of these type of materials.[28]

The goal of the present investigation is to approach the aforementioned problem by X-ray powder diffraction (XRPD) combined with Rietveld methodology.[29] This method is one of the most useful tools to obtain Quantitative Phase Analyses, QPA, directly. The method is standardless but the crystal structures of all the phases present in the sample must be known as the process comprises the comparison of the measured and calculated patterns. Rietveld QPA has been successfully applied to simple mixtures[30,31] and in the last years it has been employed to more complex industrial materials such as ordinary Portland clinkers and cements,[32–34] calcium aluminate cements,[35] mineralised Portland clinkers[36] and porcelains.[37] This methodology has several advantages over others because it uses a wide diffraction range minimizing peak overlap, preferred orientation and sample broadening effects.[38,39] The quantification of amorphous content within a given material is also possible using Rietveld methodology by adding a suitable internal standard.[40] The results obtained by this methodology for a MgO-graphite refractory have been validated with those obtained by other analysis procedures that make it possible to determine the crystalline and non-crystalline phases present in these materials.

2. Experimental procedure

2.1. X-ray data collection

A magnesia-graphite sample ground to less than 35 μm was characterised by XRPD at room temperature. The powder pattern was collected on a Siemens D5000 automated diffractometer using graphite-monochromated Cu $K\alpha_{1,2}$ radiation (1.5418 Å). The diffractometer optic used to collect the sample was: a fixed aperture slit of 2 mm, one scattered-radiation slit of 2 mm after the pattern, followed by a system of secondary Soller slits and the detector slit of 0.2 mm. The pattern was recorded between 5° and 80° (2θ) in 0.03° steps, counting 20 s per step. The sample was rotated at 15 rpm during data collection.

2.2. Rietveld refinement

Rietveld refinement was done using the GSAS suite of programs.[41] Peak shape for every phase was modelled by a pseudo-Voigt function[42] including the asymmetry correction of Finger et al.[43] March-Dollase algorithm[44] was used to correct the preferred orientation effect when it was observed, e.g. graphite along [0 0 1] direction.

The bibliographic references for the crystal structures descriptions used to calculate powder patterns are given in Table 1.[45–52] The linear absorption coefficients for Cu $K\alpha_{1,2}$ radiation are also listed. When anisotropic vibration temperature factors were reported, these were converted to the corresponding isotropic values and introduced in the Rietveld analysis. Optimised parameters in final refinement were: background coefficients, cell parameters, zero shift error, peak shape parameters, preferred orientation (when appropriate), and phase fractions.

2.3. Chemical analysis methodologies

XRPD, differential thermal analysis (DTA) and thermogravimetry analysis (TG), infrared spectrometry (FT-IR), chemical analysis by inductive coupled plasma-atomic emission spectroscopy (ICP-AES), flame photometry (FP) and induction furnace carbon/sulphur analyzer (LECO) are a set of techniques suitable to approach these types of analyses.

The following equipments and operating conditions were used: *DTA and TG*: a STA-490 Netzsch was used to heat the specimens in platinum crucibles to 1400 °C at a heating rate of 10 °C min^{-1}, in a flow of dry air. *FT-IR* spectra were recorded over the 400–4000 cm^{-1} spectral range with Fourier transformed data using a Perkin-Elmer 1760X spectrophotometer. The operating conditions were: 4 cm^{-1} resolution, 10 scans, 0.4 mV laser energy, 2000:1 resolution power. *ICP-AES*: a Thermo Jarrell Ash IRIS Advantage axial plasma spectrometer with computer controlled polychromator to analyse a pre-defined wavelength range was used. The source was pow-

Table 1
Some structural details of the investigated phases

Mineral name	Chemical formula	μ[a]	PDF file number	ICSD collection code	Bibliographic reference
Periclase	MgO	99.4	43–1022	9863	45
Graphite	C	9.3	41–1487	76767	46
Corundum	Al_2O_3	121.1	43–1484	73725	47
Silicon carbide	SiC	139.8	29–1131	15325	48
Silicon	Si	139.3	27–1402	60389	49
Aluminium	Al	129.6	04–0787	44321	50
Berlinite	$AlPO_4$	91.1	10–0423	66999	51,52

[a] Linear absorption coefficient, μ, in cm^{-1}.

ered by 2 kW crystal controlled radiofrequency generator operating at 40.68 MHz. An especial detection configuration with 262,144 individually addressable detector elements in a 512 × 512 array allows the continuous coverage of the available wavelength ranges. *FP*: A 2100 Perkin-Elmer atomic absorption spectrometer was used in flame emission spectrophotometer mode to perform the flame emission spectrometry. *LECO CS-200*: The equipment has an induction furnace that allows sample combustion.

2.4. Microstructural examination

To study the microstructure of the material several cross-sections of the refractories were mounted in epoxy resins and were progressively diamond polished down to 1 μm. Phase identification was performed using reflected-light microscopy (RLM) (Carl Zeiss Axiophot Stereomicroscope) and phase analysis was carried out using a field emission scanning electron microscope (FESEM) (Hitachi-S4700) fitted with an energy-dispersive spectrometer (Noran System Six-Thermo Electron Corporation).

3. Results and discussion

3.1. Rietveld quantitative phase analysis

A mineralogical phase identification was initially carried out. The sample contains seven crystalline phases: periclase (MgO), graphite (C), corundum (Al_2O_3), silicon carbide (SiC), silicon (Si), aluminium (Al) and berlinite ($AlPO_4$). Graphite showed preferred orientation that must be corrected. March Dollase algorithm along [0 0 1] was used and the refined parameter converged to 0.58(2) (a value of 1.0 represents an ideal "random" powder). To obtain accuracy, QPA microabsorption effect should be borne in mind. This effect may be important if the linear absorption coefficient of any phase, in a mixture, is different from that of the mixture and the particle size distribution is not homogeneous. The average linear absorption coefficient of this material is 104 cm^{-1} approximately, and the C coefficient is the farthest value from it, see Table 1. A method to partially correct this effect was developed by Brindley[53] and related to the Rietveld methodology by Taylor.[54] A detailed description of this correction has recently been presented.[55] As will be seen, Rietveld QPA results and the results of other methods match satisfactorily (Table 3). Hence, the microabsorption effect does not seem to be a problem in the present case and its correction is likely not needed. Final R_{WP} disagreement factor[56] converged to 10.3% indicating a good fit; see also the flatness of the difference curve in Fig. 1. In this figure, the Rietveld plot for the refractory is shown (20–80°/2θ) with main peaks for each phase labelled. Furthermore, the values of the phase-dependent, R_F, disagreement factor[56] are small, see Table 2, which indicates that fits to any given phase are satisfactory. Rietveld QPA results are given in Table 2.

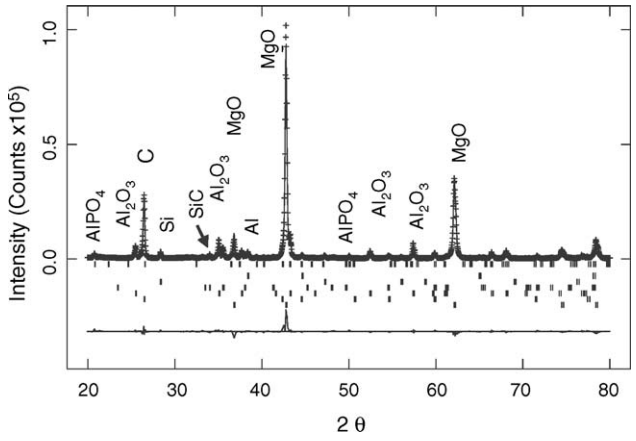

Fig. 1. Rietveld plot (20–80°/2θ) for the analysed Mg-C refractory with main peaks of each phase labelled. Observed (crosses), calculated (line) and difference (bottom line) powder patterns are shown. The marks correspond to the Bragg peaks of the different phases, from bottom to top: MgO, C (graphite), Al_2O_3, SiC, Si, Al and $AlPO_4$.

Table 2
Rietveld refinement results for the MgO-C refractory material

Phase	Wt%[a]	R_F (%)
MgO	70.1 (1)	3.8
C (graphite)	8.3 (6)	5.1
Al_2O_3	13.8 (1)	3.2
SiC	4.5 (1)	7.2
Si	0.6 (3)	5.8
Al	1.2 (1)	5.3
$AlPO_4$	1.5 (1)	12.0

[a] Figures between parentheses: standard deviation (σ) derived from the phase fraction given by the Rietveld least-squares analysis.

Rietveld results, shown in Table 2, are normalized to 100% of crystalline fraction, so the hypothetical amorphous and organic content of the sample is assumed to be negligible. Bearing in mind that the material contains 2.4 wt% of silicone acting as a binder, determined by TG and LECO,[28] data obtained by Rietveld must be fitted to 97.6 wt%, as is shown in Table 3. These results have been compared with those

Table 3
Rielveld quantitative phase analysis for a magnesia-graphite refractory material vs. other methods results

Phase	Rietveld QPA	Other methods results	
	Wt% (up to 97.6%)	Wt%[a]	Method
MgO	68.3	64.1 (3)	ICP-AES
C (graphite)	8.1	9.0 (3)	LECO
Al_2O_3	13.5	12.7 (2)	ICP-AES
SiC	4.4	4.4 (2)	Gravimetry and LECO
Si	0.6	1.5 (1)	Gravimetry
Al	1.2	2.21 (5)	ICP-AES
$AlPO_4$	1.5	0.8 (1)	ICP-AES
Silicone (polyxiloxane)	–	2.4	TG

[a] Figures between parentheses: standard deviation (σ) derived from five replicates (precision of the method).

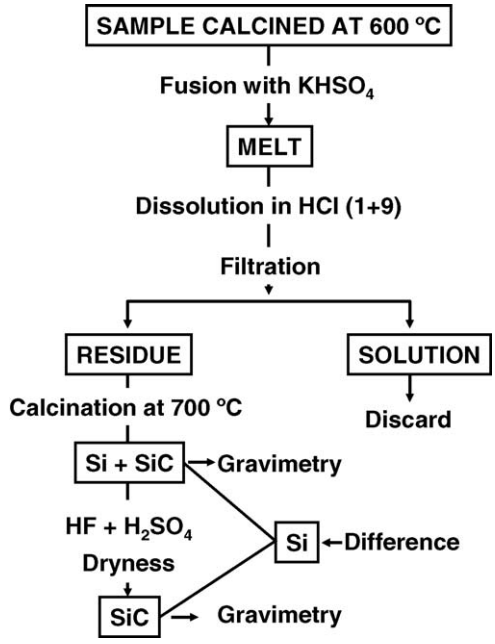

Fig. 2. Procedure scheme for determination of silicon and silicon carbide.[28]

obtained, following the described procedures (Figs. 2–5), by other methods.[28] As can be seen, Rietveld QPA and results from other methods match satisfactorily (see Table 3) and therefore it can be assumed that the amorphous phase content in the material (that includes every minor crystalline phase not defined, all non-diffracting fractions such as vitreous phases, grain boundary regions, intrinsic defects, etc.) is negligible. To confirm this point, the microstructure of the refractory was studied. Fig. 6 shows a reflected light optic microscope image of the MgO-C material, where no significant amount of glassy phase can be detected.

To put it more precisely, the difference observed for the MgO weight content (68.3/64.1) has sense due to the high amount of this phase in the refractory. In comparison, the results shown in Table 3 for Al (1.2/2.21) have a rela-

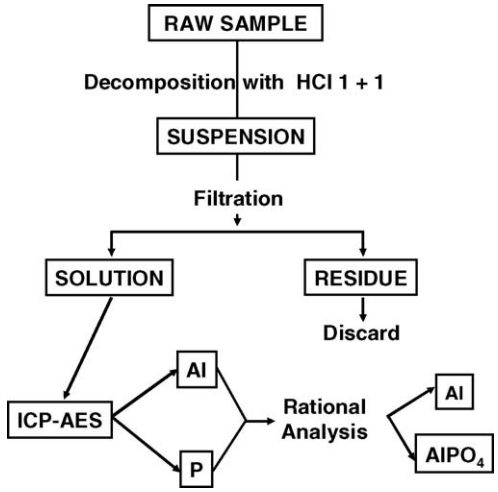

Fig. 3. Procedure scheme for determination of Al and $AlPO_4$.[28]

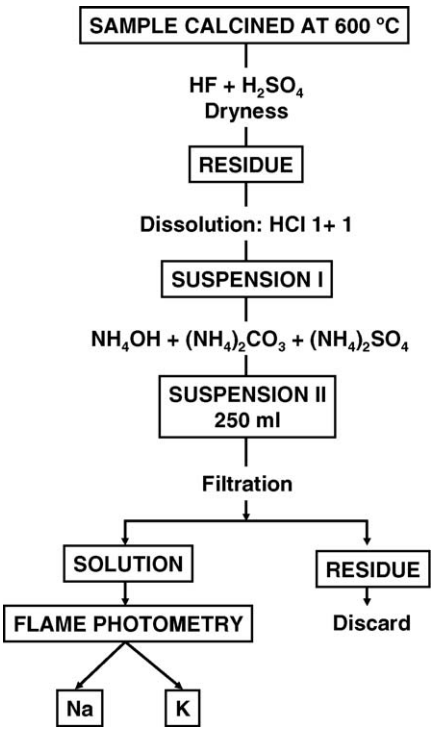

Fig. 4. Procedure scheme for determination of alkalis.[28]

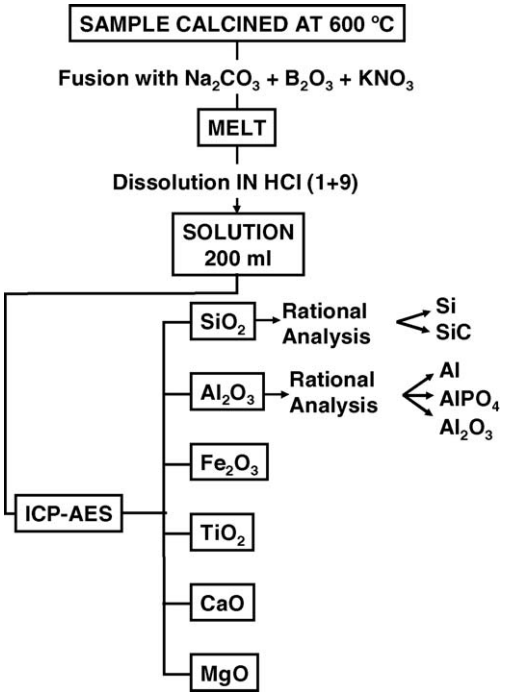

Fig. 5. Procedure scheme for determination of all the remaining components.[28]

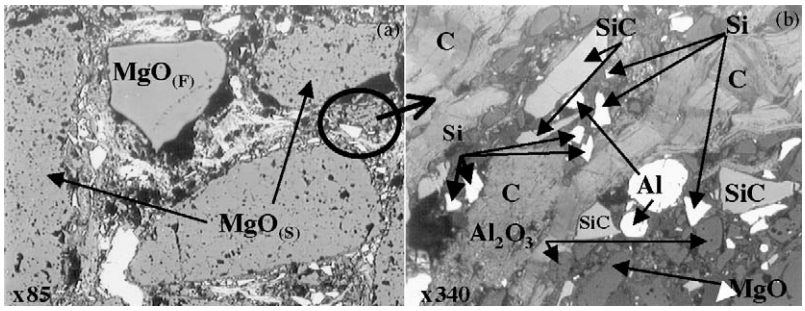

Fig. 6. Reflected light optic microscope images of the microstructure of the MgO-C refractory: (a) low magnification image (×85) and (b) higher magnification image (×380) showing a selective magnification of the refractory matrix. The main phase identified are labelled: $MgO_{(F)}$: fused magnesia, MgO(s): sintered magnesia, C: graphite, Al_2O_3: corundum, SiC: silicon carbide, Si: silicon and Al: aluminium. No significant amount of glassy phase can be detected.

tively large inaccuracy. In this particular case, the 2.21-value reported for Al was deduced by rational analysis from P and Al data obtained by ICP-AES (Fig. 3). So the aforementioned data is affected by a larger error than 1.2-Rietveld data for Al. It is worth to mention that the chemical analysis gives the existence of some impurities (wt%): $Fe_2O_3 = 0.20(2)$ (ICP-AES); $TiO_2 = 0.02(2)$ (ICP-AES); CaO = 1.40(4) (ICP-AES); $Na_2O = 0.070(5)$ (FE); $K_2O = 0.19(2)$ (FE); silicona = 2.4 (TG); moisture = 0.5 (TG).

4. Conclusions

The following concluding remarks can be made:

(a) The analysed MgO-graphite refractory material is composed by: MgO (68.3 wt%), C (graphite: 8.1 wt%), Al_2O_3 (13.5 wt%), SiC (4.4 wt%), Si (0.6 wt%), Al (1.2 wt%), $AlPO_4$ (1.5 wt%) and silicone (2.4 wt%).
(b) Rietveld quantitative phase analysis using laboratory X-ray powder diffraction is a suitable methodology to directly obtain the mineralogical composition of MgO-graphite refractories.
(c) This methodology is appropriated to be applied to quality control and to understand final performances of this type of materials.

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