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Physico-chemical characterisation of silicon carbide refractories

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Abstract

The present study was undertaken to establish a methodology for character rising silicon carbide-based refractories, as detailed information is unavailable in the literature on this point. We analysed several types of silicon carbide refractories belonging to the non-oxide and composite families of refractories, characterising each component by different methods. The phases were characterised first by X-ray diffraction (XRD). The components were then chemically characterised by different methods, which included the wet method, X-ray fluorescence (XRF) spectrometry, coulometry and inductively coupled plasma optical emission spectrometry (ICP-OES). The best method for characterising each component was determined. The proposed methodology was validated using reference materials.

Keywords: Refractories; Composite refractories; SiC; X-ray methods

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1. Introduction

A great variety of refractory materials is available. These materials can be classified, in terms of their chemical composition, in three general families of refractories[1,2]:

- oxide refractories[3];
- non-oxide refractories;
- composite refractories.

Silicon carbide refractories are found as both non-oxide and composite refractories, and may contain any or all of the following components: silicon carbide, graphite, silicon, silica, silicon nitride, periclase, mullite, andalusite, cristobalite, corundum, and other phases that contain iron, calcium, titanium, etc. as impurities. Table 1 details the principal non-oxide and composite types of refractories.

Silicon carbide-based refractories are difficult to analyse due to their refractory nature and the need to quantify each phase separately. Various studies can be found in the literature on the use of these materials,[4–7] the sintering of silicon carbide,[8–16] and the analysis of some specific component.[17–23] However, no study has been conducted on the analysis of every component in SiC refractories.

We selected several types of SiC refractories from the non-oxide and composite classes of refractories. All the components, except silicon nitride, were analysed by various methods, and the results were compared in order to identify the most appropriate analysis method for each component. Thus, the crystalline phases were characterised first by X-ray diffraction (XRD). Chemical characterisation was then done by different methods, depending on the major components. The methods used were the wet method, coulometry, inductively coupled plasma optical emission spectrometry (ICP-OES) and X-ray fluorescence (XRF). A methodology was thus established for characterising each component. The proposed methodology was validated using reference materials.

2. Experimental

2.1. Materials and experimental techniques

Five silicon carbide powders from the non-oxide family of refractories were selected and referenced SiC-1, SiC-2, SiC-3, SiC-4 and SiC-5. These powders contained $\geq$95 wt% SiC and had different average particle sizes. Five synthetic (non-oxide and composite) refractories were prepared by mixing the silicon carbide powder referenced SiC-3 with C (graphite), MgO

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Table 1
Classification of non-oxide and composite refractories

Family	Type	Major chemical components	Major phases
Non-oxide refractories	C refractories	C	Graphite
	SiC refractories	SiC	Silicon carbide
	SiC–C refractories	SiC C	α-SiC Graphite
	$SiC–Si_3N_4$ refractories	Si_3N_4 SiC	α-SiC $(\alpha+\beta)$-Si_3N_4
Composite refractories	Al_2O_3–C refractories	Al_2O_3 C	Corundum Graphite
	MgO–C refractories	MgO C	Periclase Graphite
	$Al_2O_3–SiO_2$–C–SiC refractories	SiO_2 Al_2O_3 SiC	Mullite/andalusite Cristobalite Silicon carbide
		SiO_2 Al_2O_3 SiC C	Mullite/andalusite Cristobalite Silicon carbide Graphite

(periclase), Si (metal silicon), Al_2O_3 (corundum), Si_3N_4 (silicon nitride), Al_2SiO_5 (andalusite), SiO_2 (quartz), SiO_2 (cristobalite) and $Si_3Al_6O_{15}$ (mullite). These synthetic refractories were referenced SR-1, SR-2, SR-3, SR-4 and SR-5. Tables 2 and 3 set out the characteristics of the 10 refractories used in the study.

Crystalline phase analysis was performed with a PHILIPS model PW1830 X-ray diffractometer with a Cu tube, fitted with an automatic sample changer. XRD phase quantification was done by a quantitative analysis method, in which the values of the relative intensities are related to a standard. The reference intensity ratios (RIRs)[24–26] were determined for single substance crystalline materials present in the silicon carbide-based refractories, because the method is most accurate when the RIRs are measured and subsequently used for quantitative analysis on the same instrument with the same geometry. The crystalline materials were in powder form, and a variable divergence slit and copper Kα radiation were used. The following reference materials were used for phase quantification: α- and β-Si_3N_4 (Alfa Aesar); quartz, SiO_2 (Fluka); mullite, $Al_6Si_2O_{13}$ (BCR-301); corundum, Al_2O_3 (Fluka and NBS 676); silicon carbide, SiC, with different average particle size and crystallographic nature (Alfa Aesar, Riedel-de Haën and Goodfellow); silicon, Si (Alfa Aesar); cristobalite, SiO_2 (Fluka); and andalusite, Al_2SiO_5 (SARM 34). The JCPDS files of pure crystalline substances were used to identify the components of the test materials.

Table 2
Refractory SiC powders used

Reference	Average particle size (μm)	SiC (wt%)	Supplier
SiC-1	8.6	99	Alfa Aesar
SiC-2	1.1	95	Alfa Aesar
SiC-3	21.8	98	Sigma–Aldrich
SiC-4	42.5	98.7	Goodfellow
SiC-5	22.4	98	Alfa Aesar

XRF analysis was performed with a PHILIPS model PW 2400 spectrometer, fitted with a PW 2540 VTC automatic sample changer. The samples were prepared as pressed pellets, using a solution of *N*-butyl-methacrylate in acetone as a binder; the sample was pressed in a die, 3.5 cm in diameter, at a pressure of $400\,kg\,cm^{-2}$ in a CASMON, S.A., press. The calibration curves for the XRF measurement were prepared from internal standards and subsequently validated with reference materials.

The coulometry measurements were made with a UIC COULOMETRICS INC. model CM-150 analyser, fitted with a tube furnace capable of working in a range of temperatures between 25 and 1100 °C, using alumina boats with a volume of 5 mL. The samples were diluted with Al_2O_3 from Merck for the coulometry measurements; we used Cu from Riedel-de Haën to favour the silicon carbide oxidation process.

The reagents used in the wet method were: HF, HNO_3, H_2SO_4 and $K_2S_2O_7$, all from Merck.

The ICP-OES measurement was conducted with a LEEMAN LABS INC. model Direct Reading Echelle spectrometer. Calibration and validation were performed using $1000\,mg\,L^{-1}$ solutions of each of the elements from Merck.

In order to validate the methods used we analysed the following reference materials: SRM 112b silicon carbide, supplied by the US National Institute of Standards (NIST), and CRM 781-1 silicon carbide refractory and CRM 359 nitrogen bearing silicon carbide, supplied by the Bureau of Analysed Samples Ltd. (BAS), England.

2.2. Methodology

The following methodology was adopted for characterising the crystalline phases and analysing the chemical components

Table 3
Synthetic non-oxide and composite refractories used

Reference	Family (see Table 1)	Type (see Table 1)	Composition (wt%)	
SR-1	Non-oxide	SiC–C refractories	α-SiC	89.1
			$C_{graphite}$	9.7
SR-2	Non-oxide	SiC–Si_3N_4 refractories	α-SiC	69.6
			α-Si_3N_4	26.6
SR-3	Composite	Al_2O_3–MgO–C–SiC refractories	α-Al_2O_3	50.0
			α-SiC	9.8
			$C_{graphite}$	15.1
			MgO (periclase)	25.0
SR-4	Composite	Al_2O_3–SiO_2–C–SiC refractories	α-Al_2O_3	40.3
			$Al_6Si_3O_{15}$ (mullite)	19.8
			α-SiC	9.5
			$C_{graphite}$	4.0
			α-SiO_2 (quartz)	19.9
			Si	5.0
SR-5	Composite	Al_2O_3–SiO_2–SiC refractories	Al_2SiO_5 (andalusite)	41.5
			α-SiC	21.0
			α-SiO_2 (quartz)	10.1
			α-SiO_2 (cristobalite)[a]	5.1
			$Al_6Si_3O_{15}$ (mullite)	20.5

[a] Although cristobalite is not used as a raw material in synthesising refractories, it appears during the synthesis process or in use.

of the studied refractories: first we determined the crystalline phases by XRD; average particle size was then determined by scanning electron microscopy (SEM). This was followed by chemical analysis, using different methods depending on the component to be analysed. The respective methods used for chemical analysis are detailed in Table 4.

In the XRD phase characterisation the concentration of every phase (C_r) was calculated from the equation:

$$C_r = \sum_{j=1}^{n} \frac{I_{ij}/(I_j)_0}{\sum_{j=1}^{n} S_{jr}\beta_{rj}}$$

where I_{ij} is the intensity of peak i of phase j in the sample, and $(I_j)_0$ is the peak intensity of pure phase j. In every case peak intensity means the integrated area of the peak. S_{jr} is the ratio of the intensities of peaks i and h of phases j and r, respectively:

$$S_{jr} = \frac{I_{ij}}{I_{hr}}$$

Table 4
Methods used for chemical analysis of each component

Component	Method
Free C	Wet method and coulometry
SiC	Wet method and coulometry
$SiO_2 + Si$	Wet method
Si_3N_4	–
Periclase (MgO)	XRF
Al_2O_3 from mullite ($Si_3Al_6O_{15}$)	XRF
Al_2O_3 from andalusite ($SiAl_2O_5$)	XRF
Cristobalite (SiO_2)	–
Impurities	XRF and ICP-OES

and β_{rj} is the reference intensity ratio (RIR) with respect to the reference material. In this case these coefficients have been determined from binary mixtures of pure phases and corundum (50:50 weight percentage) from the expression:

$$\beta_{rj} = \frac{K_{ij}}{K_{hr}}$$

where K_{ij} and K_{hr} are calibration constants defined as the relative areas of peaks i and h of phases j and r, respectively, in relation to corundum.

The pure phases used were either commercially available or synthesised in our laboratory.

Three factors have been taken into account in order to obtain high precision and high accuracy analysis:

(1) The material used to determine the reference intensity must have the same level of perfection as the component sought, which is relieved by the width of the diffraction lines.
(2) Sample grinding must be thorough enough to ensure optimum particle size (average diameter of 40 μm) and sample homogeneity.
(3) Sample loading into the sample holder must be free falling to avoid preferred orientation and induced packing.

In the case of free carbon the measurements were made at $d = 3.4$ Å (maximum peak intensity) and the RIR value was 13.6. The measurements on alpha silicon carbide were made at $d = 2.52$, 2.36, 1.53 and 1.42 Å and the RIR value was 2.95. The measurements on silicon, quartz and cristobalite were made at $d = 3.13$ Å, $d = 4.25$ Å and $d = 4.05$ Å and the RIR values were 4.3, 2.8 and 2.6, respectively. The measurement on silicon nitride was made at $d = 2.88$ Å and the RIR value was 0.97. The measurements on periclase, corundum, mullite and andalusite were made at $d = 2.10$ Å, $d = 2.08$ Å, $d = 5.39$ Å and $d = 4.55$ Å and the RIR values were 3.83, 1.0, 0.60 (or 0.40 in the peak between 15 and 17° 2θ) and 0.92, respectively.

Free carbon was chemically characterised by the gravimetry method (determining sample weight loss at 800 °C) and by coulometry. In the latter technique, carbon was oxidised to CO_2 at 800 °C in oxygen atmosphere in a tube kiln and the evolving CO_2 was determined by coulometry. The optimum sample quantities and test times for the coulometry experiments were 0.0400 g sample and 10 min for samples with low carbon content ($\leq 1\%$), and 0.0150 g sample and 30 min for samples with higher carbon content ($>1\%$).

Silicon carbide was chemically characterised by the wet method and by a method using coulometry. In the wet method (gravimetry) the sample was calcined at 800 °C to eliminate free carbon, etched with an acid mixture ($HF:HNO_3:H_2SO_4$ in a weight proportion of 10:1:0.5) and calcined again at 800 °C to eliminate Si and SiO_2. The last calcining operation was repeated until achieving constant weight. The sample was then etched with $K_2S_2O_7$ at 600 °C to dissolve all the components except SiC. The resulting molten mass was subsequently dissolved using HCl in order to obtain SiC without any other component initially present in the sample. This SiC was then weighed.

For the silicon carbide characterisation by coulometry a new method developed at ITC was used. In this method the sample is treated with copper to catalyse the sample oxidation process, and test conditions (reaction time, temperature, sample quantity, sample/copper ratio, etc.) are optimised. Total carbon (free carbon and carbon from silicon carbide) is determined by oxidising the carbon at 1080 °C; silicon carbide is determined as the difference between total carbon and free carbon. In order to apply this method the sample must be diluted with Al_2O_3, avoiding saturation, and mixed intimately with Cu, which catalyses carbon oxidation from silicon carbide. The optimum conditions for good results were: 5:47.5:47.5 weight proportion of Al_2O_3:Cu:sample; 0.0100 g of this mixture, heating for 60 min at 1080 °C.

Silicon and silica were chemically characterised by the wet method, jointly determining Si and SiO_2. The sample was calcined at 800 °C, etched with an acid mixture ($HF:HNO_3:H_2SO_4$ weight proportion of 10:1:0.5), dried and then calcined at 800 °C. The last calcining operation was repeated until achieving constant weight. The weight loss corresponds to the Si and SiO_2 in the sample.

MgO from periclase and Al_2O_3 from corundum, mullite and andalusite were chemically characterised by XRF after preparing the sample in the form of pressed pellets and constructing the relevant calibration curves.

Impurities (Fe, Ca and Ti) were chemically characterised by XRF and ICP-OES. For the XRF characterisation the sample was prepared in the form of pressed pellets and calibration curves were constructed. In the case of ICP-OES, the sample was acid digested and the chemical elements were determined from the solution obtained, after preparing the calibration curves.

Table 5
Crystalline phases in the reference materials used

	SRM 112b	CRM 781-1	CRM 359
Major crystalline phases	Silicon carbide	Graphite carbon Silicon carbide	Silicon carbide Silicon nitride
Minor crystalline phases	Silicon Graphite carbon Corundum	Mullite Silicon Corundum	Graphite carbon Corundum Silicon

Table 6
Free carbon content (wt%) in the studied refractories

Refractory	Theoretical values	Wet method	Coulometry	XRD[a]
SiC-1	<0.1	<0.1	<0.1	–
SiC-2	<0.1	(−1.8)	0.89	–
SiC-3	<0.1	<0.1	<0.1	–
SiC-4	<0.1	<0.1	<0.1	–
SiC-5	<0.1	<0.1	<0.1	–
SR-1	9.7	9.5	9.5	9
SR-2	<0.1	<0.1	<0.1	–
SR-3	15.1	14.9	14.8	13
SR-4	4.0	4	4.2	4
SR-5	<0.1	<0.1	<0.1	–

[a] The only carbon crystalline phase identified by XRD was graphite carbon.

3. Results

3.1. Crystalline phase identification

The crystalline phases identified in the reference materials are listed in Table 5. The table shows that all the reference materials contained numerous crystalline phases in addition to the silicon carbide phase.

3.2. Free carbon determination

The results of the free carbon and graphite carbon determinations in the test refractories and reference materials are shown in Tables 6 and 7, respectively.

The wet method and coulometry yielded the same results in the refractories and in the reference materials, except in sample SiC-2. In SiC-2 the wet method presented a negative value, while coulometry yielded a small positive value (close to 1%). This sample had the lowest average particle size, which enabled oxidation of the SiC particles to SiO_2, thus producing a negative weight loss in the wet method (increase of sample weight), as SiC molecular weight is lower than that of SiO_2, while coulometry analyses carbon from oxidised SiC.

Table 7
Free carbon content (wt%) in the reference materials

Reference material	Theoretical values	Wet method	Coulometry	XRD[a]
SRM 112b	0.26	0.31	0.25	1
CRM 781-1	37.2	36.8	36.2	43
CRM 359	0.06	<0.1	–	<1

[a] The only carbon crystalline phase identified by XRD was graphite carbon.

Table 8
Silicon carbide content (wt%) in the studied refractories

Refractory	Theoretical values	Wet method	Coulometry	XRD
SiC-1	99	99	98	[a]
SiC-2	95	–	96	[a]
SiC-3	98	99	97	[a]
SiC-4	98.7	99	98	[a]
SiC-5	98	98	97	[a]
SR-1	90.3	90	89	91
SR-2	70.5	–	–	74
SR-3	9.9	–	9	12
SR-4	9.6	–	9	9
SR-5	21.3	–	22	18

[a] Silicon carbide was not determined by XRD in these refractories because they were used to obtain calibration constants.

The wet method and coulometry therefore provided good results in analysing the studied refractories in the tested range of carbon contents (from <0.1% to 37%) when average SiC particle size was not too small.

The determination of graphite carbon content by XRD was difficult, and accuracy was poor because the maximum reflection peak of the graphite was overlapped with peaks from other components. The problem could not be solved by measuring lower intensity graphite reflection peaks, because graphite has few reflection peaks and all have low intensity. The following results were found in the XRD determination:

(1) Reference material CRM 781-1 presented a higher value for graphite carbon than the theoretical value, because one major component of the reference material was a vitreous phase whose vitreous halo overlapped with the graphite carbon maximum reflection peak in the XRD determination.
(2) In the other studied refractories the error of determination was 10–15%.

3.3. Silicon carbide determination

The results of the silicon carbide determinations in the studied refractories and in the reference materials are shown in Tables 8 and 9, respectively.

The wet method provided good results in determining silicon carbide content in the SiC refractories when average particle size exceeded 8 μm (refractories SiC-1, SiC-3, SiC-4 and SiC-5). However, the SiC content found in refractory SiC-2 by the wet method was lower than the theoretical value because the small average particle size of SiC-2 enabled partial oxidation of SiC to SiO_2, with subsequent formation of SiF_4 (a volatile compound) when the sample was etched with an acid mixture containing HF.

Table 9
Silicon carbide content (wt%) in the reference materials

Reference material	Theoretical values	Wet method	Coulometry	XRD
SRM 112b	97.37	98	97	98
CRM 781-1	36.9[a]	36.5	36	38
CRM 359	78.2	–	–	77

[a] Calculated value, not provided on the certificate.

Table 10
Joint silicon and silica content (wt%) in the SR refractories determined by the wet method

Refractory	Theoretical value	Wet method
SR-1	<0.1	<0.1
SR-2	<0.1	–
SR-3	<0.1	–
SR-4	32.4	33
SR-5	42	43

The wet method presented different results in the SiC determination in the SR refractories. The results were good in analysing SR-1. SR-2 exhibited important weight loss when the sample was acid etched (as if Si and SiO_2 were present; this was, however, obviously not the case, but was instead due to the low average particle size, which enabled oxidation of the SiC particles) and the determination could not be performed. In the case of SR-3 the results were unsatisfactory because sample weight increased with acid etching (done to eliminate all the sample components except silicon carbide), owing to the formation of stable compounds by chemical reaction between Al and Mg of the samples and the acids used. This was verified by XRD. The SiC content in SR-4 could not be determined because the formation of stable compounds as a result of chemical reaction with $K_2S_2O_7$ prevented SiC from separating from the other components. Similarly, SiC content could not be determined in SR-5 because constant weight could not be achieved when the sample was repeatedly acid etched.

Coulometry provided good results in determining the SiC content in all the studied refractories (under the test conditions set) except in the case of SR-2, probably because of its silicon nitride content.

The wet method and coulometry yielded good results in analysing reference materials SRM 112b and CRM 781-1. However, the results were unsatisfactory in the case of CRM 359, once again, due to its silicon nitride content.

The XRD determination of crystalline phase content provided good results for the SR refractories and reference materials used, although the agreement between the theoretical values and the experimentally determined values was better in the case of the reference materials because their XRD diffractograms displayed fewer overlapping peaks. In this sense XRD accuracy depends on the type of refractory to be analysed and, especially, on the number of phases present in the refractory.

3.4. Silicon and silica determination

Silicon and silica were determined jointly by the wet method (this technique does not allow determining these two components individually), and separately (as silicon, quartz and cristobalite) by XRD.

The results of the silicon and silica determinations in the SR refractories by the wet method and by XRD are set out in Tables 10 and 11, respectively. Table 11 only shows the results

Table 11
Silicon, quartz and cristobalite contents (wt%) in the SR refractories determined by XRD

Refractory	Theoretical value			XRD		
	Silicon	Quartz	Cristobalite	Silicon	Quartz	Cristobalite
SR-4	5	19.9	–	5	17	–
SR-5	–	10.1	5.3	–	10	4

Table 12
Joint silicon and silica content (wt%) in the reference materials determined by the wet method

Reference material	Theoretical value	Wet method
SRM 112b	1.23	1.1
CRM 781-1	15.6	15.4

Table 13
Silicon content (wt%) in the reference materials determined by XRD

Reference material	Theoretical value	XRD
SRM 112b	0.15	<1
CRM 781-1	4.646	5
CRM 359	0.325	<1

Table 14
Al_2O_3 and MgO contents (wt%) in the SR refractories determined by XRF

Refractory	MgO		Al_2O_3	
	Theoretical value	XRF	Theoretical value	XRF
SR-3	25.0	25	50.0	50.1
SR-4	–	–	54.0	53.9
SR-5	–	–	36.0	36.0

for SR-4 and SR-5 because they were the only refractories containing silicon, quartz and cristobalite.

The wet method presented good results when analysing SR-1, SR-4 and SR-5. SR-2 exhibited weight loss: this was not due to reaction between HF and Si and/or SiO_2, as these compounds were not present in the sample, but was again because of the small SiC particle size. The SR-3 results were unsatisfactory because sample weight rose with acid etching, owing to the formation of stable compounds by chemical reaction between Al and Mg in the sample and the acids used. This was verified by XRD.

The XRD technique yielded good results in determining the crystalline phases in SR-5. However, in SR-4 the theoretical and the experimentally determined values for quartz content did not match as well, because the quartz maximum reflection peak was highly overlapped with peaks from other components and could not be used in determining quartz content; instead, a low intensity peak (located between 20 and 21.5° 2θ) was used to determine quartz content. This low intensity peak has a greater experimental error when the sample has low quartz content and numerous crystalline phases.

Table 16
Total aluminium content (wt%) in the reference materials determined by XRF and XRD

Reference material	Theoretical value	XRF	XRD
SRM 112b	0.44	0.41	<1
CRM 781-1	4.39	4.20	4.5[a]
CRM 359	0.118	0.11	<1

[a] This Al percentage represents 6% mullite plus 1% corundum.

Table 17
Silicon nitride content (wt%) in the SR-2 refractory determined by XRD

Refractory	Theoretical value	XRD
SR-2	26.6	26

Table 18
Silicon nitride content (wt%) in the CRM 359 reference material determined by XRD

Reference material	Theoretical value	XRD
CRM 359	19.6	15

The results of the silicon and silica determination in the reference materials by the wet method and by XRD are shown in Tables 12 and 13, respectively.

The wet method presented good results when the silicon and silica contents of reference materials SRM 112b and CRM 781-1 were analysed together. XRD proved to be a good technique for determining CRM 359 silicon content; however, silicon could not be determined by XRD in the other two reference materials because the detection limit was around 1% silicon content.

3.5. Determination of periclase, corundum, mullite, andalusite, Al_2O_3 and MgO

The results of the XRF determination of MgO and Al_2O_3 in the SR refractories are given in Table 14. Table 15 sets out the results of the XRD determination of periclase, corundum, mullite and andalusite in the SR refractories. In the case of the reference materials, total aluminium was determined by XRF,

Table 15
Periclase, corundum, mullite and andalusite contents (wt%) in the SR refractories determined by XRD

Refractory	Periclase		Andalusite		Mullite		Corundum	
	Theoretical value	XRD	Theoretical value	XRD	Theoretical value	XRD	Theoretical value	XRD
SR-3	25	23	–	–	–	–	50.0	50
SR-4	–	–	–	–	19.8	20	40.3	42
SR-5	–	–	41.5	–	20.5	19	–	–

Table 19
Fe, Ca and Ti contents (wt%) in the reference materials determined by XRD and ICP-OES

Impurity	SRM 112b			CRM 781-1			CRM 359		
	Theoretical value	XRF	ICP	Theoretical value	XRF	ICP	Theoretical value	XRF	ICP
Fe	0.13	0.12	0.127	0.8061	0.79	0.802	0.1754	0.16	0.172
Ca	0.04	0.05	0.048	0.0433	0.04	0.041	0.1082	0.12	0.107
Ti	0.023	0.02	0.021	0.0320	0.03	0.031	0.0218	0.02	0.021

and corundum and mullite by XRD; these results are given in Table 16.

XRF provided good results in analysing MgO and Al_2O_3 in the SR refractories and in the reference materials.

In general XRD presented satisfactory results in determining crystalline phase contents in the SR refractories, and corundum and mullite contents in the reference materials (expressed as aluminium content to allow comparing the experimental values with the certified values), except in determining the andalusite content of SR-5. In this last case, the value obtained was much higher than the theoretical value. This was probably due to the numerous crystalline phases in the sample and/or to using a natural material whose crystallinity differed from that of the material employed in making the standard file. The relative intensities of the material used in the test can therefore vary with respect to those given in the standard file used for determining the relevant RIR value. This leads to a greater deviation in the resulting RIR values for the different peaks analysed than in other pure materials, and to inaccurate RIR values, owing to errors in phase quantification because of different crystallinity.

3.6. Silicon nitride determination

The results of the XRD determination of silicon nitride content in the SR-2 refractory and in reference material CRM 359 are shown in Tables 17 and 18, respectively.

The theoretical and experimental values for Si_3N_4 in CRM 359 do not match because it was not possible to find pure alpha-silicon nitride (α-Si_3N_4).

3.7. Determination of impurities

The results of the XRF and ICP-OES determinations of the Fe, Ca and Ti contents in the reference materials are given in Table 19.

The theoretical and experimental values match well in both techniques, although the ICP-OES technique has a lower detection limit.

4. Conclusions

A study has been conducted on the physico-chemical characterisation of silicon carbide-based (non-oxide and composite) refractories. The following conclusions can be drawn:

1. The phases have been characterised by XRD, but the quality of the results depends on the number of crystalline phases present in the sample. The greater the number of crystalline phases, the more the diffractogram peaks tend to overlap. In this study, phase characterisation accuracy has been between 5 and 15%.
2. Silicon carbide-based refractories have been chemically characterised by different methods. The best method for each particular refractory depends on the crystalline phases (silicon carbide and others) present in the sample, as well as the average size of the SiC particles (refractories containing small SiC particles cannot be analysed by the wet method because silicon is easily oxidised).
3. SiC content has been satisfactorily determined by coulometry in all the studied refractories, except in those containing silicon nitride. XRD also allowed satisfactory quantification of SiC; however, this technique requires knowing average SiC particle size and determining the reference intensity ratio (RIR) beforehand. The wet method could only be used when average SiC particle size exceeded 8 μm and no mullite, andalusite, corundum or silicon nitride phases were present in the sample.
4. Free carbon content has been satisfactorily determined by coulometry and by the wet method (calcining). For the wet method average SiC particle size needed to be larger than 8 μm to avoid SiC particle oxidation. Graphite carbon was also determined by XRD, but the quality of the results depended on the quartz and amorphous phase contents in the refractory (these phase peaks are overlapped with the graphite maximum intensity peak).
5. The MgO and Al_2O_3 contents were satisfactorily determined by XRF. Periclase, corundum and mullite phase content was determined by XRD, after previously establishing the reference intensity ratio (RIR) for the crystalline phase involved.
6. Silicon and silica contents were jointly determined by a wet method when the refractory contained no silicon nitride or periclase. XRD enabled determining silicon and silica contents separately as quartz and/or cristobalite.
7. Impurities such as Fe, Ca and Ti were satisfactorily analysed by XRF and ICP-OES; the latter technique has lower detection limits.
8. Silicon nitride could only be analysed at our laboratories by XRD in a semi-quantitative way, because no pure alpha-silicon nitride was found.

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