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Refractory products — Determination of reduced species in carbon containing refractories by XRD

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Foreword

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This document was prepared by Technical Committee ISO/TC 33 *Refractories*.

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Refractory products — Determination of reduced species in carbon containing refractories by XRD

1 Scope

This document describes methods for the determination of mineralogical phases often present as additives or reaction products in carbon containing or graphitic refractory products by X-ray Diffraction (XRD) using a Bragg-Brentano diffractometer. It includes details of sample preparation and general principles for qualitative and quantitative analysis of mineralogical phase composition. Quantitative determination of α-Si_3N_4, β-Si_3N_4, AlN, aluminium metal, Al_4C_3, silicon metal, boron carbide and BN are described. The problems encountered with some determinations are highlighted.

Additional reduced species present in some refractories could include $Al_2O_3{\cdot}AlN$ solid solutions (so called Alons), $Si_3N_4{\cdot}SiO_2$ solid solutions and $Si_3N_4{\cdot}Al_2O_3$ solid solutions (Sialons). The presence of some of these solid solution components will cause problems with both identification and quantification as they are not well-defined structures.

NOTE For rationalisation of nitrogen containing phases, the total nitrogen content, analysed in accordance with EN 12698-1 is used.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 836, *Terminology for refractories*

ISO 5022, *Shaped refractory products — Sampling and acceptance testing*

ISO 8656-1, *Refractory products — Sampling of raw materials and unshaped products — Part 1: Sampling scheme*

ISO 10081-1, *Classification of dense shaped refractory products — Part 1: Alumina-silica*

ISO 10081-2, *Classification of dense shaped refractory products — Part 2: Basic products containing less than 7 % residual carbon*

ISO 10081-3, *Classification of dense shaped refractory products — Part 3: Basic products containing from 7 % to 50 % residual carbon*

ISO 10081-4, *Classification of dense shaped refractory products — Part 4: Special products*

EN 13925-1, *Non-destructive testing. X-ray diffraction from polycrystalline and amorphous materials. General principles*

3 Terms and definitions

For the purposes of this document the terms and definitions given in ISO 836, ISO 10081-1, ISO 10081-2, ISO 10082-3, ISO 10081-4, EN 13925-1 and the following apply.

3.1
carbon containing refractories

refractory products containing greater than 20% carbon where carbon is dominantly added in the manufacturing process in the form of graphite, pitch, tar, resin or similar

Note 1 to entry: For refractories in which silicon carbide is the dominant form of carbon isare beyond the scope of this document , refer to EN 12698-2.

4 Apparatus

4.1 X-ray diffractometer

Generally comprising of but not limited to:

Bragg-Brentano X-ray diffractometer. The diffractometer will comprise of goniometer, X-ray source (normally copper X-ray tube), incidence beam optics, diffracted beam optics, specimen stage, detector and data collection system. More detail on suitable systems can be found in EN 13925-3.

The equipment should be aligned and calibrated as detailed in EN 13925-3.

The equipment should be capable of attaining the performance criteria given in Clause 5.

For samples containing a considerable amount[1] of an iron (as Fe), a Cobalt X-ray tube shall be used instead of a Copper X-ray tube due to fluorescence of the iron by the copper X-rays[1]. In the case of Cobalt X-ray tube, the diffractometer angles stated in this standard will need to be re calculated.

4.2 Software

Capable of peak matching, whole pattern fitting and Rietveld refinement for phase quantification.

5 Instrument performance

The instrument should be capable of the following performance parameters as defined in Annex C of EN 13925-3):

The peak position of major peaks for a certified reference material shall not deviate by more than 0.05° 2θ.

NOTE A suitable certified reference material to check instrument performance is NIST SRM 640f-alumina powder.

6 Sampling

Sample shaped and unshaped products using the procedures given in ISO 5022 and ISO 8656-1. When sampling large fragments, take care to collect samples from different points to ensure that the sample is fully representative.

Homogenize the sample by reducing the maximum particle size, take the test specimen from this material. Avoid, where possible, contamination during grinding. Keep sample dry and avoid heating the sample to in excess of 110 °C.

Sample splitting and or riffling of sample may be required to reduce the volume of material.

7 Procedure

7.1 Sample preparation

Grind the sample using a mill so that the resultant powder has a particle size of less than 45 µm (95% less than 45 µm as determined using a suitable methodology).

NOTE 1 Whilst a particle size of 10 µm is the ideal size for Rietveld refinement to improve sampling statistics, grinding to such a size can degrade less hard components to a non-crystalline structure. Further details are available in Jenkins & Snyder (1996)[2].

NOTE 2 Excessive grinding of the sample has been found to result in increasing the apparent non-crystalline content of the sample.

After sampling and grinding, the sample should be kept in a desiccator and analysed on removal from the desiccator. Aluminium carbide (Al_4C_3), if present, undergoes rapid hydrolysis.

Press the powder into the cavity holder from the reverse side of the cavity to that which is to be presented to the x-ray beam. Backfilling is preferred to minimise preferred orientation of the powder. The depth of the cavity shall be sufficient to exceed the critical depth of the incident radiation for the sample analysed. The dimensions of the sample holder will be such that X-rays irradiating outside of the sample volume can be avoided.

7.2 Measuring parameters

The measuring parameters will vary depending upon the mineralogy of the sample being examined.

The angular scan shall be sufficient to include all the main peaks of the phases contained in the sample, as a minimum that shall be:

start angle, 2θ 10 °;

end angle, 2θ 70 °;

NOTE If a Cobalt X-ray tube is used, the equivalent start and end angles are 11,6° and 83,5°, respectively.

In order to maximize the information-content in diffraction pattern and, at the same time, the efficiency of data collection, the experiment should be designed so that between 5 000 and 10 000 counts are accumulated for the intensities in the largest peaks in the pattern. Increased data statistics improve the accuracy of peak fitting and help to confirm the presence or absence of minor components within the sample.

The optimum step width is between one-fifth and one-third of the minimum full width half maximum (FWHM) of the peaks. Step sizes of 0.02 °2θ have been found to be suitable.

7.3 Qualitative analysis

Use an automatic or manual search to identify the different phases present. ICDD (International Centre for Diffraction Data, Pennsylvania USA) formerly known as Joint Committee on Powder Diffraction Standards (JCPDS) or equivalent databases are available to identify the relevant diffraction peaks.

In addition to carbon-based material, the main species that are likely to be encountered are one or more of the following: zircon, monoclinic zirconia, cubic zirconia, mullite, α-alumina, crystalline silica, magnesia and spinel. The reduced species could include silicon carbide (α-SiC, β-SiC), silicon nitride (α-Si_3N_4, β-Si_3N_4), silicon metal (Si), silicon oxynitride (Si_2ON_2), aluminium metal (Al), iron metal (Fe), aluminium nitride (AlN), aluminium carbide (Al_4C_3), boron nitride (BN), ferrosilicon ($FeSi_2$, FeSi), boron carbide and tungsten carbide (WC due to contamination from grinding). Additional reaction products occur in some refractories including: $Al_2O_3 \cdot AlN$ solid solutions (so called Alon's), $Si_3N_4 \cdot SiO_2$ solid solutions and $Si_3N_4 \cdot Al_2O_3$ solid solutions (so called Sialon's).

The identification and subsequent quantification of some phases is limited by overlap of adjacent peaks and is not resolvable in all cases. Such notable overlaps include silicon with monoclinic zirconia, boron nitride with graphite.

7.4 Quantitative analysis

7.4.1 General

Quantitative analysis is performed using computer-based Rietveld refinement to model the entire XRD trace. The Rietveld method uses known crystal structure models for the phases analysed rather than requiring a physical reference standard.

7.4.2 Quantitative phase determination using Rietveld Refinement

7.4.2.1 General

The Rietveld method, although initially was developed to refine the structures of crystalline materials by means of powder diffraction, is employed with great degrees of success to the quantification of mixed phase materials. For a mixture of several phases the relative abundances for the phases can be determined by minimising the discrepancies between a theoretical model of the mixture of phases and the observed (actual pattern) mixture of phases.

Rietveld refinement is carried out in a stepwise manner to minimise the differences between the observed and calculated intensities for every °2θ step of a powder pattern. Therefore, refinement takes into account all the points of a diffraction trace rather than just selected reflections. The calculated intensity (y_{ic}), for a given point on the diffraction trace is determined by summing for the background and neighbouring reflections (k) for all phases (p):

$$y_{\text{ic}} = \sum_{p} S_p \sum_{k} p_{\text{k}} L_{\text{k}} \left| F_{\text{k}} \right|^2 G(\Delta\theta_{ic}) P_{\text{k}} + y_{\text{ib}}(c)$$

where

S is the scale factor,

L_{k} is the Lorentz and polarisation factors for the kth reflection,

F_{k} is the structure factor,

p_{k} is the multiplicity factor,

P_{k} is the preferred orientation factor,

θ_{k} is the Bragg angle for the kth reflection,

$G(\Delta\theta_{\text{ik}})$ is the reflection profile function and

$y_{\text{ib}}(c)$ is the refined background.

The goodness of fit, the R_{wp} value is given as:

$$R_{\text{wp}} = \left[\Sigma w_i (y_{\text{io}} - y_{\text{ic}})^2 / \Sigma w_i y_{\text{io}}^2 \right]^{0.5}$$

where y_{io} and y_{ic} are the observed and calculated intensities respectively, at point i on the diffraction trace.

Rietveld quantification formulae:

$$W_i = \frac{S_i \left(ZMV\right)_i \big/ \tau_i}{\sum_{i=1}^{N} S_i \left(ZMV\right)_i \big/ \tau_i}$$

where

W_i is the weight fraction of i

S_i is the refined scale factor of phase i

Z is the number of particles in unit cell of phase i

M is molecular weight of phase i

V is the unit cell volume of phase i calculated from refined unit cell parameters

τ_I is the- micro absorption correction factor of phase i

7.4.2.2 Refinement procedure

The initial stage of refinement is the accurate fitting of the background, using either a polynomial term, or background subtraction.

Scale factors of each of the individual phases are then refined to allow for phase fractions. Peak positions are then refined to allow for deviations from ideal positions. The unit cell parameters, a, b, c, α, β and γ are then refined to minimise the difference between the observed and the calculated patterns.

The peak shape functions U, V and W can be refined in significant components within the sample to improve the fit. For phases that are needle or platy in shape, pressing of the powder into a sample holder can result in the preferred orientation of the crystallites. As the crystallites are no longer randomly oriented, certain peaks could show increased intensity. Preferred orientation should be refined for those phases that are subject to preferred orientation. The preferred orientation need only be refined for phases that account for more than 10% of the whole sample.

As refinement reaches completion, the χ^2 and R_{wp} values are reduced to a minimum, in ideal situations these are below 5 and 10%, respectively. A goodness of fit parameter S is also be calculated this tends to equal χ for small values. When no statistical improvement upon further refinement occurs, the data have converged. The resulting values are the quantified concentrations of the phases present.

7.5 Rationalisation of results

As phases identified and quantified have defined chemical compositions, it is preferable to compare the determined composition with directly determined chemical analysis derived from X-ray fluorescence analysis (ISO 12677) or other chemical methods as a final data check.

NOTE Due to the presence of solid solutions and non-crystalline material, a close match between the rationalised analysis and direct analysis might not always be possible.

7.5.1 Calculation refinement for α-Si_3N_4, β-Si_3N_4, Si_2ON_2, BN and AlN

The contents of α-Si_3N_4, β-Si_3N_4, Si_2ON_2, AlN and BN shall be normalized in proportion to their molecular nitrogen contents to the total nitrogen concentration. Determine the total nitrogen content in accordance with EN 12698-1.

NOTE If $Al_2O_3 \cdot AlN$ solid solutions (Alons), $Si_3N_4 \cdot SiO_2$ solid solutions and $Si_3N_4 \cdot Al_2O_3$ solid solutions (Sialon's) are present, a unique solution may not possible.