Application note

X-ray diffraction

Determination of the crystallite size of graphite in calcined petroleum coke using ARL X'TRA Companion XRD

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Introduction

Calcined Petroleum Coke (CPC) is a graphite-based material widely used in metallurgy, aluminum production, and fuel production. Derived from raw petroleum coke through a high-temperature process, CPC is known for its excellent electrical conductivity and high carbon content. The electrical conductivity, and thus the CPC's potential quality as an electrode, though, depends on the crystallite size (CS, L_c). Therefore, it is crucial to evaluate the crystallite size of CPC. X-ray diffraction (XRD) is the gold-standard method for CS determination in accordance with ASTM D5187 standard.

In that norm a procedure is described where L_c is calculated using the formula

$$\Delta po = 2(sin\theta_2 - sin\theta_1)/\lambda$$

where:

θ_1 = lower angle at half peak intensity width

θ_2 = higher angle at half peak intensity width

λ = incident wavelength

This is derived from a basic relationship between the peak width and the size of scattering domains which was established in the Scherrer equation.[1]

$$L_c = (K\lambda)/((\beta_{obs} - \beta_{inst})cos\theta)$$

K = arbitrary constant 0.89–1.39

λ. = incident wavelength

β_{obs} = measured peak line breadth

β_{inst} = instrument peak line breadth contribution

θ = angular location of the diffraction peak in degrees

From latter formulas, an expression for L_C can be derived which is valid for calcined petroleum coke.

$$L_c = 0.89/\Delta po$$

A more sophisticated approach from Williamson and Hall (the Williamson-Hall plot) is based on deconvoluting contributions of size and strain on the peak broadening[2] and thus obtaining more precise L_c values.

$$\{\beta_{obs} - \beta_{inst}\} = \frac{\lambda}{\{L_c \cdot cos\theta\}} + 4 \cdot \varepsilon_{str}\{tan\theta\}$$

$$\{\beta_{obs} - \beta_{inst}\} \cdot cos\theta = \frac{\lambda}{L_c} + 4 \cdot \varepsilon_{str}\{sin\theta\}$$

ε_{str} = strain component

Instrument and software

The Thermo Scientific™ ARL™ X'TRA Companion (see Figure 1) is a simple, easy-to-use benchtop XRD instrument for routine phase analysis as well as more advanced applications. The ARL X'TRA Companion uses a θ/θ goniometer (160 mm radius) in Bragg-Brentano geometry coupled with a 600 W X-ray source (Cu or Co). The radial and axial collimation of the beam is controlled by divergence and Soller slits, while air scattering is reduced by a variable beam knife. An integrated water chiller is available as an option. Thanks to the state-of-the-art solid state pixel detector (55 x 55 µm pitch), the ARL X'TRA Companion provides very fast data collection and comes with one-click Rietveld quantification capabilities and automated result transmission to a LIMS (Laboratory Information Management System).

Experimental

Graphite certified reference material RDC-1104 from R&D carbon was measured in reflection using Cu Kα (1.541874 Å) radiation for 2 minutes. The sample was prepared in a zero-background sample holder to minimize penetration depth error, and acquisition was performed with sample spinning.

Results

Using the Scherrer formula with the FWHM of the [002] reflection of graphite yields a L_c of 28.0 Å (see Figure 2), which is in perfect comparison to the certified value of 28.5(15) Å. The FWHM was determined by profile fitting the graphite [002] reflection with a Pseudo-Voigt function. This method complies with ASTM D5187 as it is a computational approach to determine L_c. The Williamson-Hall method has no influence on the results of this analysis as this graphite sample exhibits no strain.

Conclusion

The ARL X'TRA Companion is perfectly suited to determine the crystallite size in CPC samples according to ASTM D5187.

Figure 1: ARL X'TRA Companion diffraction system.

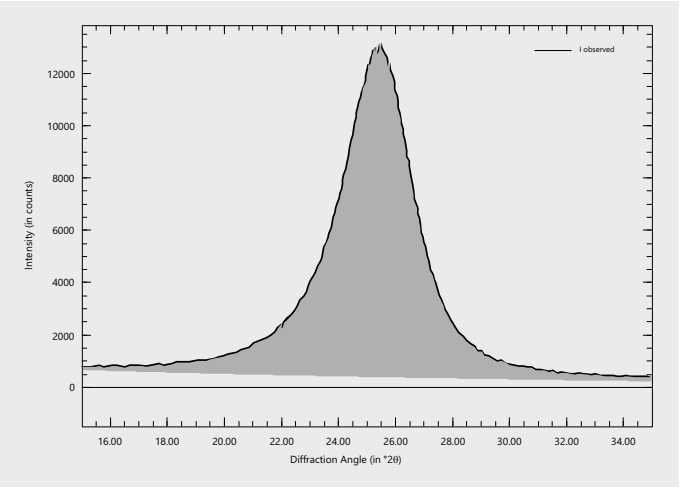

Figure 2: Measurement of RDC-1104 Graphite sample. Data were obtained at room temperature.

References

1. P. Scherrer, Göttinger Nachrichten Gesell. **1918** 2, 98-100.
2. G. K. Williamson, W. H. Hall, Acta Metall. **1953**, 1, 22-31.

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