X-ray Diffraction (XRD) – from Bath Composition towards Superheat

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Abstract

Varying raw material qualities, the use of different fluxes and increasing prices require a better control of processes and a more efficient use of energy. X-ray diffraction (XRD) is a process-critical tool to efficiently use energy during aluminium production. Traditionally quality control of electrolytic bathes, alumina and bauxites have relied on calibration-based single peak methods or more advanced full pattern techniques. Recent tests showed that the same XRD measurement used to determine composition and bath parameters can be used to predict the bath temperature and to calculate liquidus temperature and superheat. This technique saves valuable time and costs for additional temperature monitoring and allows fast counteractions on changing conditions to prevent bath solidification.

The paper shows possibilities to predict bath temperature and calculate liquidus temperature and superheat on a real-life test sample set of 69 samples together with the determination of phase composition, excess AlF_3, CaF_2 and total Al_2O_3. Measurement time per sample can reach less than one minute.

Keywords: XRD; electrolytic bath, process control, bath and liquidus temperature, superheat, PLSR.

1. Introduction

XRD analysis is a recognized analytical tool for production control in aluminium industries. Especially during the last decades with increasing analysis speed and with the use of modern techniques such as the Rietveld method XRD became a standard tool [1, 2]. Typical applications are the analysis of the mineral composition in bauxite and red mud, the alpha-alumina during the alumina extraction and the phase composition, bath ratio and excess aluminium in electrolytic bathes.

Speed of analysis and use of XRD in an automated environment are important to receive frequent feedback from the process and allow fast counteractions on changing bath conditions.

The use of statistical methods enables the handling of large data sets and extracts the maximum amount of information in the shortest possible time.

2. Methods

A first trial was set up to test if the bath temperature, liquidus temperature and superheat of an electrolytic bath can be predicted directly from the XRD measurement. A test set of 69 measurements (10 - 75 °2θ) of electrolytic bath samples with known bath compositions and corresponding bath temperatures was used to test the accuracy of the XRD analysis. The range of the bath temperatures was 931 - 1025 °C, measured with a thermocouple type k of Tyrotec and Fluke thermometer. The CaF_2 (total) content varied in the range of 6.0 - 7.6 % whereas the excess AlF_3 of the measured samples ranged from 3.3 to 13.1 % for the test set of 69 samples. Reference values for CaF_2 and excess AlF_3 for all 69 samples were determined by X-ray diffraction using the classical straight-line calibration methodology. Furthermore, an additional set of 29 bath samples with known total Al_2O_3 contents determined via oxygen combustion analysis using a Leco-O analysis for total oxygen and total alumina was used to calibrate a partial least square regression model to determine the total Al_2O_3 from the above-mentioned test set.

A Malvern Panalytical *CubiX*^{3} *Potflux* industrial diffractometer was used for the measurements, featuring measurement times of less than 90 seconds per scan. Similar tests were run on an Aeris benchtop X-ray diffractometer featuring measurement times of less than 1 minute. Data evaluation was done using the software package HighScore Plus version 4.7, incorporating the **p**artial **l**east **s**quares **r**egression (PLSR) analysis of XRD data. A combined analysis approach was used for the determination of the bath composition as well as the bath temperature, liquidus temperature and corresponding superheat. Rietveld full-pattern fitting was used to determine the phase composition, bath ratio, excess AlF_3 and liquidus temperature. In addition, simultaneously to the Rietveld analysis, the PLSR method was applied to determine total CaF_2, total Al_2O_3 and bath temperature. Alternatively, the CaF_2 content can also be calculated from the Rietveld phase composition. In addition, crystalline α-Al_2O_3 (corundum) can be accurately determined with the Rietveld method. The total Al_2O_3 content, however, including amorphous and semi-crystalline Al_2O_3, cannot be fitted as part of the Rietveld model but (like CaF_2) it can be predicted with the PLSR method [8] using a pre-calibrated model.

Partial least squares regression is a popular statistical method to predict properties directly from raw data. After calibration using a set of independently analyzed reference samples the model can be used to predict the property from unknown samples. Using PLSR [3] it is possible to predict any defined property *Y* directly from the variability in a data matrix *X*. The matrix *X* typically contains non-systematic variations (sample preparation, impurities, different grain sizes) and systematic 'measurable' variations (different quantities). Aim is to correlate the systematic variation with one known property Y. PLSR for XRD data is a full-pattern approach that totally dismisses profile shapes but still uses the complete information present in the XRD data sets. For this study, the PLSR method was used to correlate and extract the bath temperature from XRD raw data. Liquidus temperatures and superheat were calculated using the determined bath compositions from both the Rietveld and PLSR method and formulas given in the literature [6, 7].

3. Results

3.1. Bath Composition and Parameters

Prior to the tests for the prediction of the temperatures, composition and bath parameters (bath ratio, excess AlF_3) where determined applying the Rietveld method to the full XRD pattern. Figure 1 shows an example of a Rietveld quantification of an electrolytic bath sample with a standard composition, without any addition of magnesium, lithium or potassium. Eight phases were taken into account for the quantification. Depending on the bath chemistry, additional

It is shown that PLSR on X-ray diffraction data can be used to provide even more information for process control of aluminium industries. Both methods, Rietveld and PLSR, take the full XRD pattern into account and can be therefore applied on the same measurement without additional costs and time.

5. References

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