Combined Quantitative Analysis of Salt Fluxes Composition by X-ray Diffraction and X-ray Fluorescence in Process Control

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Abstract

Salt flux treatment of molten aluminium is common practice in aluminium production and recycling used to decrease oxidation and metal losses and to clean the metal. The most common class of fluxes contain a mixture of sodium chloride and potassium chloride, and minor amounts of fluoride compounds. Fluxes are specified to certain chemical compositions to produce defined process petameters, such as melting point, surface activity and refining efficiency. Thus, salt flux composition directly affects both the efficiency of the treatment operation and the final product quality.

As metal quality standards grow more demanding, it is necessary to measure the composition of delivered flux and verify that the blend matches the desired specifications. X-ray diffraction (XRD) and X-ray fluorescence (XRF) are the most suitable methods to do this in laboratory. However, in most cases the analysis is made using semiquantitative pre-calibrated programs, which does not assure the accuracy required by the industrial production. This is because neither certified reference materials nor suitable measurement techniques had been available. This paper describes a comprehensive XRD-XRF system for measuring the entire phase and elemental flux composition from major compounds to minor impurities. First, we developed and certified 14 reference materials as National or Branch Measurement Standards. Then certified measurement techniques were developed to measure main flux compounds including NaCl, KCl, AlF_3, Na_2SiF_6, K_2SiF_6 and Na_3AlF_6. Finally, we complimented the certified measurement techniques with reference-free options and formulated the methodology of how to apply them in combination to fully characterize the flux composition. In addition, the paper gives examples of industrial fluxes analyses.

Keywords: Salt flux, X-ray diffraction, X-ray fluorescence, Reference materials, Quantitative analysis

1. Introduction

The treatment of molten aluminium with salt fluxes is a common practice in aluminium production. Fluxes are mixtures of salts used to remove impurities such as alkali and alkaline earth metals and oxides, to modify the metal, or to protect it from oxidation. The most popular class of fluxes are multifunctional fluxes, which allow several operations, such as cleaning the melt from non-metallic inclusions and protecting against oxidation, to be performed in one step. The chemical composition of the flux can be tailored to adjust properties such as density, viscosity, reactivity, and wettability. The main compounds commonly found in solid fluxes are chlorides and fluorides, oxidizing compounds, and solvents of alumina.

Chlorides typically consist of NaCl and KCl. The molar ratio of NaCl and KCl in the mixtures varies as NaCl = 0,5–0,7 and KCl = 0,3–0,5. Although their reactivity with molten aluminium is negligible compared to fluorides, chlorides are used for their fluidizing effects at temperatures of 650–750 °C and act as fillers and carriers for the other compounds [1].

Fluorides play an essential role in fluxing by acting as surfactants to adjust the wettability between the salt and the molten aluminium. This ensures efficient extraction of impurities. The most commonly used additives are simple fluorides such as AlF_3 CaF_2, NaF, KF, MgF_2, and double fluorides such as Na_3AlF_6, K_3AlF_6, Na_2SiF_6 and K_2SiF_6. The amount of fluorides in the salt flux should be minimized for environmental and health reasons. However, it varies widely depending on several factors, including the desired metal quality, the concentration of inclusions in the melt, and environmental regulations [1].

Both the qualitative and quantitative composition of salt fluxes determine fluxing efficiency and affect the process economy. Moreover, the global green trend implies reducing the amount of the flux being used in casting. In this case, the highest fluxing efficiency is achieved by using of complex fluxes with a carefully adjusted composition. However, there are at least two factors that can deviate an adjusted composition. First, fluxes are generally produced from minerals, as well as by-products and wastes of aluminium production, rather than from pure salts. These raw materials are sources of impurities, the presence of which reduces the concentration of desirable components. This in turn reduces fluxing efficiency and final product quality. Second, KCl is about three times as expensive as NaCl, so flux suppliers have a strong motivation to keep the blend as close to the lower KCl limit as possible [2].

To maintain foundry technology, it is essential to verify that the blend matches the desired specifications. Concentrations of major compounds, mineral impurities, and elements degrading the metal quality should be measured quantitatively. However, there are two possible scenarios for flux acceptance in foundry practice. The first is that technologists rely only on the quality certificates provided by the suppliers. The second is that a flux is analysed in the smelter laboratory using semiquantitative pre-calibrated XRD and XRF programs that do not provide the accuracy required for the industrial production. This is because neither certified reference materials (RMs) nor suitable measurement techniques had been available.

X-ray diffraction (XRD) and X-ray fluorescence (XRF) are the most appropriate laboratory methods for quantitative analysis of flux composition. X-ray methods are non-destructive, universal, rapid and require simple sample preparation. Their combination allows complete characterization of phase and elemental composition. Due to these characteristics, both X-ray methods are widely used at aluminium smelters to measure electrolyte composition [3–4], raw material composition and by-product composition.

This paper presents the development of reference materials and a comprehensive XRD-XRF system for measuring the entire phase and elemental composition of $NaCl–KCl–Na_2SiF_6–K_2SiF_6–AlF_3$ fluxes, from major compounds to minor impurities. In addition, examples of industrial flux analyses are given.

methodology has been implemented in a casthouse laboratory and is used to make decisions on whether a flux should be accepted into the production.

8. References

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