



INFLUENCE OF FLUX COMPOSITION ON HYDROGEN CONTENT IN ALUMINUM MELTS

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ABSTRACT

The paper is aimed at evaluating the quality and performance characteristics of industrial fluxes, which are intended for refining processing of aluminum melts and used in production conditions of RUSAL JSC (Russian Federation). The results of the work were obtained using X-ray diffraction and thermogravimetric analyzes, as well as standardized procedures for determining the hydrogen content in metallic melts. It is shown that fluxes containing crystalline hydrates and hygroscopic water can be a source of saturation of aluminum melt with dissolved hydrogen. The mechanism of dehydration of crystalline hydrates in the composition of fluxes is given. According to the results of the research, technical solutions aimed at reducing hydrogen saturation of aluminum melt during flux processing are proposed.

Keywords: hydrogen, aluminum melt, fluxes, crystalline moisture.

INTRODUCTION

The quality of metallurgical products is one of the main factors determining its competitiveness in the world market [1]. Considering that in the designs of modern machines and aggregates the parts made of aluminum and its alloys are widely used, special attention is paid to the technologies for their production. It is known that the quality of aluminum alloys and products from them largely depends on the purity of the metal, including the content of impurities unspecified by state standards, namely dissolved gases and nonmetallic inclusions [2]. Gas impurities contained in cast metal adversely affect the physical and mechanical characteristics of aluminum and its alloys [3].

Hydrogen is one of the most significant gas impurities, which adversely affects both the technological properties and the mechanical characteristics of aluminum and its alloys [4-9]. Dissolved in a solid solution of aluminum, hydrogen under certain conditions promotes the formation of gas and gas-shrinkage porosity, which increases with increasing hydrogen concentration in the melt [10]. Hydrogen contained in aluminum and its alloys is very often the main problem in the way of creating new alloys with specified properties, having high specific strength, the ability to work at alternating pressures and temperatures, to withstand dynamic loads, and have high corrosion resistance [11]. Hydrogen, remaining in aluminum and its alloys after crystallization, causes premature failure of machines and mechanisms.

Despite the efficiency of using the some flux preparations for refining aluminum melts [12], in a number of cases they can serve as an additional source of saturation of the liquid metal with hydrogen [13]. Fluxes obtained by smelting the charge components in electric furnaces with subsequent granulation, and also by mechanical mixing, can absorb moisture from the air during storage with formation of crystalline hydrates, and also adsorb moisture on the surface of crystalline

compounds, as a result of which the water content in fluxes can reach several percent.

Taking into account the topicality of the issue related to the improvement of the quality of aluminum alloys and their products, we have performed comparative studies of commercially available fluxes used for the refining of primary aluminum in mixers at aluminum plants of RUSAL JSC (Russian Federation). The purpose of this research is to evaluate consumer properties of fluxes and possible risks when processing melts from the hydrogen saturation point, and also to prepare recommendations for the acceptance, storage and use of fluxes.

MATERIALS AND METHODS

The commercially available fluxes with the following component composition were used as the test materials: flux No.1 (KCl + MgCl₂) and flux No.2 (NaCl + KCl + MgCl₂ + AlF₃). Flux preparations were examined in the as-received state.

Investigations of the quality of fluxes were performed by X-ray phase analysis and thermogravimetry. Phase analysis of the fluxes was performed on a Shimadzu XRD-7000 X-ray diffractometer (Japan) using the Debye-Scherrer method, which has high reliability and the ability to carry out the analysis without destroying the sample. The analysis was performed with a scanning step of 0.001 deg. and a rate of 0.1 deg / min.

Thermogravimetric studies of fluxes were performed on a simultaneous TGA / DSC thermal analyzer SDT Q600 at a sample heating rate of 10 °C / min. Analysis of the gases released from the flux during heating was performed on a Fourier-transform infrared (FTIR) spectrometer Nicolet 380 (USA). The sample weights of the fluxes studied were 200 mg.

The automatic analyzer ALU COMPACT II (Liechtenstein) was used to determine the change in the content of dissolved hydrogen in the aluminum melt



during its processing with fluxes. Determination of the hydrogen content was made by expelling the first bubble according to the method of Gudchenko. The hydrogen content in a metal sample in cm³ per 100 g of metal was calculated as the arithmetic mean from the data of three parallel determinations.

RESULTS AND DISCUSSIONS

The phase composition of flux No.1 is represented by potassium chloride KCl, anhydrous magnesium chloride MgCl₂ and bischofite MgCl₂ · 6H₂O, which can be a source of saturation of the aluminum melt with hydrogen (Figure-1).

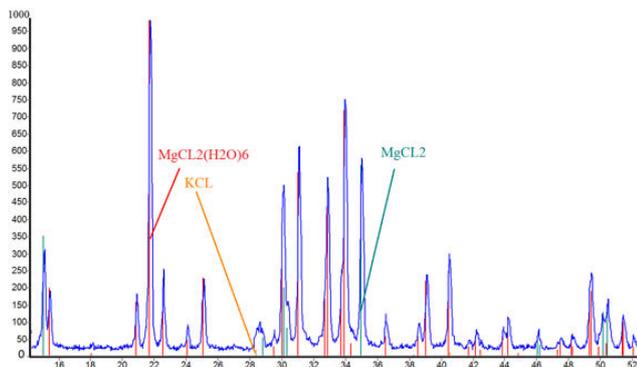


Figure-1. XRD pattern of the flux no.1.

The following compounds represent phase composition of flux No.2: anhydrous salt KMgCl₃, sodium chloride NaCl, potassium chloride KCl, aluminum fluoride AlF₃ and carnallite KMgCl₃ · 6H₂O. The latter compound is present in the form of crystalline hydrate and is a potential source of saturation of the aluminum melt with hydrogen (Figure-2).

On the derivatograms of the investigated fluxes (Figures 3, 4) several endothermic effects are observed in the temperature range up to 300 °C, indicating the removal of hygroscopic and crystallization moisture. The nature of the derivatograms allows us to establish the dehydration mechanism for carnallite KMgCl₃ · 6H₂O and bischofite MgCl₂ · 6H₂O, which are constituents of the fluxes.

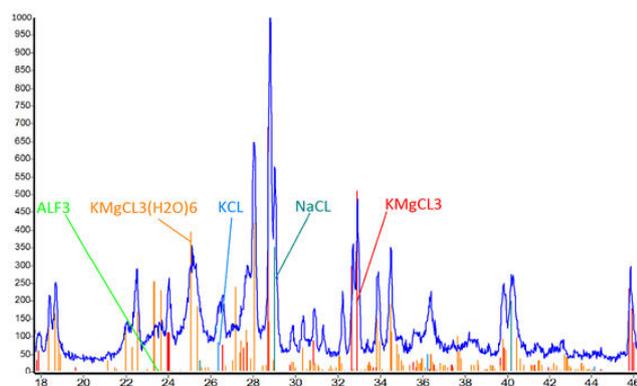


Figure-2. XRD pattern of the flux no.2.

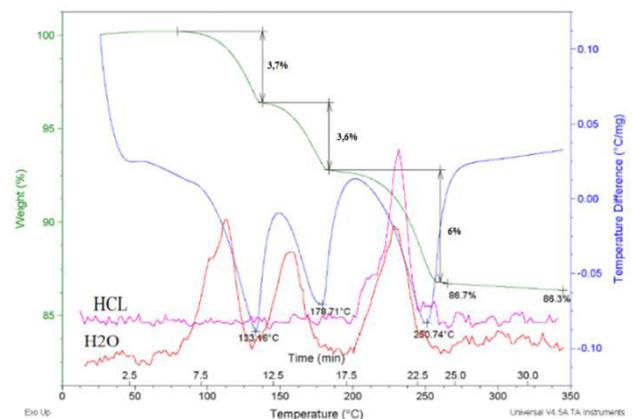


Figure-3. Derivatogram of the flux no.1.

On the derivatogram of flux No.1 (Figure-3) three endothermic effects were recorded at temperatures of 133.16 °C, 178.71 °C and 250.74 °C. These effects correspond to the successive transition of six-water magnesium chloride to a single-water:

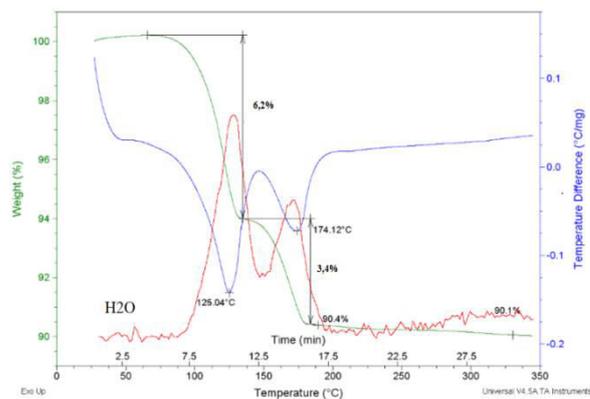
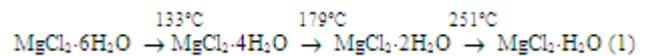
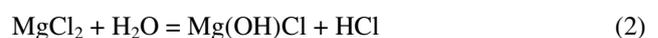


Figure-4. Derivatogram of the flux no.2.

At a temperature of 133.16 °C, six-water magnesium chloride passes into four-water and, in addition to removing the crystallization water in an amount of 3.6%, hygroscopic moisture evaporates in an amount of 0.1%. The endo effect at a temperature of 178.71 °C corresponds to the transition of four-water magnesium chloride to a two-water one and is accompanied by a loss of the sample mass of 3.6%. The endothermic effect corresponding to a temperature of 250.74 °C takes place with a loss in mass of the sample of 6%, which includes the transition of two-water magnesium chloride to a single-water and hydrolysis of magnesium chloride to form hydrogen chloride:



The total weight loss during decomposition of flux No.1 to 300 °C was about 13%, incl. ~ 10.6% due to



removal of hygroscopic and crystallization moisture and ~ 2.4% hydrogen chloride HCl.

On the derivatogram of flux No.2 (Figure-4), two endothermic effects occur at 125.04 °C and 174.12 °C, due to the release of predominantly crystallization moisture in the decomposition of carnallite. Dewatering of carnallite at atmospheric pressure in air proceeds in two stages. The first is the dehydration of the six-water carnallite to the two-water one. This transformation begins at 85 °C and ends at 145 °C. The second stage - dewatering of two-water carnallite to anhydrous KMgCl_3 - is completed at 190 °C. The total amount of hygroscopic and crystallization moisture released from flux No.2 was 9.6%. The presence of crystalline hydrates of carnallite $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$, and bischofite $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, as well as the presence of hygroscopic moisture can be caused by a violation of the technology of flux manufacturing from suppliers or unsatisfactory storage conditions. The use of fluxes containing hygroscopic and crystallizing moisture is unacceptable, since it, along with to additional saturation of aluminum with hydrogen, increases flux consumption and increases emissions of halogenated gases into the working zone.

Experimental melting was carried out for verification of the obtained data and estimation of the effect of processing with fluxes in the delivery state on the content of dissolved hydrogen in the aluminum melt. For this purpose, high purity aluminum (99.99% Al, ingot) was melted in an induction furnace. When the melt temperature reached 700 °C, the metal sample was taken for hydrogen test. The concentration of hydrogen in the sample was 0.22 cm³/ 100 g. The metal was further refined with flux No.1 and when the melt temperature reached 700 °C, the sample was taken for hydrogen, which was 0.34 cm³/ 100 g. After that experiment was repeated using flux No.2. After refining with this flux, the hydrogen content in the melt was 0.32 cm³/ 100 g. The amount of fluxes was taken according to the recommendations of the manufacturers.

The obtained data indicate that the use of flux preparations for refining melts is unacceptable without preliminary drying operations. Optimizing the drying modes of fluxes to ensure a minimum amount of bound moisture can be the subject of additional investigations. An alternative approach is degassing by purging with inert gases [14], as well as using degassing methods based on external physical influences on aluminum melt [15].

CONCLUSIONS

a) As a result of the conducted researches it was established that the investigated industrial fluxes contain crystalline hydrates: carnallite $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ and bischofite $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, which is confirmed by the results of X-ray diffraction analysis. In addition, according to the differential-thermal analysis the fluxes contain hygroscopic moisture. With the help of the ALU COMPACT II hydrogen analyzer, it has been established that after processing with fluxes, additional aluminum melt hydrogen

saturation on 0.10...0.12 cm³/ 100 g can occur, which adversely affects the quality of metallurgical products.

b) As technical solutions for eliminating the additional hydrogenation of aluminum melt with fluxes, it is recommended to store fluxes under conditions that exclude their saturation with hygroscopic moisture. It is also necessary to establish an input quality control of the fluxes, if necessary, to dry the fluxes and, if possible, prepare the sample of fluxes in a sealed package for dosed loading into the mixer. The proposed set of actions will help to avoid saturation of fluxes with atmospheric moisture, reduce the consumption of flux per ton of metal and reduce the saturation of the aluminum melt with hydrogen, which will reduce the cost and improve the quality of the finished product.

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