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Evaluating the Chemical Composition and the Molar Heat Capacities of a white Aluminum Dross

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Abstract

The present study evaluates the chemical composition and the molar specific heat of white aluminum dross skimmed from a gas fired reverberatory metal holding furnace during the alloying process. The chemical composition was determined using the energy dispersive analysis (EDS) technique while the specific heat were measured isothermally using micro-reaction calorimeter (μRC) from 303.15 K to 353.15 K at an interval of 5 K. The molar specific heat is extrapolated to elevated temperatures from 363.15 K to 1323.2 K based on a linear model that is developed from the measured range and in house elemental specific heat model. Also, the thermal conductivity and enthalpy of the dross was predicted using the JMatPro software and the aluminum component phase change has been determined. The EDS shows that the composition of metallic aluminum found in the dross was high with the inclusion of other impurities and this metallic aluminum can still be further recycled in order to acquire considerable amount of aluminum in the secondary recovery process. The determined weight percentage of chemical composition of the aluminum dross consists of Al (42.52%); C (6.09%); O (22.82%); Mg (15.54%); Fe (10.15%); Nb (0.51%) and K (2.37%).

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Keywords : White Aluminum dross, Chemical Composition, Molar Specific Heat, EDS Analysis ,Micro-Reaction Caliormeter

1. Introduction

Aluminum is the earth's third most abundant element and it can never occurs as a free element in nature [1] .The production of aluminum is energy intensive process and a lot of dross are produced as a waste product during remelting or refining aluminium. This hazardous waste poses a bigger threat and challenge to aluminum industry due to figuring out a better way of safely disposing this waste. Dumping of this waste is an environmental hazard to plants, animals, and even human beings [2, 3]. Aluminium dross consists of metal, salts oxides, and other non-metallic substances. Dross can be classified as either black or white dross; black (or dry) dross has lower metal content and higher amounts of oxides and salts. It

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tends to be in granular, like sand. White (or wet) dross has extremely high metal content and smaller amounts of oxides and salts. It tends to form into large clumps or blocks. [4-6] .Saltcake contains contaminants like oxides, carbides and sulphides as well as metallic aluminium which is entrapped in the salt and traces of pollutants polychlorinated dibenzo-p-dioxins and dibenzofurans. In contact with water it emits flammable gases such as acetylene (which in turn can cause explosions), and is liable to give off toxic gases, such as ammonia, in dangerous quantities. Dross represents 0.5 to 5% of the total remelting furnace load depends on the type of remelted scrap. White dross can be reprocessed to produce aluminium and black dross. Black dross can be converted to useful commercial products. These products are harmful to the environmental and the cost of disposal of this waste is very high hence a lot of research is geared towards recycling these waste as useful products [7-10]. Studies and new advances in new technologies like the oxy-fuel rotary furnaces have shown that up to 80% of aluminum could be recovered from aluminum dross through the secondary production of aluminum which needs just 5% of energy and emits just 5% of greenhouse gases of what is used in the primary production of aluminum [11] .This product has shown a great prospect as an engineered material which can be used in refractories, as aluminum composites and as a high temperature additive for de-sulphurizing of steels [12]. Detailed Characterization of the physical and chemical properties (bulk density, salt content, particle size, distribution of the elements in different fractions and the composition) of the aluminium dross where reported in literature [13] while in this study the chemical composition and the thermo physical properties of the white aluminium dross were investigated. The aluminium dross can be utilized in different applications like they can be used as a raw material for refractories [14]. The recovery of secondary aluminum from the aluminum dross requires a significant amount of energy [15]. Also, a direct relationship between the thermal conductivity of aluminum dross at higher temperature and its metallic aluminum content was found [16]. Full energy assessment was investigated for the Al remelting and holding furnaces; however, this analysis was unable to give a precise information about the amount of waste energy that is carried out by the dross due to the missing information of the dross specific heat [17, 18].

The main goal of this study is to provide an accurate thermo-physical database for the white dross that is generated during the alloying process while aluminium molten metal is in hold in gas fired reverberatory furnace. Experimental measurements of the dross elemental composition and calorimetric specific heat analysis are completed using cut edge technology techniques.

2. Experimental Procedures

The fine sized sample of white aluminum dross which in form of a powder materials as shown in Fig 1, was placed on conductive tapes. An elemental analysis of the test materials was carried out using the energy dispersive analysis (EDS) technique. A FEI Quanta 3D dual beam scanning electron microscope (SEM) that is equipped with a focused ion beam (FIB) coupled with an Energy Dispersive Spectrometry (EDS) was used and all the standard procedures were followed. This SEM functions permit microscopic observations of the sample, the FIB functions allows cutting of the sample (not used in this case) while the EDS helps in the elemental (composition) analysis of the aluminum dross sample.

For the SEM and subsequent EDS examination, the powdered sample obtained from the white aluminium dross waste was mounted on a metal stud. This sample was constrained unto the stud by using a double-sided carbon tape. Because the sample is non-conducting, it was coated with gold-palladium (Au/Pd) particles of 45nm thickness to prevent charging and for clear imaging in the electron microscope. The prepared sample was mounted into FEI Quanta 3D dual beam scanning electron microscope (SEM) that is equipped with a focused ion beam (FIB) coupled with an Energy Dispersive Spectrometry (EDS) and all the standard procedures were followed. The EDS spectrum was obtained using the EDAX software at an accelerating voltage of 20kV and low magnification for better focus.

The specific heat was measured using a Micro Reaction Calorimeter provided by Thermal Hazard Technology (THT) UK. Heat capacity was measured at temperature ranging from (303.1 to 353.15) K. The measurement of the heat capacity was achieved by making a "step-change" in the temperature of the cell in comparison to an empty vial. At each temperature, the heat was repeatedly measured 3 times with a step of ± 0.5 K. First, blank test was conducted with an empty vial. Then, approximate (0.7-1.5) g of absorbent was placed in the sample analysis vial and conducted test with the same condition used for the blank. The heat capacity was calculated using the equation below,

$$C_p = (Q-Q_{blank})/m\ \Delta T \quad (1)$$

Where, C_p (J.mol^{-1}.K^{-1}) is the heat capacity of absorbent, m is the mass of sample (g), ΔT is the temperature step (1 K), and Q (J) and Q_{blank} (J) are the heat change of analysis cell with sample and without sample respectively.

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Fig.1. Samples of the white dross aluminum

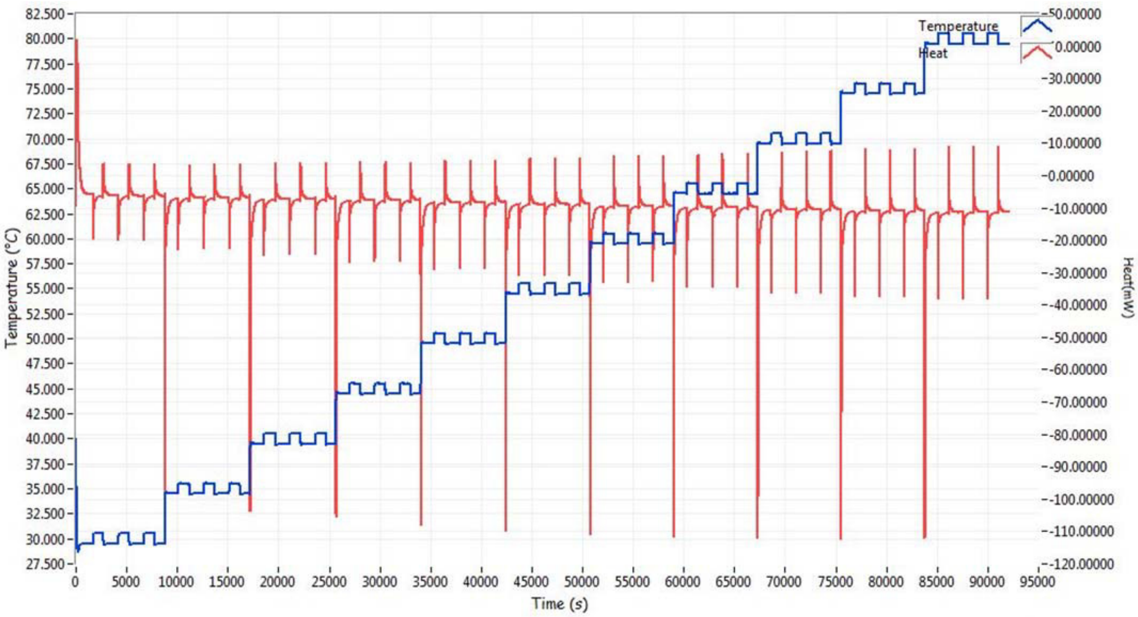

Fig.2. An example of the heat flow and three step change in the reactor's temperature for measuring the heat capacities recorded as a function of time from start to the end of one experiment

3. Results and Discussion

The crystal morphology of a white aluminum dross sample was imaged using the SEM, the results as illustrated in Fig. 3 shows a non-uniform morphology plate [3]. The sample was further examined using EDS operated under high vacuum at an accelerating voltage of 20kV with a low magnification. The chemical composition of aluminum dross (expressed in weight percentage) was determined: Al (42.52%); C (6.09%); O (22.82%); Mg (15.54%); Fe (10.15%); Nb (0.51%) and K (2.37%). The EDS analysis showed that the composition of the metallic aluminum that is found in the white dross sample was high with the inclusion of other impurities and this metallic aluminum can still be further recycled in order to acquire considerable amount of aluminum in the secondary recovery process. The resulting spectrum and tabulated results reveal that Al, C, and O are the main elements present with Al being the most abundant in the selected field as shown in Fig 4. The concern about recycling the aluminum from the dross is the alloy degradation that my need to be readjusted.

The Aluminium dross heat specific heat is measured using the micro-reaction calorimeter from 303.15 to 353.15 K (instrument limitation). The experimental results are extrapolated beyond the instrument temperature range using specific heat model in Eqn. 2. The measured and modelled specific heat results are plotted as shown in Fig. 5. It can be seen from this plot that the capacity of the dross sample increases linearly with the temperature.
The molar specific heat of the elevated temprature from 363.15 K to 1323.2 K were extrapolated, using the linear model in Eqn. 2. This model is generated from the element mixing based on the elements' molar specific heats and their EDS concentration. The uncertainity in this model came from the fact that the elemental O obtained from the EDS analysis doesn't necessarily mean oxygen exist as an identity element on its own but most likely as aluminum oxide. The other source of uncertianity is the aluminum component phase change that would happen while heating up the dross sample.

$$C_P = 12.645 + 0.0208\,T \tag{2}$$

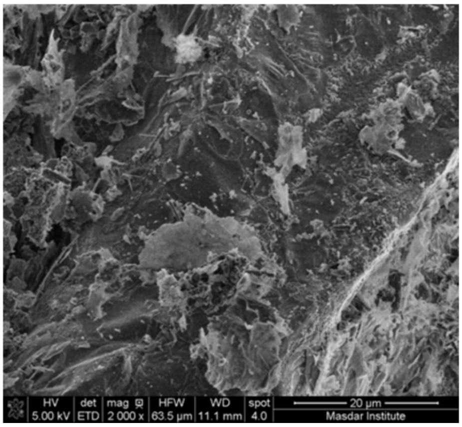

Fig. 3. SEM Image of white Aluminium Dross

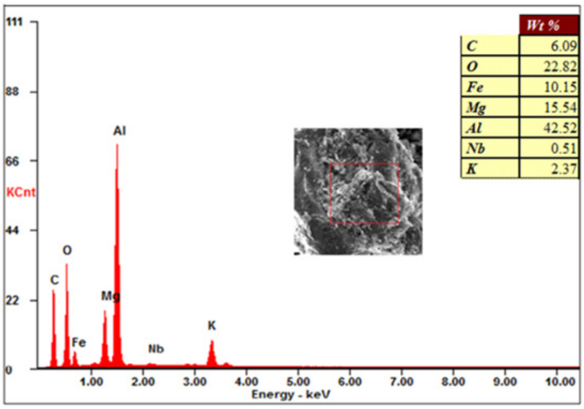

Fig. 4. Energy Dispersive Analysis (EDS) of white Aluminium Dross

Since, the specific heat of white aluminum dross does not appear in literature, a metal thermodynamics software, JMatPro [19], is used to predict the possible phase change temperature using the EDS dross analysis. The EDS dross composition analysis is recalculated after taking out the O, Nb, and K components and the new element analysis (57%Al, 14%Fe, 21%Mg and 8%C) is inputted to JmatPro. The dross enthalpy results in Fig. 5 and the thermal conductivity in Fig. 6 depict a dross sample phase change at 624 K. Figure 7 shows the specific heat as it varies with temperature, the specific heat is jumped to 10.08 J/g.K (not shown in Fig. 7 because of the large scale change) due to the latent heat contribution while phase change occurred. Therefore, the linear extrapolation specific heat model will not be valid beyond the phase change temperature. However; it can be readjusted after the phase change occurs because of the linear behavior of the specific heat after phase change. For validating the JmatPro data, the specific heat experimental results has been used for the same range of temperature and a comparison is plotted in Fig. 8. It can be seen that there is a bias difference between the measured and predicted plots. The main reason for this bias is the lack of information of what in the O composition as metals oxide. As it can be seen in Fig. 8, the aluminum composition can be readjusted to match the experimental data and then the final composition can be used for extrapolating the specific heat values to higher temperature because of the privilege of the linearity.

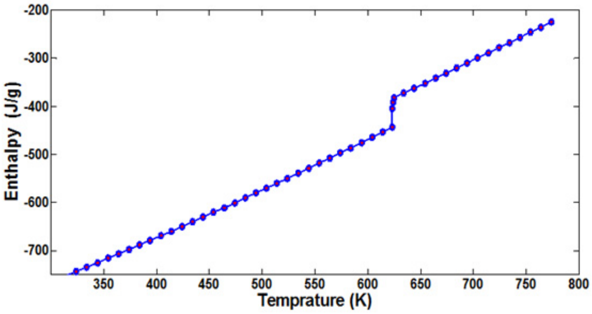

Fig. 5. JmatPro results for dross enthalpy Vs temperature

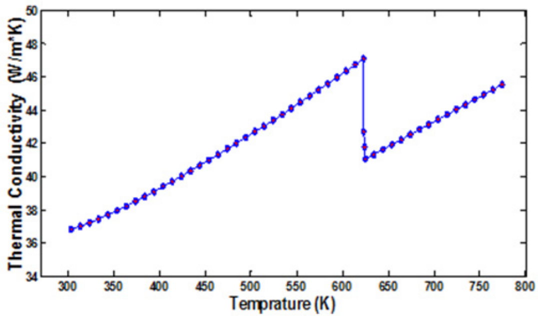

Fig. 6. JmatPro results for dross thermal conductivity Vs temperature

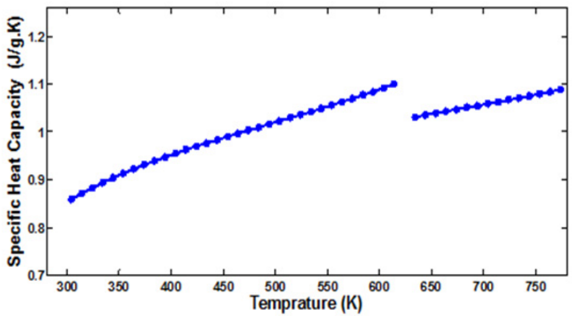

Fig. 7. JmatPro results for dross specific heat Vs temperature

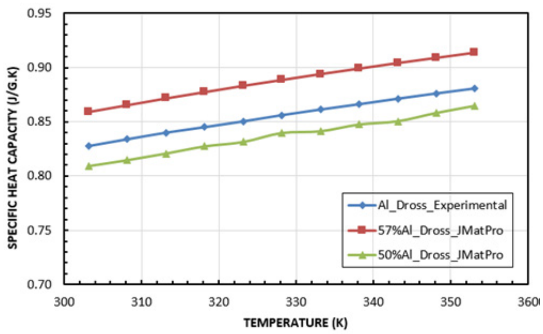

Fig. 8. Experimental vs. JmatPro results for dross Specific Heat

4. Conclusions

Aluminium dross is not only waste of metal but also a waste of energy in the aluminium industry. Preliminary thermodynamic analysis for how much metal would be recovered from the dross and how much energy would be saved by reducing the dross formation needs an accurate measurement for the dross composition and dross thermo-physical properties. The scan electron microscopy (SEM) with energy dispersive analysis (EDS) at Masdar Institute is used to characterize the white aluminium dross skimmed from a reverberatory gas-fired metal holding-furnace. The Micro Reaction Calorimeter is used for measuring the specific heat of the same dross sample. The energy dispersive analysis dipicts a significant amount of aluminum alloy (at least 42.5%, not mentioned what would be recovered from the oxide composition, O) can be recovered from the dross sample. Also, the composition analysis gave a prcise information about the other alloy components that would help in adjusting the recovered alloy degredation in adition to caculating the dross molecular wieght. the molecualr whieght analyis and the measured molar specific heat will help in prdicting the amount of energy carried out by the dross skimming as well as the amount of energy that would be needed for smelting the aluminum from the dross. It can be concluded as there is much merit if the dross that is formed could be recycled a gain since it has an ample amount of Aluminium in it. This study has tackled the dross composition and the thermophysical properties of the aluminium dross in the region that have not being investigated before.

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Biography

Mohamed Ibrahim Hassan Ali is assistant professor in the mechanical and materials engineering department of Masdar Institute of Science and Technology. Dr. Ali earned his PhD in mechanical power engineering on a channel program between the University of Helwan, Cairo, Egypt, and the University of Michigan, Ann Arbor, Michigan, USA.