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AN INDUSTRIAL THERMOGRAVIMETRIC/DIFFERENTIAL THERMAL ANALYSIS (TG/DTA) FOR MEASURING HUMIDITY AND ORGANIC CONTENT IN INCOMING ALUMINIUM SCRAP

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Abstract

In recycling plants, especially those specialized in the recycling of low-grade aluminium scrap for wrought aluminium alloys, timely and accurately information about the amount of organics and other impurities in the incoming scrap is an important parameter in achieving both economic benefits and standard metallurgical quality of the recycled metal. As a prerequisite for using aluminium scrap combined with organics as a valuable and good-quality source of aluminium for producing wrought aluminium alloys of standard quality, its metallurgical composition and the content of organic and other impurities should be quickly and cost-effectively analyzed on representative samples, typically with a mass of 20–50 kg. Due to the enormous growth of the secondary-aluminium industry, the development of an industrial method for determining the amount of organics and other impurities in representative samples of incoming scrap has become very important.

In this work, an industrial thermogravimetric/differential thermal analysis (TG/DTA) of representative scrap samples was developed as an efficient analytical methodology for analyzing the humidity and organic impurities in incoming scrap. When performed in continuous mode, under a flowing atmosphere of argon with 1 wt. % of oxygen, this methodology enables a routine measurement of the humidity, the quantity of organics and the carbon content in representative samples of incoming scrap in less than 15 min within an accuracy of ±0.5%.

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Introduction

The suitability of aluminium scrap with organics as a proper (valuable and of sufficient quality) source of aluminium for the production of wrought aluminium alloys of standard quality depends on its metallurgical composition and the content of organic and other impurities (humidity, non-metals such as oxides, non-oxides etc.) [1]. The metallurgical composition of the incoming scrap, influenced by the mix of alloys appearing in it, is routinely determined in recycling plants by standard optical emission spectroscopy. However, a similarly fast and cost-effective method for analyzing the amount of organics and other impurities in representative samples of incoming scrap is still under development [2, 3].

In recycling plants that are specialized in the recycling of low grades of aluminium scrap, timely and accurately information about the quantity of organics and other impurities in the incoming scrap is the ultimate vital prerequisite when it comes to achieving a higher net added value. The goal is, considering the amount of organics and other impurities, to recycle each grade of scrap using an optimal recycling procedure both from the economic and metallurgical points of view.

From the economic point of view, the content of organics and other impurities (the part of non-aluminium phases) defines the cost of the scrap and therefore is absolutely indispensable in the commercial issues of scrap buying as well as the added-value engineering of the entire process of recycling [1].

With respect to the metallurgy, the amount of organics and other impurities determines the key technological parameters of the recycling and the process of refining the molten metal for achieving a standard uniform quality for end products. First of all, the amount of organics determines the exothermic/endothermic behaviour of the incoming scrap and the volume of gaseous products liberated during the early stages of recycling. In addition, the concentration of organics and other impurities favours the formation of inclusions that influence the quality of the molten metal [4].

Aluminium scrap, especially grades with organics, represents a highly exothermic input (e.g., scrap with approx. 6 wt. % of organic impurities is exothermic enough for self-melting). During the melting of such an input, a huge amount of energy and gases are generated simultaneously, influencing the productivity and the cost of recycling as well as the quality of the obtained molten aluminium – in particular its suitability for the production of wrought aluminium alloys for highly demanding end products.

The inclusions that appear as various solid particles present in the molten aluminium or aluminium alloy could be classified into two main groups: (i) indigenous or *in situ* inclusions and (ii) exogenous inclusions. The growth of indigenous inclusions is caused by chemical reactions taking place in the melt due to the existing chemical composition and the applied processing parameters (temperature, time, atmosphere, etc.). In contrast with that, exogenous inclusions already exist as a separate phase in the system before melting and are introduced to the melt by raw materials, alloying elements, additives, refractory materials and furnace atmosphere [4].

Exogenous inclusions can be effectively removed by filtering. On the other hand, the presence of indigenous inclusions may be effectively prevented only by mastering the overall reactivity in the system – by selecting and keeping the proper chemical composition of the melt and the processing parameters.

Regarding the overall reactivity in the system, it is particularly important to note that the level of impurities and, therefore, the chemical reactivity in remelted aluminium

scrap with organics (painted scrap) is quite different to those in primary metal or remelted clean scrap. The organic component of paint can be volatilized during decoating and pyrolysis, but paint often contains inorganic compounds (fillers and pigments) that do not respond to thermal processing or convert to oxides or other (usually binary) compounds, remaining on the surface of the pyrolized scrap as exogenous inclusions. Many of these exogenous inclusions may also react with molten aluminium and/or alloying elements dissolved in the melt, creating indigenous as well as new exogenous inclusions.

Note that fillers and pigments can react either with molten aluminium and/or in parallel with some of the alloying elements dissolved in the melt. Therefore, in real scrap mixtures, with a very complex chemical composition of the impurities originating from the organics, it is very important to take into account all the thermodynamically possible chemical reactions that enable the formation of inclusions. The aim of such a consideration is a careful prescription of the tolerance limits for all the recycled alloy constituents (incoming scrap), including the impurities originating from the organics.

Due to the enormous growth of the secondary-aluminium industry, the development of an industrial method for determining the amount of organics and other impurities in incoming scrap has become very important. This is particularly the case in recycling plants and cast-houses where low grades of scrap are also dedicated for the production of wrought aluminium alloys. As a result, the purpose of this paper is to present an industrial method for determining the amount of organics and other impurities in representative samples of incoming scrap.

Determination of the amount of organics and other impurities in representative samples of aluminium scrap

The method for characterizing aluminium scrap with organic contamination used in this work is thermogravimetric/differential thermal analysis (TG/DTA) applied on an industrial scale. The goal was to develop an industrial method for a fast and cost-effective compositional characterisation of the incoming aluminium scrap as part of an integral quality-control system and an acceptance procedure for the input raw materials. If we consider the high value of aluminium scrap, then this testing procedure is also crucial in negotiating the final cost of scrap and addressing eventual claims to scrap suppliers.

Generally, aluminium scrap with organic contamination contains both organic and inorganic impurities and also some level of humidity. Organic impurities are usually in the form of various coatings, such as lacquers, paints, polymers, inks, phenolic resins, thermolacquers, oils etc., while inorganic are mostly in the form of various non-volatized solid oxides such as aluminium oxide (Al_2O_3), oxides of alloying elements (silicon, iron, copper, manganese, magnesium, chromium, nickel, zinc, lead, tin, bismuth, titanium and others) as well as oxides obtained by the thermal decomposition of pigments or used in organic coatings as filler (in particular TiO_2).

The principle of the TG/DTA analysis of aluminium scrap with organic contamination is in determining the mass loss of representative scrap samples caused by heating in a controlled atmosphere.

Based on the measured experimental values of the intermediate masses, the following scrap characteristics can be calculated:

- humidity, Δm_{A1} and Δm_{B1},
- content of volatile products liberated during dried scrap pyrolysis, Δm_{A2},
- content of carbon in pyrolysed scrap, Δm_{A3},
- content of volatile products liberated during the burning of dried scrap, Δm_{B2}.

The above-listed scrap characteristics are determined using the following formula:

$\Delta m_{A1} = m_{A1} - m_{A1}' = m$(wet scrap-sample A) – m(dried scrap-sample A) (1)
$\Delta m_{B1} = m_{B1} – m_{B1}' = m$ (wet scrap-sample B) – m(dried scrap-sample B) (2)
$\Delta m_{A2} = m_{A1} - m_{A1}'' = m$(dried scrap-sample A) – m(scrap after pyrolysis-sample A) (3)
$\Delta m_{B2} = m_{B1} – m_{B1}'' = m$(dried scrap-sample B) – m(scrap after burning-sample B) (4)
$\Delta m_{A3} = m_{A1}'' - m_{A1}''' = m$(scrap after pyrolysis-sample A) – m(scrap after burning-sample A) (5)

The total amount of organics in the scrap samples A and B corresponds to $\Delta m_{A2} + \Delta m_{A3}$ and Δm_{B2}, respectively.

By combining Eqs. (3) and (4), the sum $\Delta m_{A2} + \Delta m_{A3}$ representing the total content of organics in the scrap can be rewritten as:

$$\Delta m_{A2} + \Delta m_{A3} = m_{A1} – m_{A1}''' \quad (6)$$

Therefore, under the proper experimental conditions (optimal burning time in order to minimize the oxidation of aluminium), the content of organics in sample A (processing route A) and sample B (processing route B) should be the same:

$$\Delta m_{A2} + \Delta m_{A3} = \Delta m_{B2} \quad (7)$$

At the same time and under the same experimental conditions, the content of non-organics in samples A and B should also be the same:

$$m_{A1}''' = m_{B1}'' \quad (8)$$

Note that the content of non-organics means the total content of aluminium, mAl, inorganics, minorganics, and ashes, mashes:

$$m_{A1}''' = m_{B1}'' = m_{Al} + \text{minorganics} + \text{mashes} \quad (9)$$

ΔmB2 – the amount of organics in dried scrap (sample B) is a very important parameter for the proper planning of the initial stages of contaminated scrap processing in a cast-house.

On the other hand, the experimentally determined Δm_{A3} value corresponds to the carbon content in the scrap's organic phase, although for determining the stoichiometric carbon content the amount of carbon present in the fraction of volatile products of pyrolysis (Δm_{A2}) should also be considered. However, carbon in volatile products represents a minor part of the total carbon content and could be neglected or even estimated from the average carbon content in the exhaust gases.

Finally, the level of inorganic impurities can be estimated by extracting the aluminium from scrap samples remaining at the end of processing routes A and B. However, in that case the recycling efficiency, ηR, of the applied recycling technology should also be considered:

$$\eta R = m_{Al}/ m_{A1}''' = m_{Al}/ m_{B1}'' \quad (10)$$

Thermogravimetric analysis of the humidity and organics content in aluminium scrap – experimental procedure

Sampling

The typical mass of representative scrap samples is 20–50 kg, which is far above the maximum capacity of commercial TG/DTA devices, designed to analyse just a few tenths of a milligram of input material. For this reason, an effort was made to develop an industrial TG/DTA method/device for a thermo-gravimetrical analysis of representative samples of incoming scrap.

Two representative scrap samples taken from the same scrap lot (mix of painted profiles including some with a thermal bridge) were analyzed in this work: sample A with mass mA1, planned for treatment using a batch processing route, and sample B with mass mB1, planned for a continuous processing route. Samples A and B were taken from a scrap lot of approx. 10–20 t, according to the general rules of representative scrap sampling.

Batch and continuous procedures of TG analysis

The industrial TG/DTA analyses performed in this work were run as either batch or continuous processes.

Following the batch procedure, scrap sample A was heated, starting from room temperature up to 560 °C, in a flowing atmosphere of pure and dried argon. At approx. 120 °C, the mass plateau, m_{A1}', of the dried scrap was recorded. After that, sample A was heated to the mass plateau m_A'' at 560 °C. During that stage of heating, the organic impurities were first completely pyrolysed, resulting in a carbon-coated scrap surface and, in continuation, heated at the same temperature in an atmosphere of Ar+1 vol. % of O_2 to the mass plateau m_A''', corresponding to the mass of aluminium and all the present inorganic impurities. A histogram of the mass changes of sample A is presented in Fig. 1.

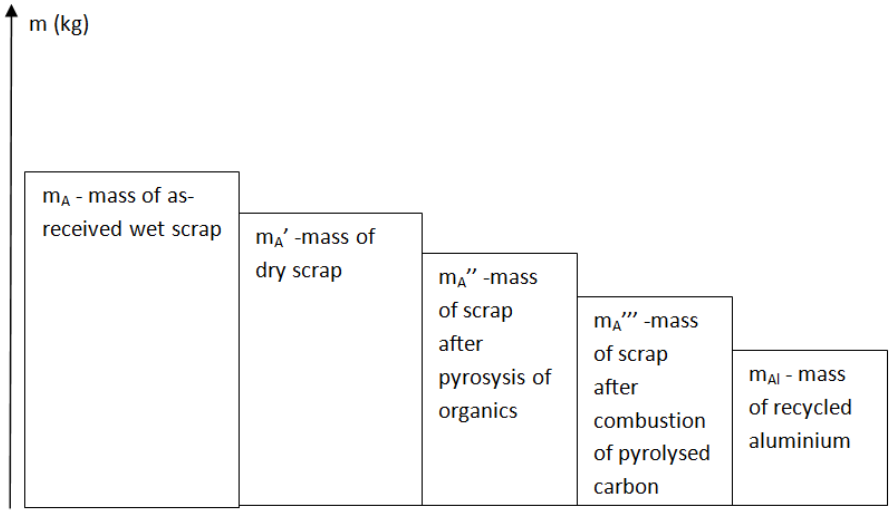

Fig.1: The histogram of mass changes of sample A during TG/DTA performed using batch mode.

In the continuous process, sample B was exposed in a flowing atmosphere of argon with 1 wt. % of oxygen to two constant temperatures: 120 °C and 560 °C. At 120 °C, the mass plateau m_{B1}' of dried scrap was recorded. At 560 °C, the organic impurities were completely burned to volatile products. The remaining scrap surface was covered only with Al_2O_3 and ashes, which corresponds to the mass plateau m_B''. The histogram of the mass changes of sample B is presented in Fig. 2.

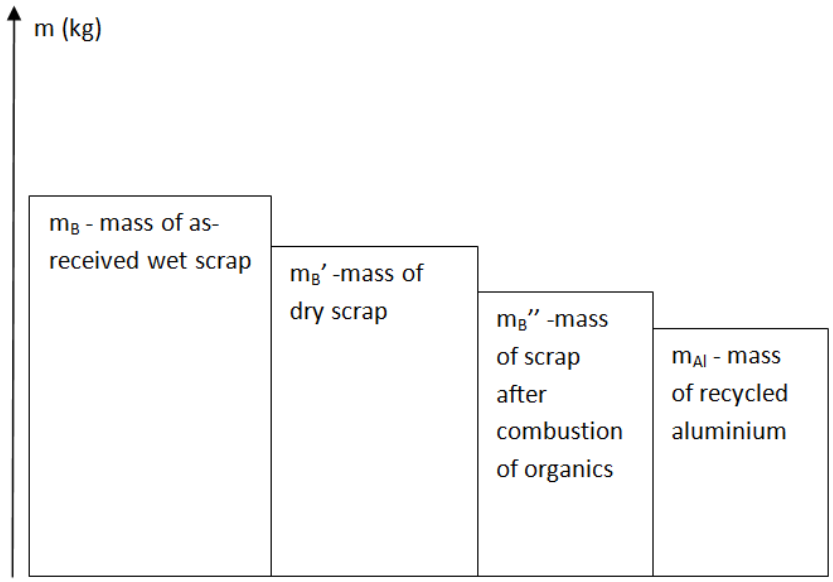

Fig. 2: The histogram of mass changes of sample B during TG/DTA performed using continuous mode.

The batch TG/DTA device is schematically represented in Fig. 3. The central part of such an industrial TG/DTA unit is an electrically heated furnace with fully programmable heating regimes and a sufficient volume capacity for processing balled, and various kinds of non-balled, incoming scrap samples. The complete unit is mounted on a balance with an average absolute error of about ± 100 g. Because of the significant amount of gaseous products and ashes generated during the various stages of TG, the furnace is equipped with the appropriate fume hood for exhaust gases mounted on the top and an ashes trap placed below the perforated supporting plate for scrap. The furnace operates in inert (argon) and oxidising atmospheres (e.g., Ar+1 wt. O_2), which are controlled by a computerized gas cabinet. In addition, the furnace door has sufficient sealing to prevent any contamination of the furnace atmosphere with air.

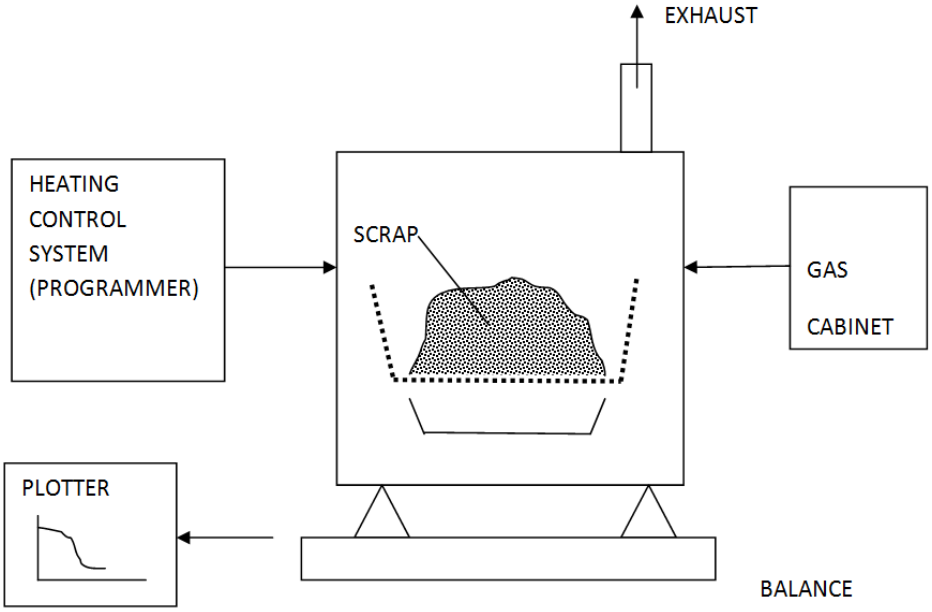

Fig. 3. An industrial TG/DTA device operated in batch mode.

The TG/DTA analysis of the incoming scrap samples was performed as a convenient batch process. An individual scrap sample was introduced into the furnace and placed on the perforated supporting plate. The door was closed and the proper initial atmosphere was adjusted. The sample was heated up with the selected regime and under the desired atmosphere, which was also regulated automatically. Total mass losses (in %) of the scrap sample were monitored as a function of time, temperature and atmospheric composition, resulting in a plotted TG/DTA curve (Fig. 4) or a final report with the calculated humidity and organics content (Table 1) .

However, as confirmed by the experiments, the batch method of analyzing scrap has low productivity and because of that it is not so suitable for industrial application. The representative sample of scrap should be analyzed starting from room temperature, which requires a relatively long time for heating and, at the end of the process, also for cooling the empty device before another start-up. The typical scrap heating time is about 1 hour. A similar period of time is necessary for cooling the device to room temperature, which means that a maximum of four representative scrap samples could be analyzed during one shift. An additional disadvantage is the need to change the composition of the furnace atmosphere – from pure argon to argon with 1 wt. % of oxygen – at the end of the process.

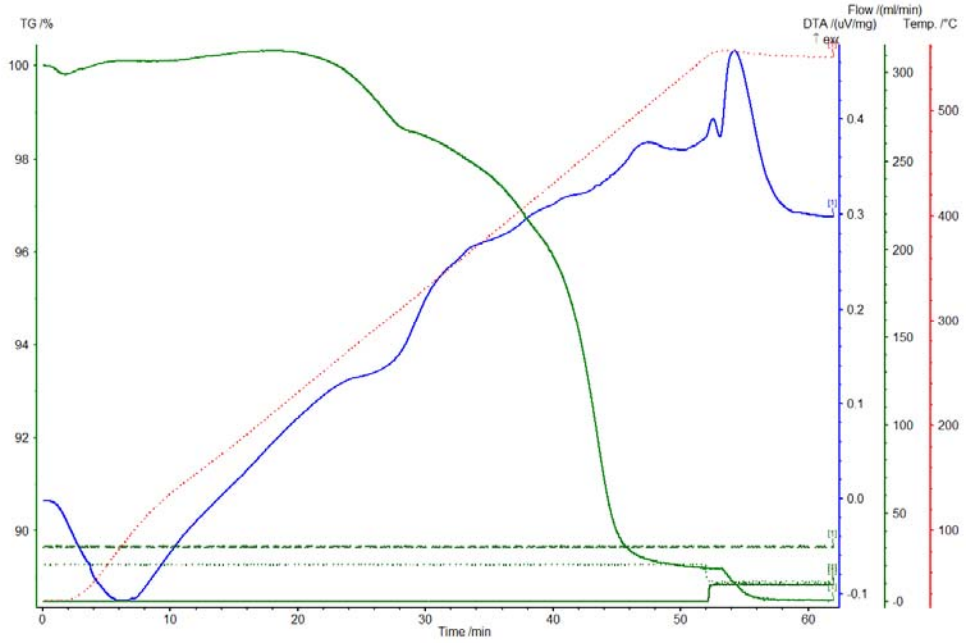

Fig. 4. TG/DTA curve obtained using the batch-processing mode.

Table 1. Comparison of the experimental results for aluminium-scrap TG/DTA analyses obtained using the batch and continuous modes

Scrap lot 1	Sample A, batch mode	Sample B, continuous mode
Humidity (%)	0.7±0.02	0.8±0.02
Content of organics (%)	15.6±0.4	14.1±0.4
Content of non-organics including aluminium (%)	84.6±2	85.8±2
Recycled aluminium * (%)	73.6±2	74.7±2

* According to Eq. 11, the estimated recycling efficiency, η_R , was 0.88

A significantly higher productivity for the scrap analysis can be achieved by using the TG/DTA unit presented in Fig. 5, which operates continuously. The main part of the unit is a vertical, two-chamber furnace with the possibility to select the holding temperatures in both chambers separately. The upper chamber is dedicated to a measurement of the humidity and is usually controlled at 120 °C. The bottom chamber is for the thermal decomposition of organics and is heated up to 520–560 °C. The chambers are separated by an intermediate door with a computerized door-opening/closing system. The door has a hole in the middle and the scrap sample, placed in a basket with perforated walls, is hung from the computerized balance by a steel wire directed through the hole. Such an arrangement ensures that a representative scrap

sample can be quickly and continuously TG/DTA analyzed at two different temperatures in the selected furnace atmospheres (argon with 1 wt. % of oxygen). After finishing the TG/DTA monitoring of the sample in the upper chamber heated at 120 °C, the door is opened automatically – when the constant weight of the basket is achieved in the upper chamber – and the scrap sample is introduced into the bottom chamber at 520–560 °C. Immediately after, the door is automatically closed in order to prevent any temperature fluctuations in both chambers. The TG/DTA analysis to a constant weight of the sample usually takes less than 60s, which means that a complete TG/DTA scrap analysis (including the humidity measurement in the first chamber) is finished in approx. 10–15 min. Also, the results of the TG analysis can be presented as a plotted TG/DTA curve (Fig. 6) or as a final report with the calculated humidity and the percentage of organics (Table 1).

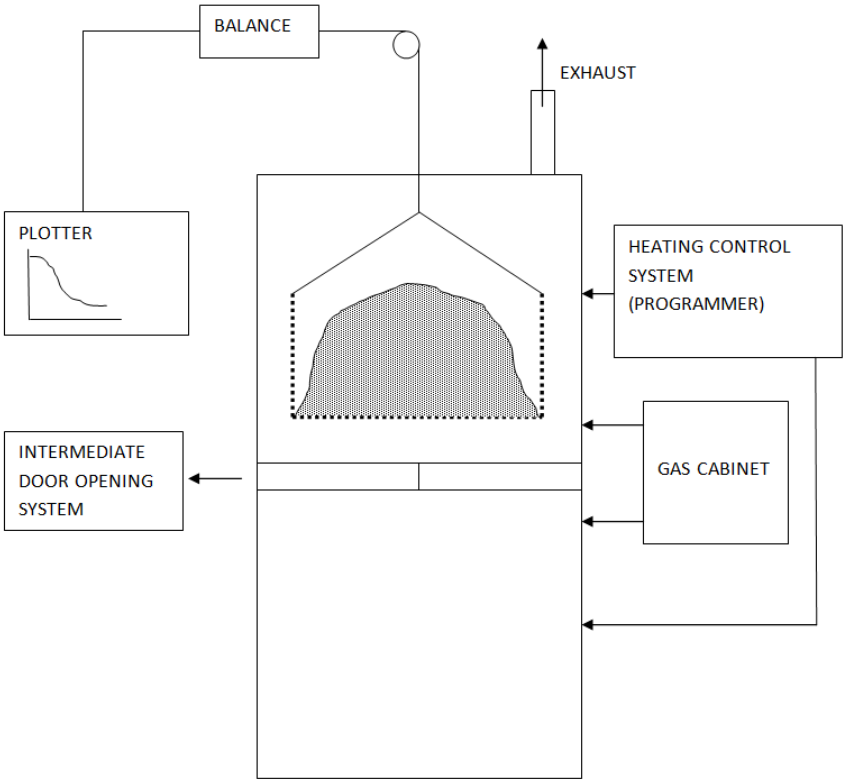

Fig. 5. An industrial TG/DTA device capable of operating in both continuous and batch modes.

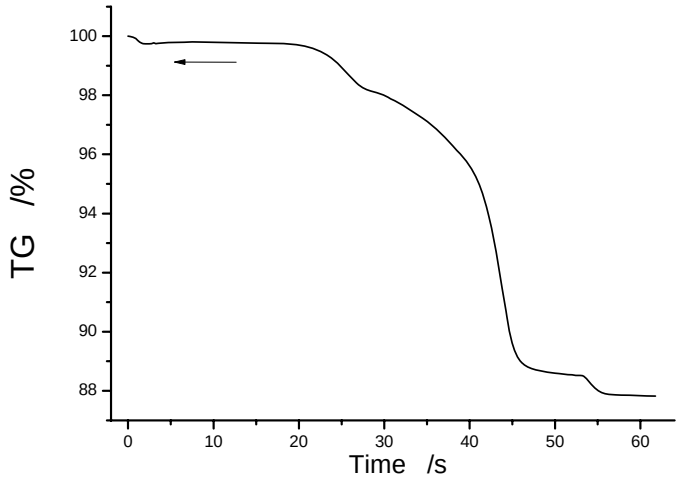

Fig. 6: An example of a TG curve generated using the continuous mode.

The accuracy of the measurement of the humidity and organic content using the batch method (in an inert atmosphere) depends on the sensitivity of the applied balance. This was determined to be ±50 g, corresponding to a maximum relative error of about 1%. The lowest relative error was in the samples with minimum weight losses (minimal content of organics). For example, the relative error of the measurement of organic content in a sample with an initial mass of 50 kg and approx. 10 kg of organics is about 0.25%, while in a sample of the same initial mass but having 80% of organics the relative error of the measurement is 1%. However, in both cases, the relative error of the measurement is within the expectation of industrial users.

The accuracy of the measurement of humidity and organic content by the continuous method (in an oxidizing atmosphere of argon with 1 wt. % of oxygen) depends in the same way on the sensitivity of the applied balance and, in addition, on the time and temperature of the thermal degradation of organics and is usually lower than in the batch mode of processing. The most important prerequisite for achieving the highest accuracy of the measurement in the continuous mode, similar to that achieved in the batch mode, is an efficient minimizing of the oxidation of the aluminium during the thermal degradation of the organics in the scrap sample. Due to the fact that the molar mass of aluminium oxide is almost two times higher than the molar mass of the stoichiometrically equivalent amount of aluminium, any oxidation of aluminium during the TG/DTA measurement will be detected as an increase in the mass of the remaining scrap sample and correspondingly interpreted as a smaller amount of organics.

Two basic approaches are practiced for minimizing aluminium oxidation during the TG/DTA measurement performed in continuous mode: (i) a prolonged exposure of the scrap sample at a lower temperature (480 to 520 °C) or rapidly heating the scrap to a temperature just below the melting point (560 to 620 °C). The right combination of temperature and time strongly depends on the scrap morphology (thick or thin gauge), the kind of organics (soluble oil, mineral oil, paint, plastic or lacquer) and the percentage of the organic phase. For this reason, for each particular lot of incoming scrap in which the

organics content is going to be analysed by an industrial TG/DTA measurement made in continuous mode, the proper time and temperature of complete organics removal with minimal aluminium oxidation should be defined in advance. The best way of selecting the proper temperature and time is based on results (humidity, content of organics, content of non-organics including aluminium) obtained on a representative sample using the batch mode as the reference. According to that, the parameters of the continuous mode (temperature and time) should be selected to reproduce the same results, with the same accuracy level as determined using the batch mode.

It is important to note that the industrial TG/DTA device developed for working in continuous mode (Fig. 5) can quite easily operate also in batch mode. This can be done by heating the sample in the bottom chamber, starting from room temperature in an atmosphere of pure argon. The decisive advantage of such an industrial TG/DTA device is in its internal flexibility to operate in both modes. For this reason, the optimizing of the processing parameters (temperature and time) for operating in continuous mode with the same level of accuracy as in the batch gained reference counterpart, become an end-user friendly and routine operation, easily applicable for a wide spectrum of incoming aluminium scrap. By following this methodology, the batch measurement should be completed first, irrespective of the scrap morphology, the kind of organics and the percentage of organic phase, providing the complete reference values for the scrap analysis. After that, in a second step, the main processing parameters (temperature and time) of the continuous mode should be tuned in order to ensure, within the same accuracy level, comparable results for the scrap analysis.

The comparison of the experimental results obtained with the TG/DTA analysis performed in batch and continuous modes (Table 1) clearly confirms that the parameters of the continuous mode applied in this work (temperature: 560 °C, holding time: 60 s) were selected properly, resulting in the comparable values of humidity, the content of organics and the content of non-organics including aluminium.

Conclusions

The TG/DTA of representative scrap samples presented in this work is an efficient analytical methodology for determining the humidity, the amount of organics and the carbon content in incoming scrap. The continuous TG/DTA industrial methodology, which ensures accurate, fast and cost-effective incoming-scrap characterization with excellent measuring certainty, is particularly effective. As demonstrated, the humidity and organic content in samples of incoming scrap having a mass of 20–50 kg were routinely measured in less than 15 min within accuracy of ± 0. 5%.

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