The Influence of Pyrolythic Reactions on the Aluminum Dross Formation during the Twin Chamber Remelting Process

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Abstract

After a coated aluminum product has reached the end of life cycle it needs to be recycled in an economical way. State of the art is the thermal removal of the organic fractions by pyrolysis. In modern multi chamber furnaces this step is realized in a separate pre-heating and melting compartment of the furnace. The incidence of aluminum losses can be traced back to the contained organic components, which lead to an aluminum burn off and thus increase dross production. The influence of typical scrap package structures on the de-coating step and the impact of released organic components on the dross quantity are investigated in this work. Lab-scale experiments have shown that the average residence time is too short to complete the pyrolysis. It has to be considered that the pyrolysis continuous while the scrap bale is submerged in the aluminum melt.

Introduction

Within the aluminum recycling process large amounts of aluminum scrap usually are contaminated with organic material. This organic layer, for example, paint, oil or cellulose compounds, represent a significant carbon input into the process route of the aluminum recycling industry. This carbon may have impact on the quantity and quality of the recycled aluminum. At the same time, the organic components could also be converted using pyrolysis to potential thermal energy, so that the fuel consumption and thus the recycling costs are reduced. The combination of pyrolysis with subsequent remelting of the scrap is achieved by the use of twin chamber furnaces. A ramp or shaft which is used for the pyrolysis step is located inside the melting chamber of modern furnace.

The aim of this part of a current project is to investigate a more complete picture of the impact of de-coating time and scrap properties and to determine the exact duration of the pyrolysis process. The obtained results are subsequently compared with each other and with those of a multi chamber furnace to show the potential for improvement. [1]

Basics of thermal decomposition of organic material

In general the thermal decomposition of carbon material with and without oxygen is divided into three reactions. To make a distinction between these reactions called pyrolysis, combustion and gasification the air number λ is defined. The air number λ is the ratio of total air amount in the system and the required air for stoichiometric total combustion.

For the combustion of carbon containing material e.g. lacquer the air number is higher than one, So that for the reaction of every mol carbon one or more mol of oxygen is available. Such combustion reactions generate a lot of heat energy as shown in equation 1.

$$C(s) + O_2(g) = CO_2(g) \qquad \Delta H = -393,5 \ \frac{kJ}{mol} \qquad\qquad (1)$$
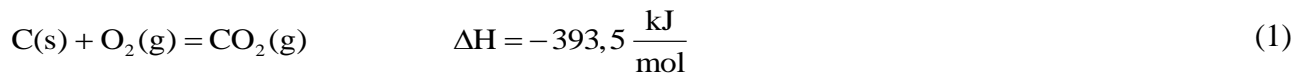
At variance with the combustion, the air number range for gasification is between 0 and 1. Because of the low oxygen concentration ($<<$ 1 %) in the pre-heating chamber of the furnace the leading carbon decomposition reaction is pyrolysis. Due to considerable fluctuations of the oxygen level during the scrap charging step, combustion and gasification reaction are also possible. The interaction between these reactions is complex and not well known. Furthermore the consequences of temporary increasing of oxygen concentration are unidentified for carbon decomposition reactions.
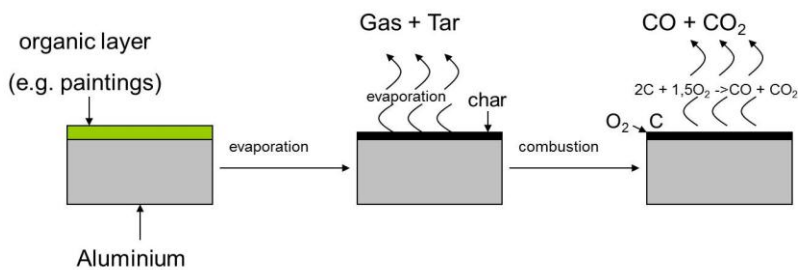

Figure 1:   De-coating mechanism [2]

Figure 1 shows the reaction during an industrial pyrolysis process with the aim to reduce the total amount of organics covering aluminum scrap. In the first step the organic components evaporate by forming gas and tar. On the surface of the scrap remains a carbon-containing tar residue. In the second step of the reaction remaining carbon on the surface reacts with the added oxygen and burn controlled to CO or CO_2 [2, 5].

Organic(s) = Coke(s) + gaseous Components   (2)

Equation 2 shows the overall pyrolysis reaction. Parallel to the gasification process at sufficiently high temperatures, an auto-thermal pyrolysis can be generated. In such a state simultaneously pyrolysis and combustion reactions are running. Before an auto-thermal pyrolysis can be achieved, the pyrolysis process runs through several phases. Which reactions take place in these phases depends on temperature.[1,3,4].

Influence of de-coating on aluminum yield

The de-coating of aluminum in twin chamber furnaces is common. One of the main arguments is the saving of natural gas by burning gaseous pyrolysis products for example methane. Therefore the charging process of scrap should be as short as possible to avoid uncontrolled increasing of oxygen level in the furnace. On the one hand aluminum oxidation will increase due to this on the other hand the pyrolysis reaction will be replaced of an uncontrolled combustion reaction. It is also well known, that a pretreatment of aluminum to decrease the carbon adhesive content related to the organic coatings, increases the aluminum yield. Unfortunately there is the majority opinion that de-coating time decreases the furnace productivity so that the charge to charge time is not a question of de-coating grade but of aluminum bath temperature. The typical de-coating time for aluminum scrap packages in twin chamber furnaces is between 20 to 30 min.

To investigate exclusively the influence of de-coating on the metal yield, lab scale experiments in a resistance heated furnace have been performed. The experiments were divided into the two steps pyrolysis and melting. Further information of the experimental setup of the de-coating step

can be found in *"Conditions of Pyrolythic Processes in Multi Chamber Furnaces for Aluminium Recycling"* published in EMC 2011 proceedings [1]. The pyrolysed aluminum scrap was molten at 750°C. After 30 min holding time dross was skimmed and aluminum casted.
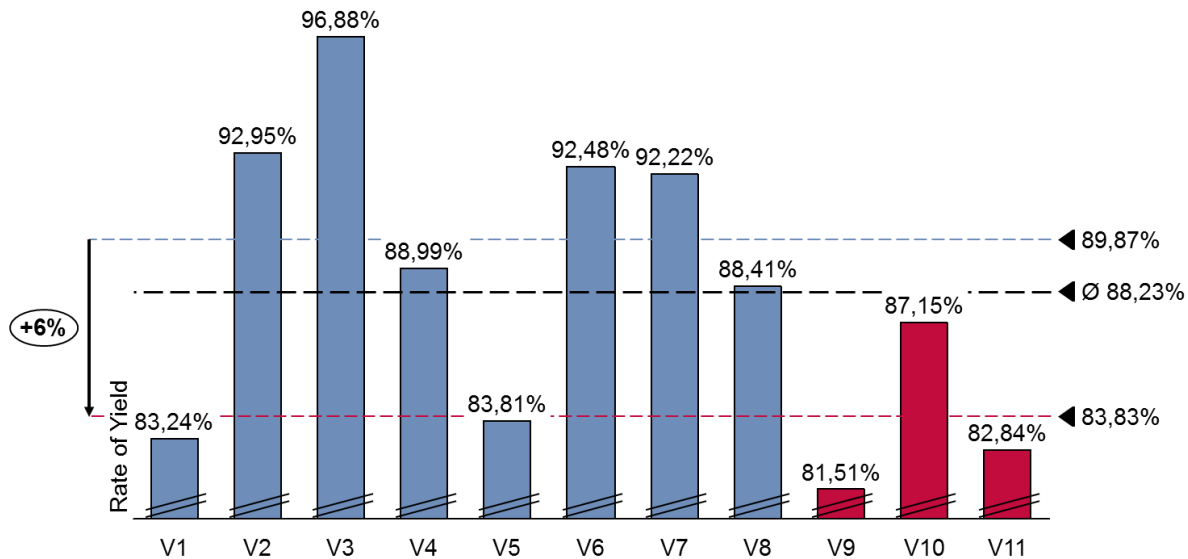The influence of the de-coating step on the melt yield can be seen in figure 3.

Figure 3:   Aluminum yield comparing pretreated (blue) and untreated scrap (red)

The comparison of 89.87 % average recycling yield for de-coated material and 83.83 % average yield for untreated material shows a significant difference. Such an overall increase of the recycling rate for more than 6 % is a huge increase of produced secondary aluminum, too.

To get a feeling of needed de-coating time experiments and simulation using the Euler difference scheme have been performed to assess the optimum ratio between de-coating time and melting rate.

Preheating of scrap bales

Typical baled scrap causes some challenges. Compacted beverage can production scrap, which is typical for the salt free recycling process has a bale density of only 0.76 g/cm³ comparing to solid aluminum density of 2.7g/cm³ and respectively 2.3g/cm³ for liquid aluminum. Together with the bale volume this leads to high bale porosity. The ratio of bale volume to bale density is the bale porosity.

$$\delta_g = 1 - \frac{\rho_{package}}{\rho_{Al}} \tag{1}$$

Usually the bale porosity of these small size bales is between 0.5 and 0.8. The high porosity together with the low package density leads to floating of single bales on the melt and a long contact time between furnace atmosphere, dross and aluminium bale. In addition, the heat transfer coefficient and thermal conductivity are changed to the worse, so that it is assumed, that the industrial de-coating time is too short for a complete pyrolysis of the organic adhesions. For a simulation of the temperature profile in the scrap bale during the pyrolysis process under inert gas atmosphere the use standard literature data for metallic aluminum is not meaningful due to the inhomogeneous structure and low density of the scrap bale and its adherent coating layers. Two different procedures are performed: The calculation of one-dimensional, instationary temperature field with the Euler method and the calculation of two-dimensional, instationary

temperature field with the computer software MATLAB. In general heat conduction problems as in the present case can be solved due to their complexity only approximately and assuming several simplifications.

The effective heat transfer coefficient λ_{eff} is given by:

$$\lambda_{eff} = A_c \, \lambda_{sol} \, (1-\delta_g) \qquad\qquad (2)$$

First simulations based on literature data showed that it is essential to generate some experimental data to get a specific temperature profile for our special case. Therefore some scrap bales were prepared with type k thermocouples to measure the heat flow. With the help of these experiments the thermal conductivity λ and the heat transfer coefficient α were identified.

The experimental setup is shown in Figure 4. To simulate the twin chamber furnace conditions, a resistance heated furnace with four heating zones excluding the furnace bottom and ceiling was used. A constant argon or nitrogen gas flow through a steel box which was installed inside the furnace realized the required inert atmosphere. At the same time there was no direct radiative heat transfer from the resistance heating elements to the bale. The furnace was preheated up to 800 °C to compensate the high heat losses during charging of the bale. While over the experimental time the furnace temperature was regulated at 500 °C. The experiments were finished by reaching 500 °C at the package centre. To avoid melting of aluminum the temperature of the experiments was limited to 600 °C.
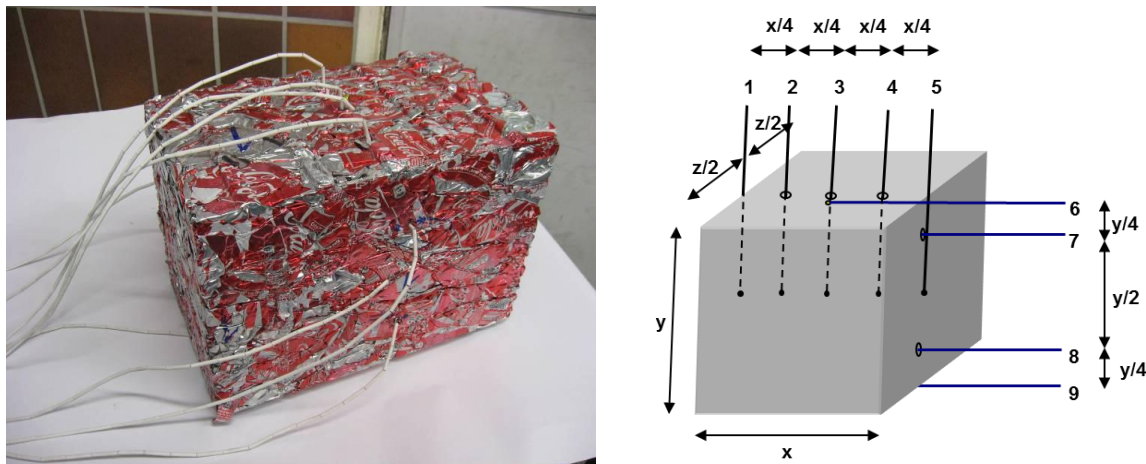

Figure 4: Temperature profile measurement of an industrial scrap package

Figure 5 illustrates one of the experimental results. Here the temperature profile of the bale can be considered (Figure 4). Comparing the bale centre with the surface the temperature lag over time is obvious. To reach the ideal Temperature of 500°C in the centre it takes up to 3600 seconds.

In industrial twin chamber furnaces the temperature of the furnace ceiling can reach up to 1200 °C, at which the atmosphere temperature is around 1000°C. Furthermore the bales are charged as a bulk so that the position of the considered bale has also an influence on the heat transfer. For our purposes, the experimental setup is the right choice.
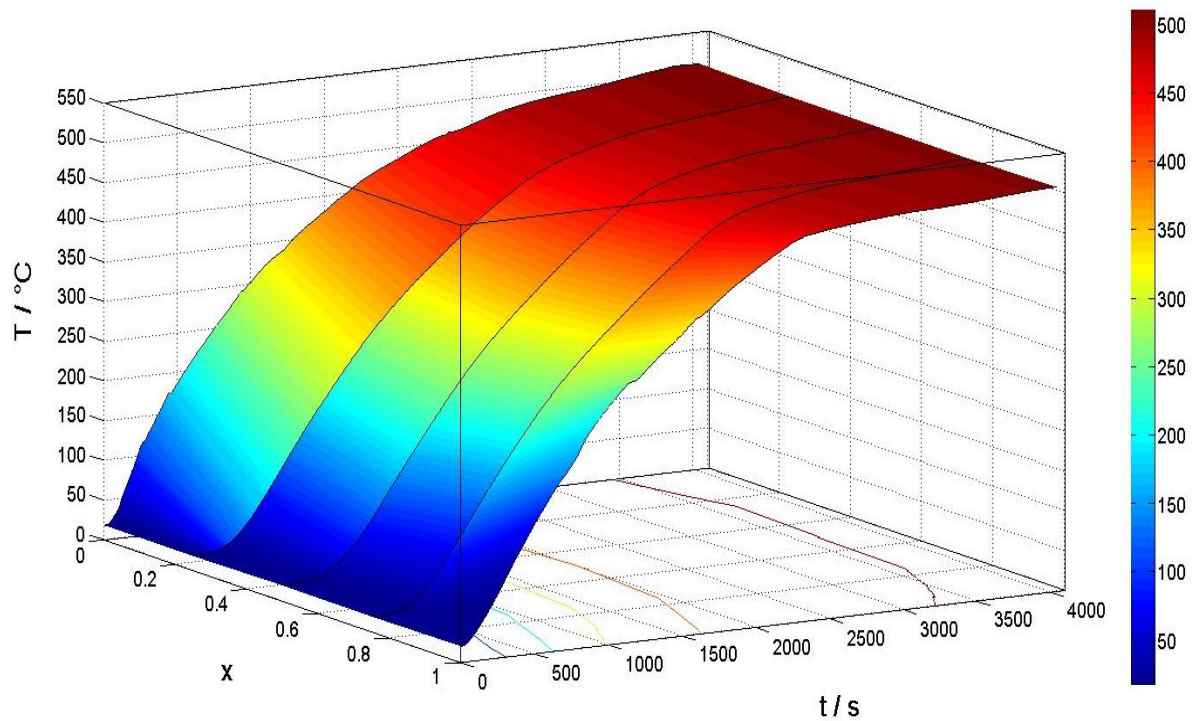
Figure 5   Typical temperature profile of a scrap bale

Finally, in order to adjust the exact development of the temperature field, both the values of the thermal conductivity, as well as heat transfer coefficient were calculated until an approximate match between simulation and reality was reached. Therefore the thermal conductivity was indirectly adjusted by variation of heat transfer resistance. The relationship of both variables has been explained already in Eq. (2). A lower thermal conductivity results in a stronger curved shape of the graph from edge to center, while the surface is inclined in the direction of higher temperatures with increasing heat transfer coefficient. The result of this improved simulation is shown Figure 6. For a better illustration, a side view of the three-dimensional graph is chosen.
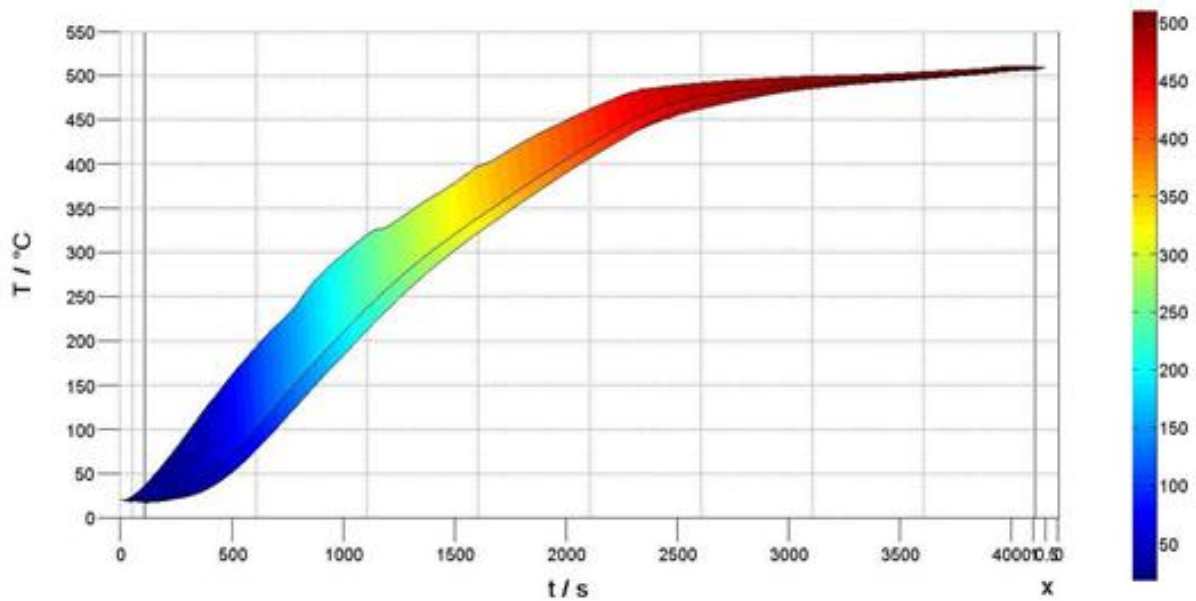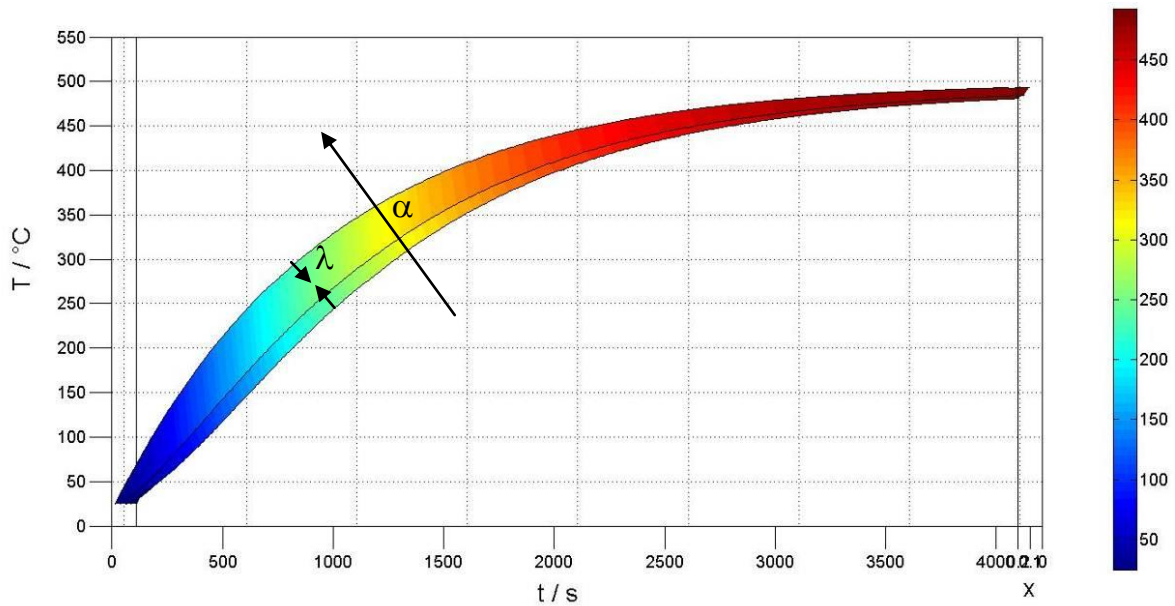
Figure 6: Comparison of Experiment data (top) and matched simulation (bottom)

As can be seen above in the figure 6, the temperature field can be realistically reconstructed expect of a few deviations with use of the Eulerian finite-difference method. Matching the figures results in a thermal conductivity coefficient of 6.75 W/(mK), or rather a thermal resistance of 0.1 and a heat transfer coefficient of 20 W/(m²K). To achieve a pronounced edge curvature, as shown by the temperature field, the boundary condition of the simulation for λ is set 0 W/(mK).

The approximate real heat transfer coefficient α can be calculated with Eq. (3) and the experimental results, so that the following relationship is obtained.

$$\alpha \quad = \quad \frac{m \cdot [\Delta H + c_p \cdot (T_f - T_i)]}{A_{conv} \cdot (T_\infty - T_{Paket}) \cdot t_{Pyrol}}$$

(3)

T_f = 500 °C

T_i = 30 °C

T_∞ = 500 °C

T_{Paket} = 265 °C

Since the bale temperature continuously changes during the process, the average temperature is used. Accordingly, α results to 17.87 W/(m²K). Nevertheless, this value is close to the used one in the adjusted simulation. Furthermore, the time interval can be changed in this simulation, in contrast to previous calculations with a useful output. This is mainly a result of the smaller number of local steps.

Comparing Simulation Result with Industrial Data

To verify the simulation method using the Euler difference scheme on its validity, results from previous experiments were used. These experiments were performed in 2004 at *Hydro Aluminium GmbH, Bonn, Germany*.

In these experiments the temperature profile of lithography scrap bale with a bigger size were analyzed. The organic content of the scrap bales were between 0 and 6.5%. Although the experiments at Hydro Aluminium were performed at the same temperature range, the oxygen content of the furnace atmosphere was 21%. Due to the presence of oxygen, the preferred reaction is combustion instead of pyrolysis, so that the mechanism is not endothermic, but exothermic. It is essential to consider this aspect in the following results.

The recording of the temperature profile was done in a similar manner. In the lower diagram of Figure 6 shows the results of the simulation of the temperature curves at the bale top side and in the bale center of original data from a heating trail under open atmosphere (upper diagram). Comparing the temperature curves of the heating experiments and the simulation (lower diagram), a good correlation was achieved.
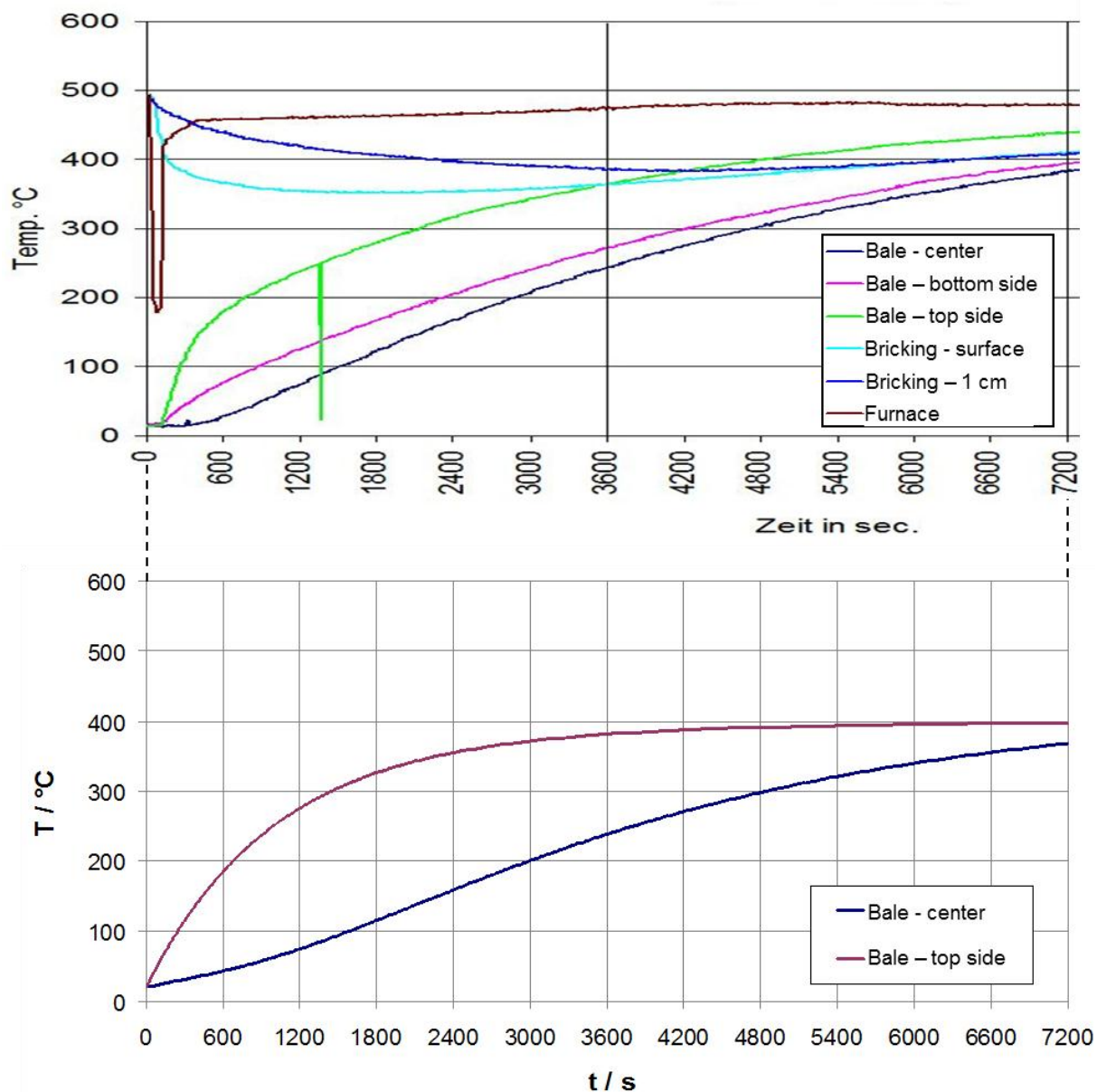

Figure 7:   Comparison of up heating experiments and simulation

A similar result shows the simulation of the temperature curve in the middle of an organic free bale. Here, the absence of a pyrolysis or combustion reaction is considered.

Table 1 summarizes the parameters used in the performed simulations. Because of the different dimensions of the scrap bales various step sizes are used for the simulations. Conspicuous is the low heat transfer resistance, resulting in very low thermal conductivities. The apparently higher thermal conductivity of the organic contaminated package can be a consequence of the exothermic combustion due to the availability of oxygen. The heat transfer coefficient results to 12 W/(m²K), while for solid aluminum a heat transfer coefficient of 50 W/(m²K) can be found in literature.

Table 1: Used parameters for simulation

	Simulation Parameters	
	With combustion of organic impurities	Without organic impurities
x / m	0,22	0,15
y / m	0,4	0,3
z / m	0,603	0,605
Dichte / gcm^{-3}	1226,4	1513,3
λ (bale) / W(mK)$^{-1}$	1,8	1,0
Λ (surface) / W(mK)$^{-1}$	0,015	0,001
Thermal resistivity	0,018	0,008
A / Wm^{-2}K^{-1}	12	12
T (furnace) / °C	485	600
Δ x / m	0,02	0,01
Δ t / s	10	10

For the experiments without combustion reaction, the heat transfer coefficient is calculated with equation (3). The equation results in a value for α of 12.9 W/(m² K). With a deviation of 7%, this corresponds approximately to the adjusted value of the simulation (table 7). Furthermore, with respect to the constraint very small numbers are used for the thermal conductivity, resulting in S-shaped profiles as seen in the simulated curves as shown in figure 7 and Figure 8. According to the shown numbers, the thermal conductivity of pure solid aluminum is 208 W/(mK). In addition, the curves (figure 7) runs not parallel for package center and surface, this is also a consequence of the lower thermal conductivity at the surface. Whether the almost identical real temperature profile is also based on this fact, however, remains open.

To control the de-coating effect of the performed experiments, untreated and de-coated scrap were visual considered under a scanning electron microscope (SEM). The de-coated scrap (Figure 9, right), shows a clear decrease in coating thickness. After pyrolysis only 30 % of the original thickness of the outside coating is remaining. The clear coating inside the beverage cans had a thickness of only about 2.5 µm after treatment, which also corresponds to a decrease of approximately 70 %.
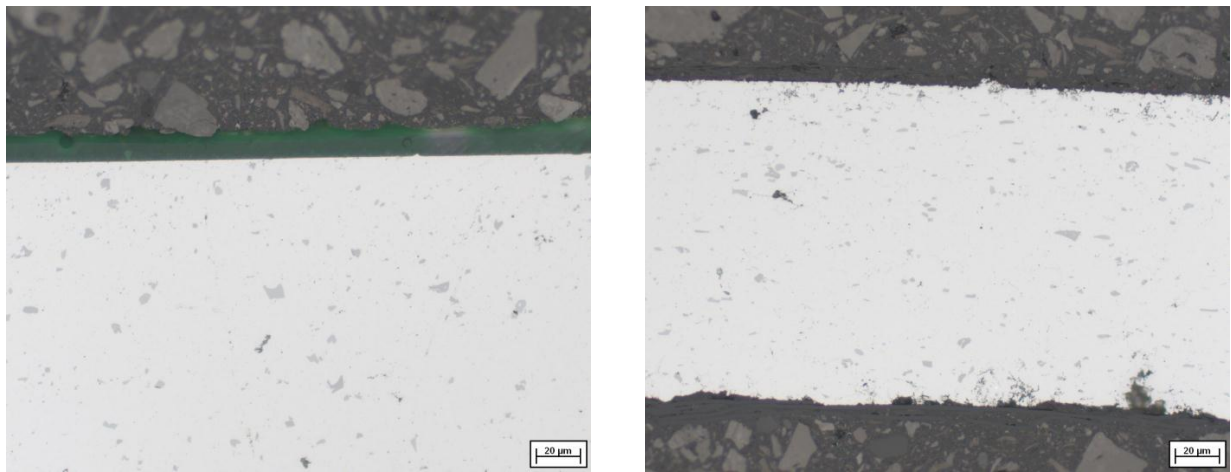
Figure 9: SEM observations of the interior and exterior lacquer untreated (left) and pyrolysed (right); 500x magnification

Conclusions

Organic scrap impurities amongst others are one of the main factors of increasing dross formation in twin chamber furnaces. To avoid interactions between pyrolysis products, for example gaseous components, tar and remaining carbon with aluminum melt, it is recommended to pre-treat the used scrap. The optimal de-coating process for scrap is a result of temperature, time and scrap type. Especially the common compacted scrap bale design causes a lot of challenges. The compacting of scrap is a result of high volume of cuttings and due to the compacting the logistics is much easier. The experiments have shown that the complete de-coating of a typical industrial scrap in a reasonable process time is not practicable. One of the main reasons is the low density - and as a result - the high porosity, so that the heat transfer and the thermal conductivity are low comparing to solid aluminum. Even if the pyrolysis time would be sufficient according to the structure, the pyrolysis products cannot leave the package so that they stay inside the package until it is molten, so that gaseous and solid de-coating products will react with the liquid aluminum and increase the dross amount.

The behavior of the reaction dynamics in a twin chamber furnace can only carried out partially based on the performed experiments. The interactions of pyrolysis products, different oxygen levels and the aluminum melt and therefore the produced dross amount can vary significantly through increased scale and should therefore be tested in 1 ton scale up trials in March 2012.

The previously described situation leads to two consequences for the production of recycled aluminum in twin chamber furnaces. First, not all of the calorific value of the organic material adhering to the scrap will be used for the remelting process, since the residence time is not sufficient for this purpose. Thus, there is an increased natural gas consumption, which offset the amount not recovered pyrolysis. As a second consequence of the incomplete pyrolysis, the carbon input into the aluminum melt and the subsequent carbide formation is increasing. This amount can be reduced by pyrolysis and different furnace and scrap design. A reduction in carbon input will have positive effects on the purity of the obtained secondary aluminum and reduce the inefficient formation of dross.

Outlook

In order to understand the distribution of carbon impact within the mass-streams of a twin chamber furnace more precisely, further investigations will be carried out. The focus will be on determining real carbon mass flow through the dross and the recycled aluminum. In addition, the effects on melt purity and the amount of dross formation caused by the remaining carbon content on the scrap will be investigated. The current work shows that the pyrolysis process is still running when the scrap block is pushed under the melt. It is assumed that formed gases have a long contact time inside the melt. This gas/liquid reaction will increase the dross formation. A longer pyrolysis time could prevent these effects. A longer de-coating time will reduce the furnace productivity and is unpopular. An alternative is the change in scrap design and a separate pre de-coating step or a controlled temporary oxygen increase during the de-coating to activate the organic combustion without oxidation of aluminum.
However, to find the best way between complete transformation of organic material into furnace atmosphere and a high furnace performance is the challenge.

Acknowledgment

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