THE EFFECT OF Mg-CONTENT ON THE EFFICIENCY OF METAL RECOVERY BY THE THERMO-MECHANICAL TREATMENT OF ALUMINIUM MELTING DROSS

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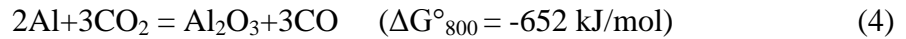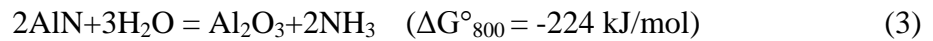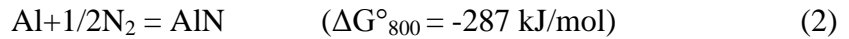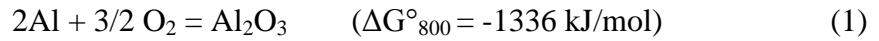kekesi@uni-miskolc.hu

Abstract

Scrap based aluminium production is increasing rapidly, however it generates significant amounts of dross of high metallic content. It is common to treat the dross at high temperature in a rotary "converter" furnace to recover most of the entrapped metal. The efficiency of this process depends on many factors, and the Mg content of the metallic phase is important. We have examined an extensive industrial data base and carried out experiments with a laboratory scale rotary furnace to compare the tapped metal yields from dross tapes divided in groups by the Mg-concentrations of the "mother alloys" generating them primarily. It has been found that a medium Mg-content in the metallic phase can offer the best yields.

1.Introduction

As the demand for aluminium increases rapidly, the importance of secondary resources has become evident. Nowadays, more than 30% of the worldwide aluminium production is based on secondary resources [1]. The energy needed to produce primary Al is 186 MJ/kg, as opposed to 11,7 MJ/kg required for the secondary production [2]. The scrap based aluminium production starts by re-melting different types of alloyed or unalloyed Al-scrap. This process however involves the production of some dross caused by the oxidation of the reactive metal and the inclusion of contained non-metallic phases. The amount of dross produced depends on various factors, including the Mg-concentration of the produced Al alloy. Among all the technically important metals, aluminium is the second most reactive after magnesium. The isolating effect of the formed oxide layer on the surface of metal drops results in the difficulty to form a coherent aluminium metal bath and causes more metal loss [3]. Dross processing is important, firstly because its valuable metal content, and secondly, to minimize the hazardous waste material that needs to be stored in landfills afterwards [4]. The dross layer acts as a "sponge" incorporating much metal in the heterogeneous structure. As it is removed by mechanical means, shown in Fig. 1, it may also contain a significant amount of metal. Thus the ratio of the metallic phase in the melting (primary) dross can reach as high values as 70 − 80 % [5]. This metal content can be mostly removed by thermo-mechanical treatment in a rotary furnace, where the material is heated and agitated at the same time. The main steps of the hot dross treatment in the "converter" are shown in Fig. 1.

Usually, the primary dross (from scrap melting) is loaded into a rotary furnace – available on-site - with fluxing salt. The energy is provided by an air- or oxy-fuel burner. The hot refractory lining can transfer heat also from below the charge. Moreover, the rotation, serves yet another purpose: it helps to brake the oxide layer that entraps the metallic Al. Beside the main process of physical heating and the separation of the metallic phase as a liquid bath, the following side-reactions can occur with the Al content of the metallic phase:

$$2Al + 3/2\ O_2 = Al_2O_3 \qquad (\Delta G^\circ_{800} = \text{-1336 kJ/mol}) \qquad (1)$$

$$Al + 1/2 N_2 = AlN \qquad (\Delta G^\circ_{800} = \text{-287 kJ/mol}) \qquad (2)$$

$$2AlN + 3H_2O = Al_2O_3 + 2NH_3 \quad (\Delta G^\circ_{800} = \text{-224 kJ/mol}) \qquad (3)$$

$$2Al + 3CO_2 = Al_2O_3 + 3CO \qquad (\Delta G^\circ_{800} = \text{-652 kJ/mol}) \qquad (4)$$

Small amounts of aluminium carbide (Al_4C_3) may also be formed [6]. It also implies that the thermo-mechanical treatment may cause some further metal loss by the formation of these non-metallic compounds, which will be present in the final (residual) dross after tapping the rotary furnace (often referred to as "converter"). In many cases magnesium is the main alloying element of aluminium. Its concentration in the alloy can go as high as 5 %. If the alloy being re-melted contains magnesium, the dross will contain some magnesium oxide (MgO) mostly in the form of a complex spinel form ($MgAl_2O_4$). The oxidation of Mg is even more vigorous than that of aluminium, evidenced by the very large negative value of the relevant Gibbs free energy change [7]. For this reason, the Mg concentration in the recovered metal will be significantly lower than that of the metallic phase in the charged dross.
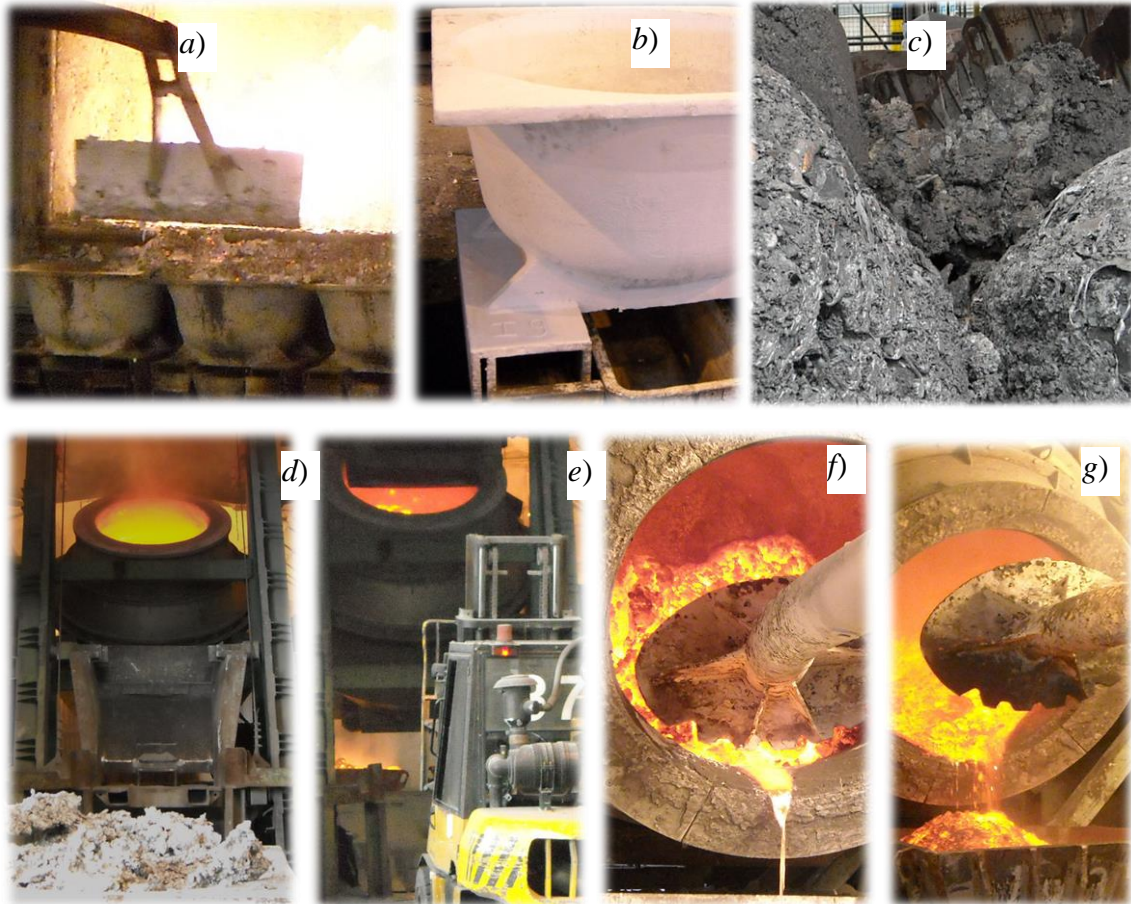

Fig. 1 Technology a) dross skimming, b) dross ladle c) primary dross d) dross charging, e) converting f) metal tapping, g) residual (secondary) dross from converting.

2. The performance of industrial thermo-mechanical treatment

A database was built which contains the important parameters of more than 750 rotary furnace heats. This refers to several months of operation for the particular furnace. We have determined the amount of dross and salt flux fed to the furnace, the recoveries, the gas and oxygen volumes consumed during each operation, and the relevant processing times. The database also contains the measured Mg content in the recovered aluminium and the composition of the alloys produced related to the treated dross batches. It must be noted that there is a plenty of uncertainties, when it comes to analysing industrial data, because of the technological circumstances. The greatest uncertainty is related to the metal content of the dross batches, depending strongly on the skimming technique used to remove the dross layer from the surface of the molten metal bath. A higher entrained metal content will result in a consequently higher amount of the metal tapped at the end of the thermo-mechanical treatment, thus the recovery results may not only depend on the converting parameters. As the examined facility offers a wide range of different aluminium alloys, each batch has been categorised into one of four groups, based on the nominal Mg content in the alloy prepared in the melting furnace, from which the dross has been skimmed. The categories applied are the following:

- "Negligible Mg": ~ 0.09% Mg
- "Low-Mg":~ 0.9% Mg
- "Medium-Mg":~ 2.4% Mg
- "High-Mg":~ 4% Mg

The magnesium concentration of the metallic phase may influence the recovery by the excess heat produced by its oxidation. In the case of Mg, the heat of oxide formation is especially high. The heat released when 1 mole of MgO is formed (601 kJ) can affect the recoveries in either a positive or negative way. Higher local heat generation may allow better fusion of the metallic and the salt phases, however it may also accelerate harmful oxidation reaction causing metal loss. The average recoveries for each Mg groups are shown in Fig. 2.
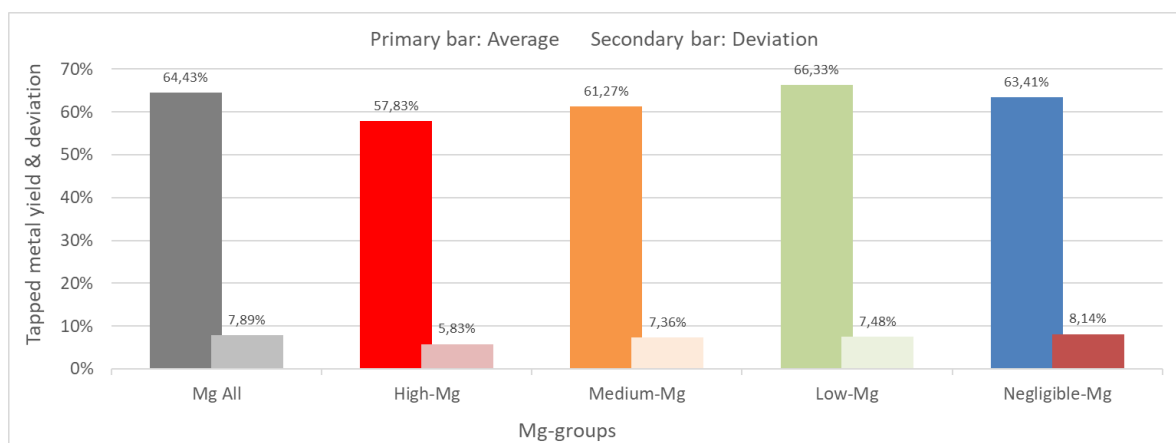

Fig. 2 The average metal recoveries of individual Mg groups.

Apparently, the most metal was recovered from the dross batches that contained low amounts of magnesium (~ 0,9%). In this case an average of 66,33% aluminium was recovered relative to the mass of the charged dross. Whereas the worst average recovery (57,83%) belongs to the high-Mg group. In the case of the negligible Mg group, the heat released when the Mg oxidised is so little that it hardly has any effect on the recovery. The

heat generated *in situ* by the vigorous oxidation of Mg makes it easier for the salt flux to melt, thus becoming more effective at the physical and chemical reactions that enhance the coalescence of the metal. In the medium and the high Mg groups, the recoveries were significantly lower. The worst recovery can be observed in the high-Mg group, where the average was ~ 10 % lower. The higher amounts of Mg in the metallic phase of the dross can increase the temperature and accelerate oxidation. Moreover, heat is released intensively and *in situ* in the charge as MgO, or at higher temperatures $MgAl_2O_4$ spinel is formed.

N. Cochran et al found [8] that in the magnesium containing alloys, first the matrix may form some amorphous Al_2O_3 and MgO nucleates around it. The MgO formed then reacts with Al_2O_3 to form spinel. The continuous spinel formation results in rapid oxidation which in turn leads to large amounts of dross formation. The formation of MgO and especially of $MgAl_2O_4$ from the metals is a highly exothermic reaction. This is also called "breakaway oxidation", it usually continues at an accelerated speed until the Mg content is depleted around the surface of the melt [9]. As a practically important consequence for melting Mg containing Al-alloys, the protective oxide layer does not form while spinel is being generated, as it consumes both Al_2O_3 and MgO. This means the metallic aluminium melt is exposed to air, and is free to bond with oxygen, resulting in a heavier melt loss and excess heat evolution. There is also, an excessive stress that is being generated during the formation of spinel, which can cause the already existing oxide film to rupture, thus releasing the covered metal. It also leads to more breakaway oxidation. In Al alloys with higher Mg content, the duration of this process is longer which results in more dross formation.

Another important factor may be the processing time in the rotary (converter) furnace. This factor varied in a wide interval, although it is not clear how the technology or the furnace operator decided the actual length of the treatment. The batches containing higher amounts of metal require longer time to melt, and this may lead to more breakaway oxidation. However, the uncertainty of the ingoing metal content makes it difficult to indicate the effect. As demonstrated in Fig. 3, the metal recovery seems to be continually increasing with the batch time. Due to the above mentioned influence of the technological circumstances, no strong correlation can be revealed, nonetheless longer process times seem to have a positive effect on the efficiency of the hot dross treatment.
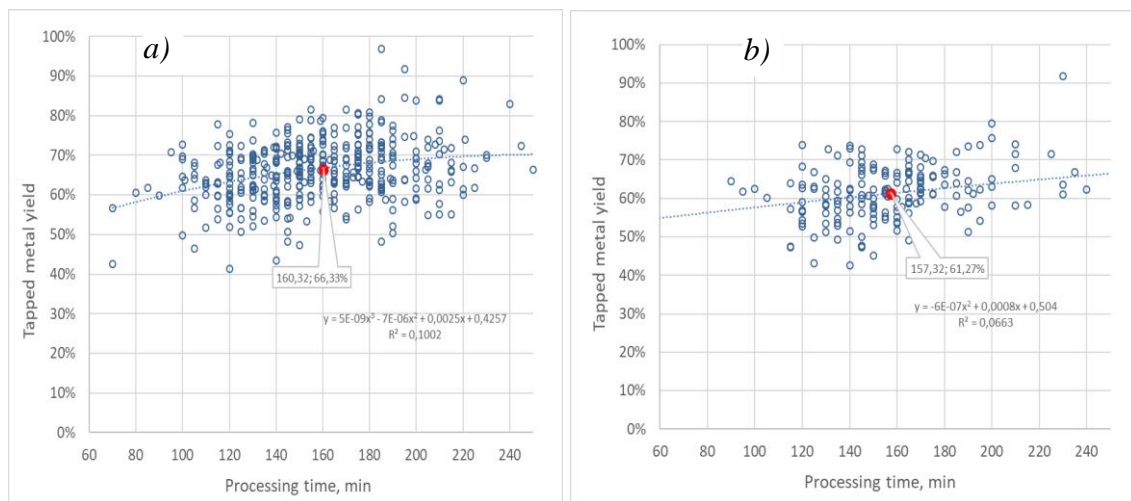

Fig. 3 *The effect of processing time on the recovery (a – Low-Mg, b –Medium-Mg).*

Despite the danger of oxidation, longer processing may not appear harmful to the recovery because the majority of the metallic phase in the dross will form a flat molten bath shortly after the suitable temperature is reached. Once the molten metal bath is formed, the specific surface of the metal drops and the bath surface is covered with its own oxide skin. Thus the oxidation of the coalesced metal is barred by kinetic factors. Its increased oxidation can only take place if the rotation of the furnace is so fast, that the molten metal often breaks out from its protective layer. On the other hand, a significant part of the metallic phase in the dross may still be entrapped in the non-metallic matrix, rolling above the metal bath in the rotary furnace. As the thermo-mechanical treatment proceeds, the suspended droplets may eventually coalesce, thus ending up in the metal pool. This may compensate for any additional loss caused by oxidation during the prolonged batch time.

The concentration of Mg in the metallic phase - as shown in Fig. 2 - can greatly influence the efficiency of the aluminium recovery from the primary dross by the thermo-mechanical treatment. In order to indicate this effect further, we have compared the nominal Mg concentrations of the alloys produced in the primary melting furnace to that analysed in the metal recovered from the dross by the thermo-mechanical treatment in the rotary furnace. The results of this comparison can be seen in Fig. 4.
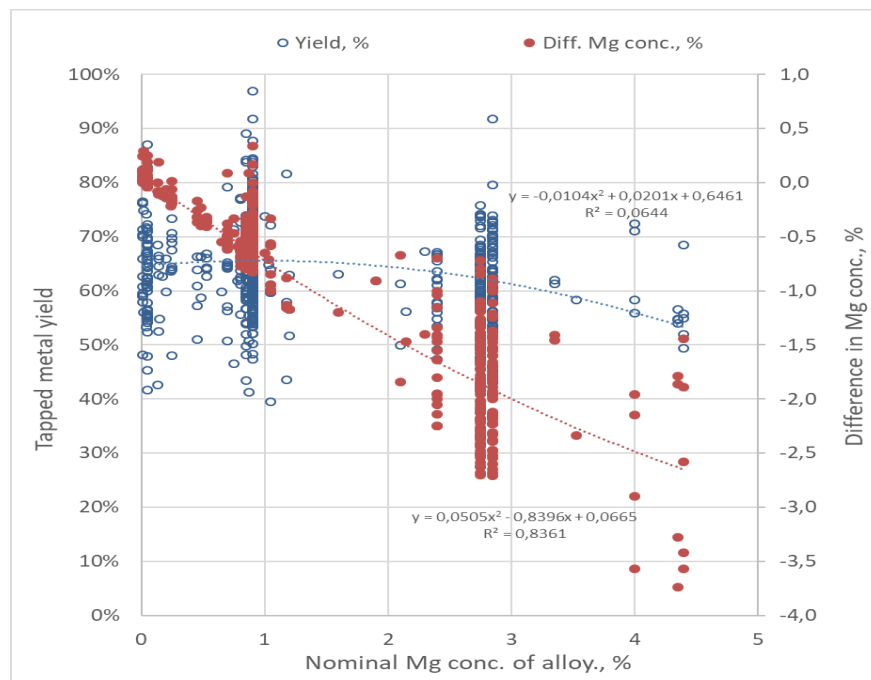

Fig. 4 The metal yield (vs. charged dross mass) and the difference in the Mg-concentrations of the produced alloy and of the metal recovered from its dross.

The actual Mg-concentration in the metallic phase of the treated dross is unknown, as the dross is skimmed off before adding the alloying elements into the molten bath of the alloy production. However, the composition of the charged scrap is usually close to the targeted alloy grade. Thus, it's reasonable to assume that the metallic phase in the primary dross has a somewhat lower Mg concentration than the nominal value referring to the alloy produced, but the two values may be mostly similar and changing in parallel with each other. Another cause of inaccuracy is the analysis by the handheld x-ray fluorescence spectrometer. This method is less accurate, even if multiple points are analysed on the solidified and machined sample taken from the tapped metal. Despite these difficulties,

Fig. 4 clearly shows that the difference in the Mg concentrations grows with the nominal value in the alloy. The increasing loss of Mg by oxidation during the thermo-mechanical treatment offers another proof to the interpretation of the Mg content causing higher metal losses.

3. The large laboratory-scale modelling of the thermo-mechanical treatment

The effects of certain parameters on the efficiency of the aluminium dross treatment could not be determined accurately by evaluating the collected data from the industry because of the uncertain initial metal content in the primary dross and the inaccurate measurements/recordings. These shortcomings were to be eliminated or reduced by modelling the hot treatment on a large-laboratory scale. A rotary tilting furnace, shown in Fig. 5, was built for this purpose with an inner diameter of 22 cm and a useful length of 50 cm. The energy for melting was provided by an air-fuel burner fitted in the door beside the off gas outlet. For each experimental run, the heat consisted of 2000g dross with the addition of 400g (20%) of the same type of salt flux used in the industry. The necessary processing times (~ 40 minutes in the current experimental series) were determined by a series of preliminary experiments. The dross types fed into the furnace were divided into the same four groups (Negligible -, Low -, Medium- and High-Mg) categories as applied in Chapter 2. The metal content of the experimental batches was obviously lower, than in the industry because of the controlled method of sample collecting. The temperature of the heated charge was measured in every 10 minutes with a digital thermometer and an N-type thermocouple placed into the charge, to record the average of the lowest and the highest measured temperatures. The main stages of the furnace operation are shown in Fig. 5.
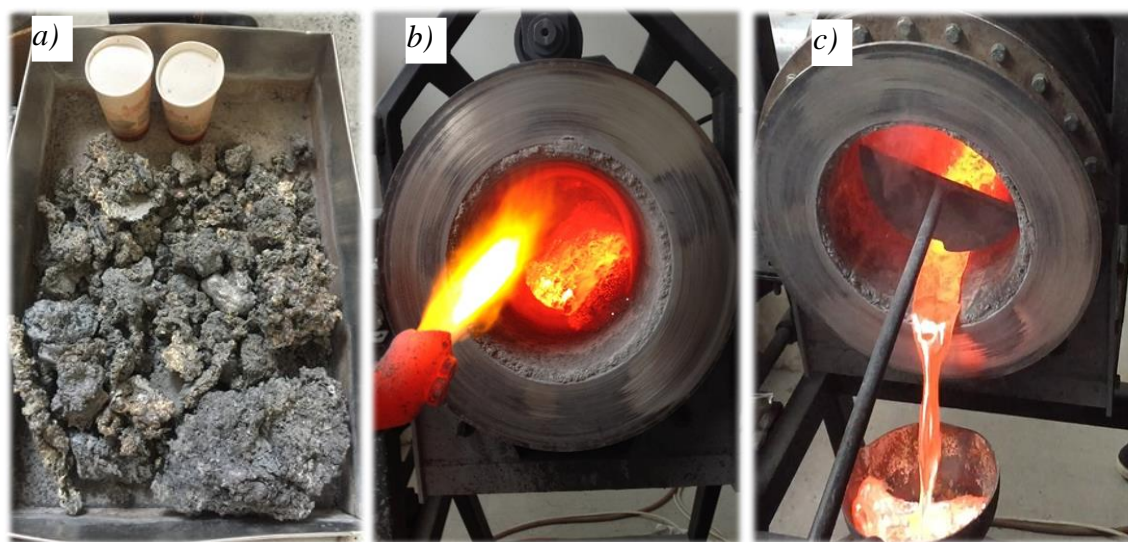

Fig 5 The operation of the furnace: a) an average batch, b) heating, c) tapping.

The amount of the metallic phase contained in the charged primary dross (Fig. 5.*a*) remained as the major factor of uncertainty still with the (visually) controlled collecting of the samples at the industrial site. In this series of the experiments, the mechanical effect exerted on the charged and heated dross arose only from the rotation of the furnace. Tapping was carried out after equal durations of hot processing. The main numerical result was obtained by measuring the solidified blocks of the recovered metal, expressed as the tapped yield relative to the mass of the charged primary dross sample. In each Mg

category, 5 individual charges were processed and the average of the obtained yields were accepted as the representative result. In this way the scattering of the metal phase ratio in the charged dross samples was considered mostly balanced and cancelled. The tapped metal yields (relative to the charged mass of the dross) are shown with the solid bars in Fig. 6, whereas the results of the parallel experiments are also given as empty bars.
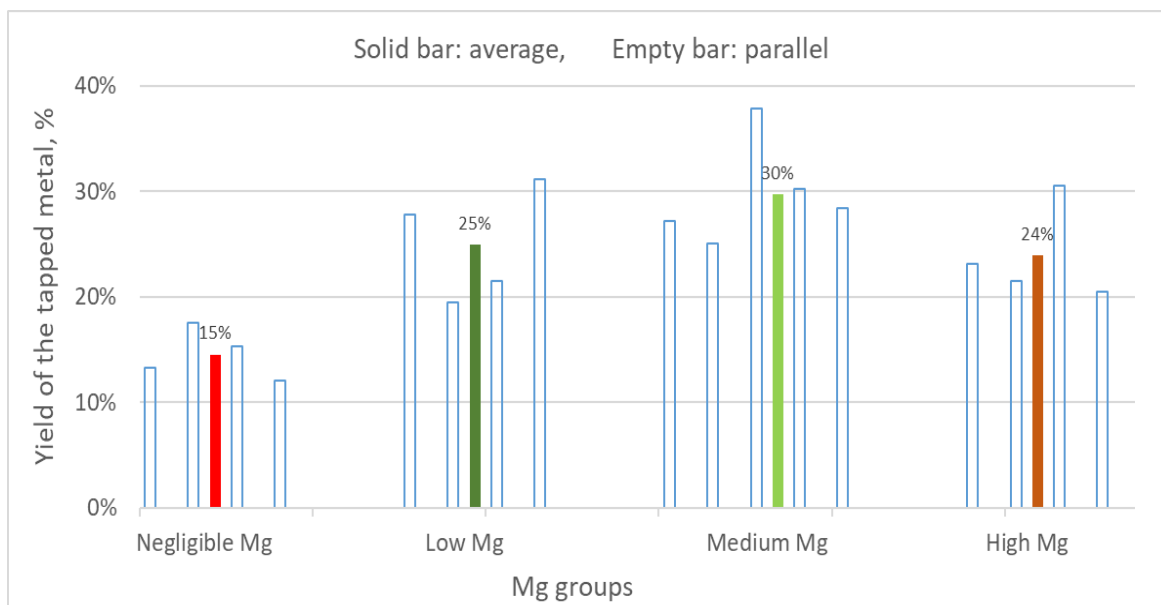

Fig. 6 The metal yields of the parallel heats in the different Mg groups.

The highest yield of the tapped metal was obtained from the charges belonging to the medium Mg group, while the lowest from the negligible Mg group. It appears that the absence of Mg can greatly decrease the efficiency of the thermo-mechanical treatment. With the low Mg group (where the mother alloy contains 0.9 % Mg) however, the average yield was 10% higher, and with the primary dross samples obtained from the melting of 2,4% Mg (medium Mg) alloys the highest average yield was achieved. This tendency did not continue with the dross samples obtained from the 4% (high) Mg alloy production.

The results from the experiments with the laboratory rotary furnace do not correspond to those derived from the industrial database (Fig. 2). This may be principally caused by the great difference in the mechanical actions at the laboratory and the industrial sizes. The small diameter of the laboratory furnace could not exert the necessary pressure on the heated dross to liberate the molten drops of the entrapped metallic phase. This shortcoming can however be compensated by introducing some external pressing action in the continued investigations. Also, the residual dross may be examined for the still remaining metal content which we have found partially liberated in larger lumps and coarse granules, but they could not be merged in the tapped pool. Therefore, the laboratory treatment with the introduced procedure could show the effect of the changing Mg content in the metallic phase on the degree of liberation for the entrapped metallic phase to form a united molten pool. Although the yielded amount of the metallic phase in tapped form does not represent the total amount of the recoverable metal.

Another indication of the effect made by the Mg content on the dross, is the maximum temperature achieved before tapping. These results are shown in Fig 7 for the examined groups of Mg-content in the mother alloy generating the treated dross.
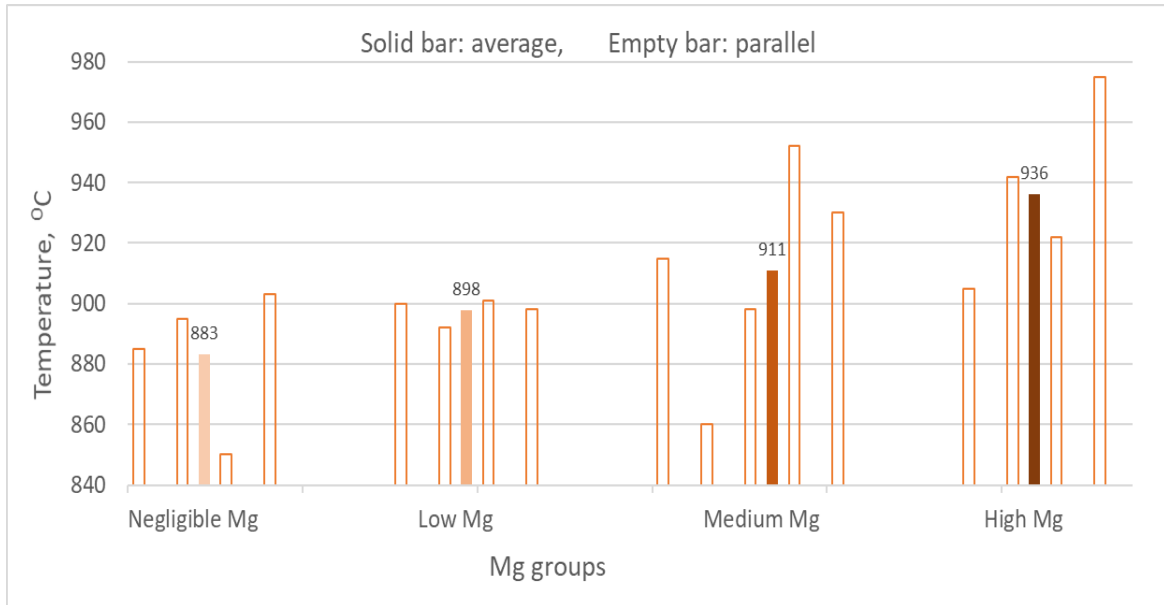
Fig 7 The average maximum temperatures of each Mg group.

As the oxidation of Mg is highly exothermic, and the heat is generated *in situ*, the temperature of the charge can rise faster and to higher degrees. It must have a beneficial effect, which is demonstrated by the achieved higher yields of the tapped metal in the same order as the Mg content of the metallic phase in the dross increased. Although the actual Mg concentration can be lower than the indicated nominal value, as explained above, the tendency is evident. The intensity of heating seems to outweigh the importance of direct loss of the oxidised metal under the examined conditions. While at low temperatures the separation of the metal from the dross matrix cannot be sufficient enough, extremely high temperatures should be avoided, as "breakaway oxidation" [8] would definitely cause lower yields.

4. Conclusions

The efficiency of the thermo-mechanical processing, the yield of the metal tapped from the rotary furnace the primary dross from aluminium scrap melting is treated is strongly dependent on the Mg content of the metallic phase in the dross. The analysis of the database constructed from a large number of data from the industrial technology suggested that too high and too low concentrations of Mg may are not advantageous. The best yields were obtained with the dross type generated by the melting of moderately low-Mg (0.9%) mother alloys. However, experiments applying the laboratory scale rotary furnace showed that the Mg-concentration of the metallic phase in the dross may have a continually beneficial effect on the separation and coalescence of the molten metal drops from the oxide matrix. The significantly different temperatures reached during the experimental runs with the dross types of different Mg groups indicated that the contained Mg acts to generate directly in the charge allowing a better action also of the added salt and resulting in better coalescence of the dispersed metal drops. This beneficial effect was more important under the experimental conditions than the obviously higher rate of oxidation causing some direct loss of metal. The results obtained from the industry were more distorted by the uncertainty of the ratio of the metallic phase in the charged primary drops. While in the laboratory experiments this disturbing factor was attempted to be mitigated by a careful composition of the charge, at least by visual

appearance. Despite of this inherent uncertainty, the average results of parallel runs may be considered as reliable to draw conclusions from. In further work, the residual dross will be also examined for the partly liberated and still entrapped amounts of the metal. Further experiments will target the effects of various salt additions, applied in different ratios, the influence of the processing time and also that of the combustion parameters, while the gentle mechanical effect of the rotation in the laboratory furnace of small diameter will be attempted to be increased by external pressure to help the liberation of the molten metal drops from the oxide matrix of the dross.

Acknowledgment

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