AES/GT/11-19 Zinc Removal from Aircraft Aluminium-alloy scrap

April-June 2011 C.R. Boeree

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Title : Zinc Removal from Aircraft Aluminium-alloy scrap

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TA Report number : AES/GT/11-19

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Summary

This report introduces a method for the removal of zinc from aircraft aluminium-alloy scrap. The driving force for this research is the demand from the secondary aluminium industry for a low zinc content in the Al-alloy scrap, and the growing demand for aluminium in the world. Meanwhile large amounts of obsolete aircraft are stored because of the problems during recycling of the aluminium.

The influence of coating on the aircraft scrap recycling is studied by treating the scrap in a de-coating process, regarding its influence on the melting process of the scrap. The coating accounts for approximately 1,6 wt% of the scrap. On a small scale, the melting of de-coated scrap shows much better results in coalescence and the separation of alloy from slag. On a larger scale, the melting results are also better for de-coated scrap, while the melting process of not de-coated scrap forms a reasonably coalescent alloy piece.

The recyclability of aircraft scrap is studied in the presence of different salt fluxes. The addition of 10 wt% cryolite promotes the coalescence of the alloy and the separation of alloy and slag. However, this salt flux removes magnesium from the alloy. Addition of magnesium fluoride maintains or even increases the magnesium content in the alloy, but gives poor results in the melting process. The use of a higher salts-to-alloy ratio does not improve the melting results and possibly even counteracts the evaporation of zinc for both cryolite and magnesium fluoride as an addition.

To improve the zinc removal from the aluminium alloy, a lance is used to blow argon gas into the alloy melt. The argon gas reduces the partial pressure of zinc, thereby promoting the evaporation of zinc from the melt. The tests are performed on an alloy with an initial zinc content of 2,42 %. A test with argon blowing lowers the zinc content to 1,88 %. However, a similar test without argon blowing results into an alloy with a zinc content of 2,11 %. The argon blowing only reduces the zinc content with 0,23 % compared to the similar test in which the same alloy is molten but no argon is blown into the melt.

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The contents under this text box are confidential and therefore cannot be displayed.

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1. Introduction

1.1 Demand for aluminium

The demand for aluminium has grown at a fast rate for the last decades, up to 38 million tons in 2010, as can been seen in figure 1.1. Properties like ductility, corrosion resistance, formability and its relatively low weight have made it an important metal for the construction, transport and packaging industry, amongst others. Growing economies like China and India are the major contributors to the increase in demand for aluminium [1]. In most cases aluminium is alloyed with other metals to create a material with specific properties that are required for its application. As a part of the transportation sector, aircraft are mainly made out of aluminium alloys.

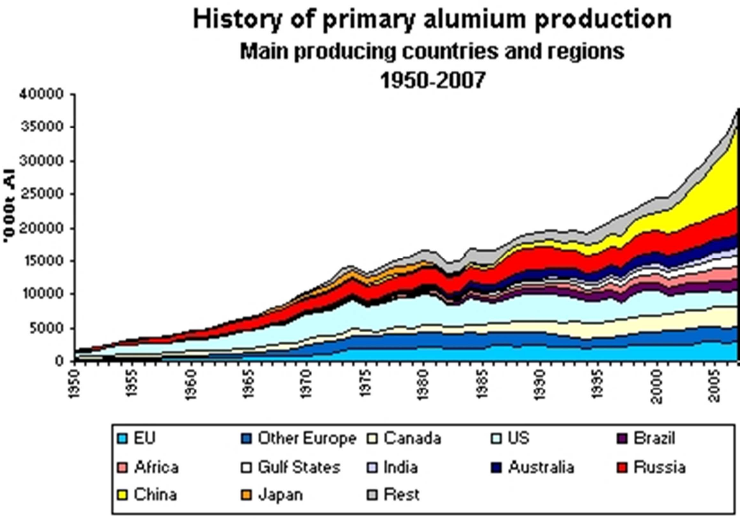


Figure 1.1: Increase of primary aluminium production [1].

1.2 Secondary aluminium production

In the secondary aluminium production industry, scrap aluminium is loaded into rotary or hearth furnaces in which the scrap is melted [2]. These furnaces often are fired by gas or oil. The addition of salt fluxes and slag are used to remove the impurities. Other uses of salts can be found in chapter 3. After melting, the aluminium is usually treated further in converters to refine the product, and alloyed with other metals. The metals are cast into bars or processed into the desired form.

Figure 1.2: Tapping of molten aluminium.

The recycling of aluminium is a process that consumes a lot less energy than the primary production from bauxite ore. The primary production consumes about 45 kWh/kg of metal product, while the secondary production uses only 2,8 kWh/kg [3]. This is not only a large saving of energy, but also the emission of CO_2 and other polluting gases are reduced, especially when the electric energy for the primary aluminium production comes from the burning of fossil fuels. Since the power companies have to pay for the emission of these gases this also results into a saving of money and therefore cheaper energy. With increasing metal prices the use of secondary resources becomes more and more attractive. Also primary production has an impact on the environment in the form of waste rock from the mining process and *red mud*, a toxic waste product from the production of alumina from bauxite ore. Furthermore aluminium can be recycled for 100%. In total it is of great concern for any country that as much aluminium as possible is being recycled.

1.3 Driving forces for this research

A great amount of the aluminium used in aircraft is alloyed with zinc, in order to increase the strength of the metal. The current secondary Al producers operate by mixing different types of Al-scrap into the composition that is asked for by the costumer. If one wants to compose an Al-alloy with low zinc content, a large amount of pure Al-melt would have to be added to reduce the Zn-content to the 0,05-0,25% that is conventional in other Al-alloys. For this reason it is desirable to remove a substantial amount of Zn from the Al-alloy before it is recycled.

In the past few decades thousands of obsolete aircraft have been placed in so-called 'aircraft graveyards' (figure 1.3), where they are abandoned because there is no suitable large scale recycling process available for the metal bodywork, which mainly consists of Al-alloys. The interior, like chairs, the electronics and the engine are taken out, and the remaining aircraft frame is left over. One famous military aircraft graveyard is located in Tucson, Arizona in the United States of America. For a satellite view, one can type the following address into Google Earth: *South Kolb Road, Tucson, Arizona.*

Figure 1.3: Aircraft graveyard in Arizona, USA. *[Google Earth 2011]*

The scrapping of aircraft is done with a special scrapping machine, mainly consisting of big saws or scissors. In practice it has been proven that it is very hard to separate parts that are made out of different alloys, since they are nailed or welded, or the geometry of the saw does not allow this kind of separation. Therefore the scrap will be a mixture of these materials, and possibly other metal alloys.

In a perfect world, the aircraft scrap could be recycled for new aircraft, since the composition of the Al-alloys used for new aircraft does not differ greatly with the alloys used in old aircraft. However, the fact that the scrap is a mixture of different Al-alloys plus other metal alloys complicates the recycling process. The different types of Al-alloys are explained in section 1.4.

Another reason why no secondary material is used in new aircraft is because the aviation industry has a belief that recycled material has a lower quality than primary materials. The safety of aircraft is the number one priority for all the aircraft construction companies. Whether primary material is better than secondary metal to satisfy the high demands of the aviation industry is a point of discussion beyond the scope of this research.

Because there is no main application of zinc-rich Al-alloys except for the aerospace industry, the price of this metal is relatively low compared to aluminium of higher purity. Sometimes these alloys are used in military applications, like armored vehicles and military bridges, but this market is very small and the industry also demands very high quality standards. The main goal of this research is to create a process to lower the Zn-content in the Al-alloy. After that, the metal is hoped to be more suitable for the current secondary aluminium production, and aircraft dismantling companies can sell the metal for a better price.

1.4 Aluminium-alloys

Wrought aluminium alloys are divided into several series, ranging from 1000 to 8000 [4]. The main Al-alloys used for aircraft are the 2000 and 7000 series, alloyed respectively with copper and zinc as main alloying elements. In aircraft construction, the frameworks, like the circular ribs in figure 1.4, are made out of 2000-series Al-alloy and the plate work is made of 7000-series Al-alloy. The alloying metals of several Al-alloys are given in table 1.1.

Series:	**Al alloyed with:**
1000	>99% Aluminium
2000	Copper
3000	Manganese
4000	Silicon
5000	Magnesium
6000	Magnesium and Silicon
7000	Zinc
8000	Other elements (Li, Fe, Sn, Ni etc.)

Table 1.1: Several Al-alloy series [4].

When the Al-alloy scrap material from aircraft is melted it contains a substantial percentage of zinc. The exact percentage is unknown because it is a mixture of 2000 series and 7000 series alloys. Therefore the percentage of zinc will be around the 5 to 7 percent in a pure 7000 series Al-alloy, but it will be lowered by the 2000 series Al-alloy and other metals that are present in the scrap.

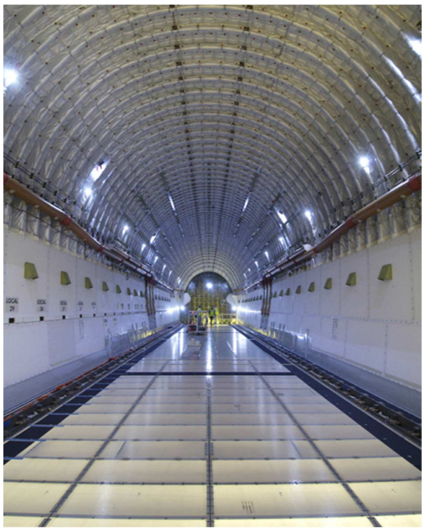


Figure 1.4: The inside of a plane, with circular ribs visible on the ceiling and plate work on the sides. *http://blog.theavclub.tv/post/big-plane*

2. Theory

2.1 The aluminium recycling industry

The production of secondary aluminium in Europe is classically done by melting the scrap in an oil- or gas-fired rotary drum furnace [13]. The scrap is covered by a layer of salt flux, mainly to prevent oxidation of the metal. Some other functions of the salt flux are explained in section 2.2.1.

The rotary drum furnace causes good mixing of the salt flux and the metal charge. This way organic materials, oxidations and other impurities are separated from the molten metal. For that reason the process is able to handle heavily contaminated scrap. The required amount of salt flux directly depends on the contaminations in the scrap. In average 500 to 600 kg of salt slag is produced per tonne of secondary aluminium. The salt slag is cleaned in a special installation and re-used.

Scrap from manufacturing processes like the car industry is relatively clean and is referred to as ‘new scrap’. The more contaminated scrap is the ‘old scrap’ which comes from used products like beverage cans or old cars. This scrap often has a layer of coating or plastic, which is hard to separate physically and will end up in the smelter.

During the melting process alloying metals can be added to create the right composition of the metal. When the right composition is reached, the metal is casted into ingots or transferred to the foundry as hot metal.

2.2 Effects of salt flux

2.2.1 Functions of flux

In most primary and secondary aluminium production salts are used for various reasons. These salts are most often based on chlorides and fluorides. The types of salt fluxes include [5]:

- *Cover fluxes*: to protect the liquid metal from oxidation and absorption of atmospheric hydrogen, and cause the agglomeration of small beads of aluminium, improving the metal recovery. Especially on alloys that oxidize rapidly, for example alloys with a high Mg content (+2 wt%), cover fluxes are important. The cover flux should be liquid at the metal melting temperature.
- *Slagging fluxes*: to increase the separation of molten aluminium in the slag. These salts are reacting with the melt and generating heat. The fluidity of aluminium is increased and aluminium can flow down in the melt more easily.

- *Cleaning fluxes*: to remove oxides from the melt. Furnace and crucible walls often have a remainder of metal oxides.
- *Refining fluxes*: to remove certain metallic elements in the aluminium. These salts are thermodynamically favorable to react with specific elements and form compounds that will form slag.

The main salts used in this research are KCl and NaCl, which serve as cover fluxes. Furthermore, MgF_2 and Na_3AlF_6 (cryolite) are used. These salts can dissolve the aluminium, and improve the coalescence between droplets of Al to obtain a satisfying metal yield. Reactions with certain elements will occur to purify the melt and react with impurity elements in the aluminium melt. For example, cryolite reacts with magnesium to remove it from the melt and form $NaMgF_3$. MgF_2 can be used when it is not desirable to remove magnesium from the alloy.

Because of the high melting points of magnesium fluoride and cryolite, these salts thicken the melt and therefore the use is limited. Also the disposal of fluoride salts is obliged to much stricter environmental regulations than chloride salts.

2.2.2 Flux Composition

For the experiments in this research, salt fluxes of NaCl and KCl are used. In addition, different amounts of Na_3AlF_6 and MgF_2 were used, as will be explained in chapter 4. To determine the right composition of the salt flux, the phase diagram of KCl-NaCl in figure 2.1 is regarded. The aim is to let the salt flux melt at the lowest possible temperature, so that it will cover and protect the aluminium. A mixture of NaCl and KCl has a eutectic point at 657 °C. At this point the composition of the mixture is 50,6 mole% KCl and 49,4 mole% NaCl, so almost equimolar. To convert this to weight percentage, the molar masses of KCl and NaCl are needed. These are shown in table 2.1.

Salt	**Molar mass**	**Melting Point**
KCl	74,56 g/mole	771^{o}C
NaCl	58,44 g/mole	801 ^{o}C

Table 2.1: Molar weights and melting points of KCl and NaCl [6].

Now the required weight percentages are calculated:

$$0{,}506 * 74{,}56 = \ 37{,}68\ g$$
$$0{,}494 * 58{,}44 = 28{,}87\ g$$
$$\frac{37{,}68}{37{,}68 + 28{,}87} = 56\ wt\ \%\ KCl$$
$$\frac{28{,}87}{37{,}68 + 28{,}87} = 44\ wt\ \%\ NaCl$$

This means the composition of the salt should be 56% KCl and 44% NaCl to let the salts melt at the lowest possible temperature. The addition of cryolite or magnesium fluoride will increase the melting point of the salt flux, since these fluorides both have a melting point above 1000 °C. The melting point of cryolite is 1020 °C, and the melting point of magnesium fluoride is 1263 °C [6]. It will also lead to a higher viscosity of the flux.

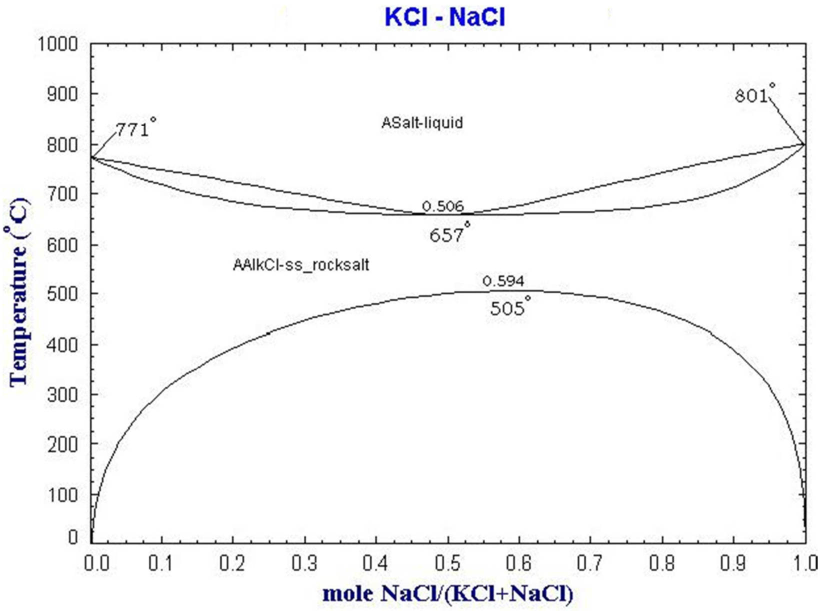


Figure 2.1: KCl-NaCl phase diagram [7].

2.3 Metal volatility

One theoretical way to separate Zn from Al-alloys is to employ the difference in melting and boiling point between Al and Zn. As can be seen in table 2.2, the melting points of Al and Zn are respectively 660˚C and 419˚C, and the boiling points are 2519˚C and 907˚C. When melting the alloy near 900˚C, the Zn will start to evaporate, while the Al remains liquid due to its very high boiling point of 2519˚C. The environment in which this volatility of Zn is used has to be protected. Any oxygen inside the reactor will oxidize Zn into ZnO, or Al into Al_2O_3. For this type of degassing, the temperature must be high enough to provide a good metal melt and volatility of zinc.

Metal	Melting point [˚C]	Boiling Point [˚C]
Aluminium	660	2519
Aluminium-oxide	2072	2977
Zinc	419	907
Zinc-oxide	1975	2360
Magnesium	650	1091
Iron	1538	2862
Copper	1085	2562
Manganese	1246	2061
Silicon	1414	2355
Chromium	1907	2671
Titanium	1668	3287

Table 2.2: Melting and boiling points of several metals and metal oxides [6].

2.4 Lowering Zn partial pressure by argon gas blowing

At every temperature there exists an equilibrium for the reaction $Zn(l) \leftrightarrow Zn(g)$. By blowing inert argon gas into the reactor at high temperature (i.e. near Zn boiling point), the partial pressure of Zn in the reactor can be lowered. To maintain the equilibrium, liquid Zn will evaporate. The evaporated Zn is transported by the gas flow. Once the zinc reaches an environment with a lower temperature, it will condensate to a liquid and eventually solidify. Another possibility is that zinc reacts with any oxygen left in the reactor to form zinc-oxide. Zinc-oxide has a very high melting temperature, so it is solid at the reactor temperature. In practice it will be very hard to create an environment without any oxygen at all, because of gas leaks or a low concentration of O_2 in the argon gas.

To improve the contact area between the argon gas and the alloy melt, the argon gas can be blown into the melt through lances. The next sections deal with the theoretical aspects of this method. The bubbles of argon gas are injected in the lower section of the melt and because of its buoyancy the bubble will move upwards, out of the melt into the atmosphere of the reactor. The amount of zinc that evaporates into the gas bubble depends on several factors [8]:

- The mass transfer coefficient of zinc from the melt into the gas bubble. This is also related to the partial pressure of zinc, which is related to the zinc content of the melt.
- The velocity of the gas bubble through the melt, i.e. the time it remains in the melt.
- The volume and surface area of the gas bubble. This is related to the Reynolds number of the bubble.
- Flow regime: laminar, turbulent or transition. This can be determined by calculating the Reynolds number.
- Bubble breakup: if a bubble gets too large, it can break up into several smaller bubbles.

The next paragraph deals with the partial pressure of zinc. The velocity of the gas bubble through the melt had been summarized in several models by Zhang et al [8, page 208]. The velocity of the bubble is mainly dependent on its size and shape. One of the simplest models is from Szekely (1979) [9]:

$$U_B = 0{,}74 * \sqrt{g * d_B}$$

In which U_B stands for the bubble velocity, g stands for the gravitational constant and d_B stands for the bubble diameter. The other models use different constants or take different parameters into account, like the viscosity of the melt, the Reynolds number or the volume of the bubble (assuming that it is not spherical). Also models exist to predict the breakup of a bubble, which is a very difficult factor to predict. Assuming that the method works, the optimal rate of bubble generation can only be found by testing.

In practical applications it is not attractive to use argon gas, because of its high price. Nitrogen is less inert than argon, but also has a price that is about 10 times lower than the price of argon. When melting in a nitrogen atmosphere, the nitrogen will form nitrides with the metal. The formation of nitrides like AlN will have consequences for the quality of the alloy.

2.5 Thermodynamic calculations for zinc evaporation

2.5.1 Partial pressure of zinc

The reaction for the evaporation of zinc is:

$Zn\ (l) \rightarrow\ Zn\ (g)$

To describe the partial pressure of zinc, the following empirical formula is used from Kubaschewski and Alcock (1979) [10]:

$$\log p(Zn) = -\frac{6620}{T} - 1{,}255 \log T + 12{,}33\ [mm\ Hg]$$

To convert the unit millimeters of mercury into Pascals, the correction factor is 133,332.

$$\log\left(\frac{p(Zn)}{133{,}332}\right) = -\frac{6620}{T} - 1{,}255 \log T + 12{,}33\ [Pa]$$

This results into the graph of figure 2.2, describing the partial pressure of zinc in a pure zinc solution between melting and boiling point. Furthermore, Raoult's law states that the vapor pressure of a component in a mixture is equal to the vapor pressure of the pure component times its mole fraction in the liquid phase [11]:

$p_j = x_j p_j^*$

Therefor the partial pressure of zinc can be taken as its mole fraction in the melt. Figure 2.2 also shows the vapor pressure for lower mole percentages of zinc in the melt.

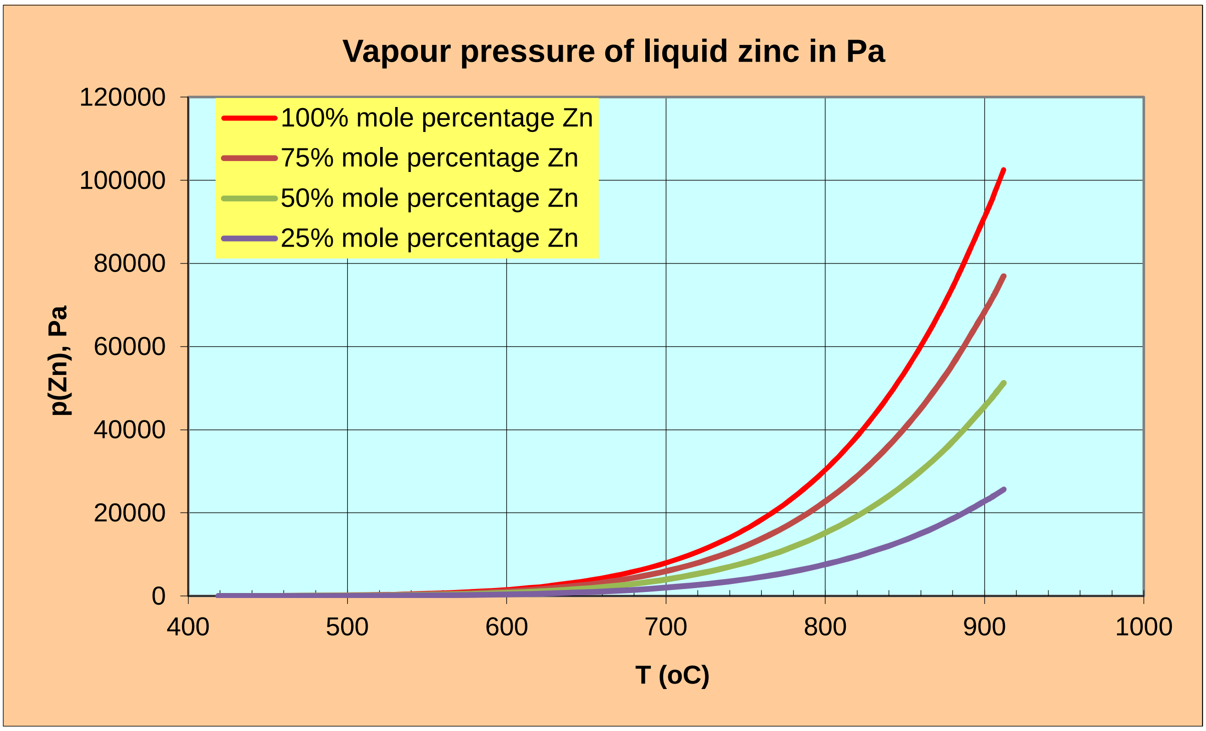


Figure 2.2: Vapor pressure of liquid zinc as a function of temperature.

The vapor pressure in a melt of Al-alloy at a fixed temperature can be calculated as a function of the zinc percentage. This results into the following linear graph:

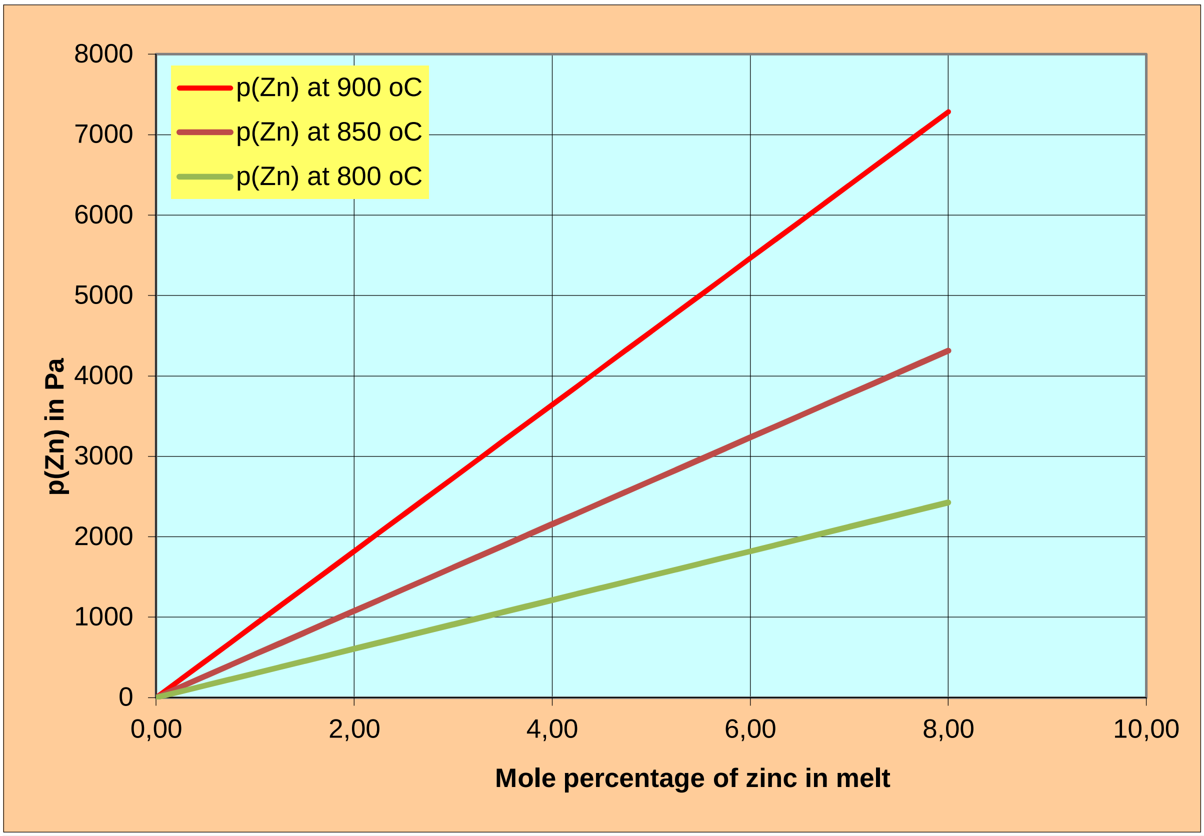


Figure 2.3: Vapor pressure of Zn at 800, 850 and 900 ^{0}C in the melt.

The mole fraction of zinc can be obtained with:

$$x_{Zn} = \frac{\frac{m_{Zn}}{M_{Zn}}}{\sum \frac{m_i}{M_i}}$$

Where m_{Zn} can be calculated by multiplying the sample weight and the weight ratio from an XRF test, and M_{Zn} stands for the molar weight of zinc.

$\sum \frac{m_i}{M_i}$ stands for the sum of the element weights in the alloy (i.e. the sample weight) divided by their molar weights (molar weights of the contributing elements). The molar percentage is equal to 100 times the mole fraction.

2.5.2 Temperature dependency

For the following calculations the program HSC Chemistry [6] is used to calculate various equilibrium compositions.

To study the theoretical effects of the temperature in which the process of zinc evaporation will occur, HSC Chemistry is used to plot the equilibria of the different phases of zinc as a function of the argon flow. The graph is meant to illustrate the effect that when the amount of argon gas in the reactor is increasing, zinc will start to evaporate to maintain its partial pressure. On higher temperatures this effect is enhanced. In practise argon gas will constantly be added to the system, and to maintain a standard pressure argon gas with zinc vapor comes out on top of the system. This way zinc is removed from the system.

Since a reactor has a fixed volume, the number of gas moles in the reactor can be approximated with the ideal gas law pV = nRT, where the pressure is 1 atmosphere and R = 8,314 J K^{-1} mol^{-1}. So at a certain reactor volume the temperature relates direcly to the number of gas moles in the reactor. From there, the ratio Zn/Zn(g) can be read from the graphs.

The weight of the alloy is 1 kg, which consists out of 92 wt% Al, 6 wt% Zn and 2 wt% Cu. In these graphs Zn stands for the sum of Zn(s) and Zn(l).

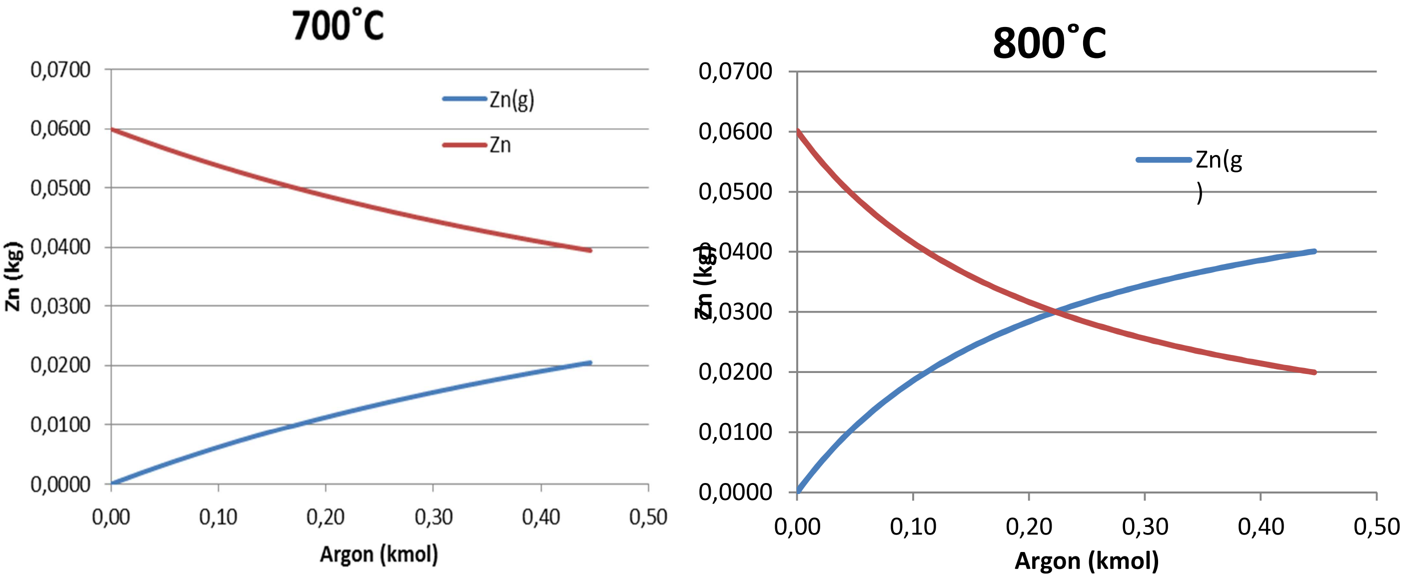


Figure 2.4.1: Equilibrium compositions as a function of argon flow at different temperatures.

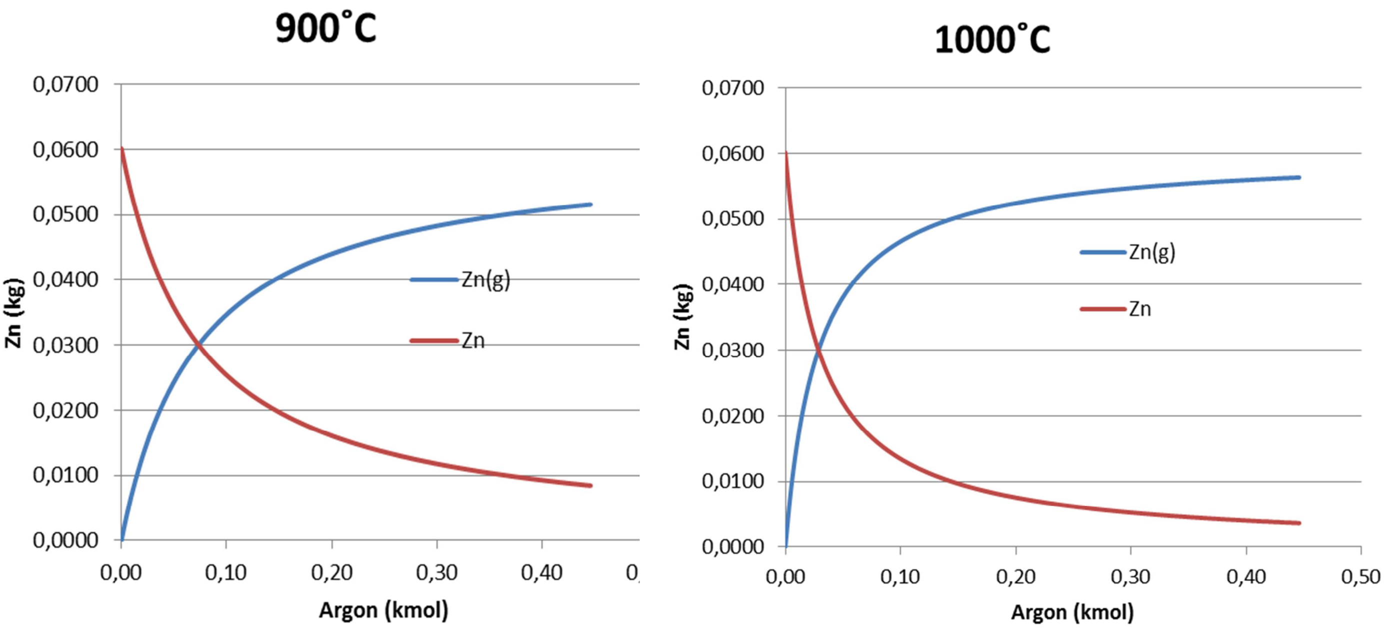


Figure 2.4.2: Equilibrium compositions as a function of argon flow at different temperatures.

From these graphs it is clear that at a higher temperature less argon is required to create an equilibrium in which Zn(g) is the dominant phase over Zn. Since the boiling point of Zn is 907 ˚C this is an obvious result.

2.5.3 Argon flow dependency

To study the effects of the amount of argon in the system, graphs are made in HSC to plot the zinc equilibrium compositions as a function of temperature at different amounts of argon gas in the system. Again, the weight of the alloy is 1 kg, and it consists out of 92 wt% Al, 6 wt% Zn and 2 wt% Cu.

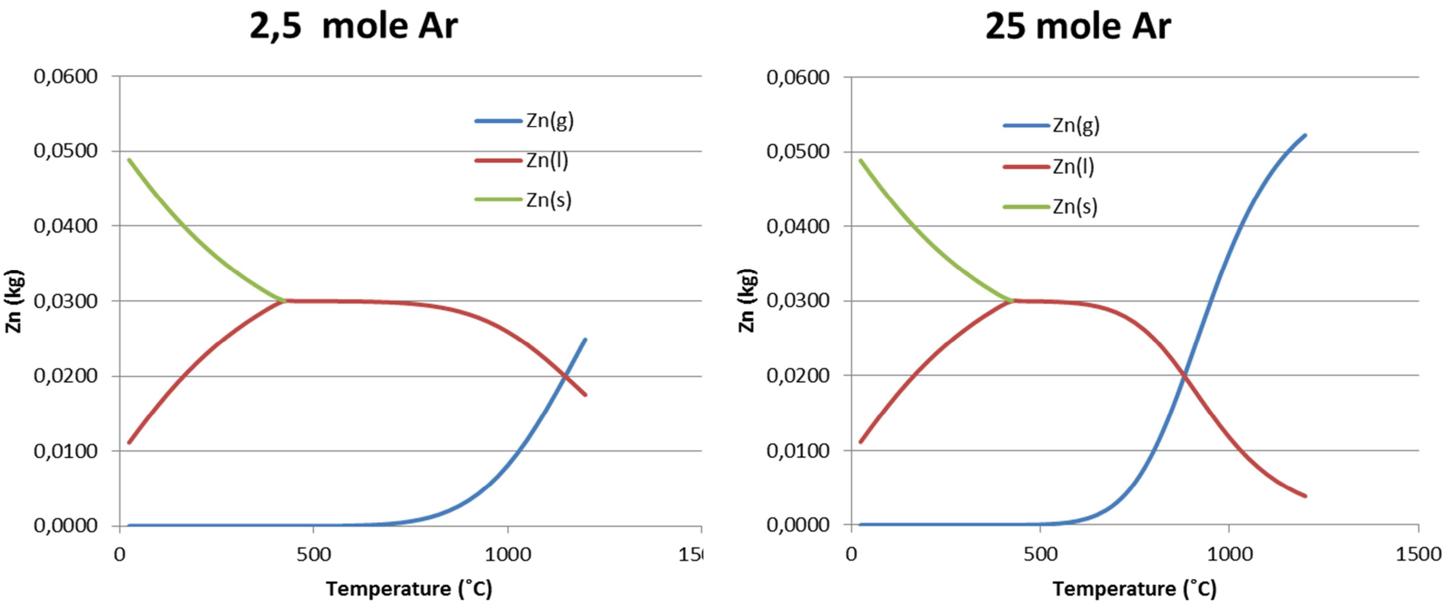


Figure 2.5.1: Equilibrium compositions as a function of temperature for different amounts of argon

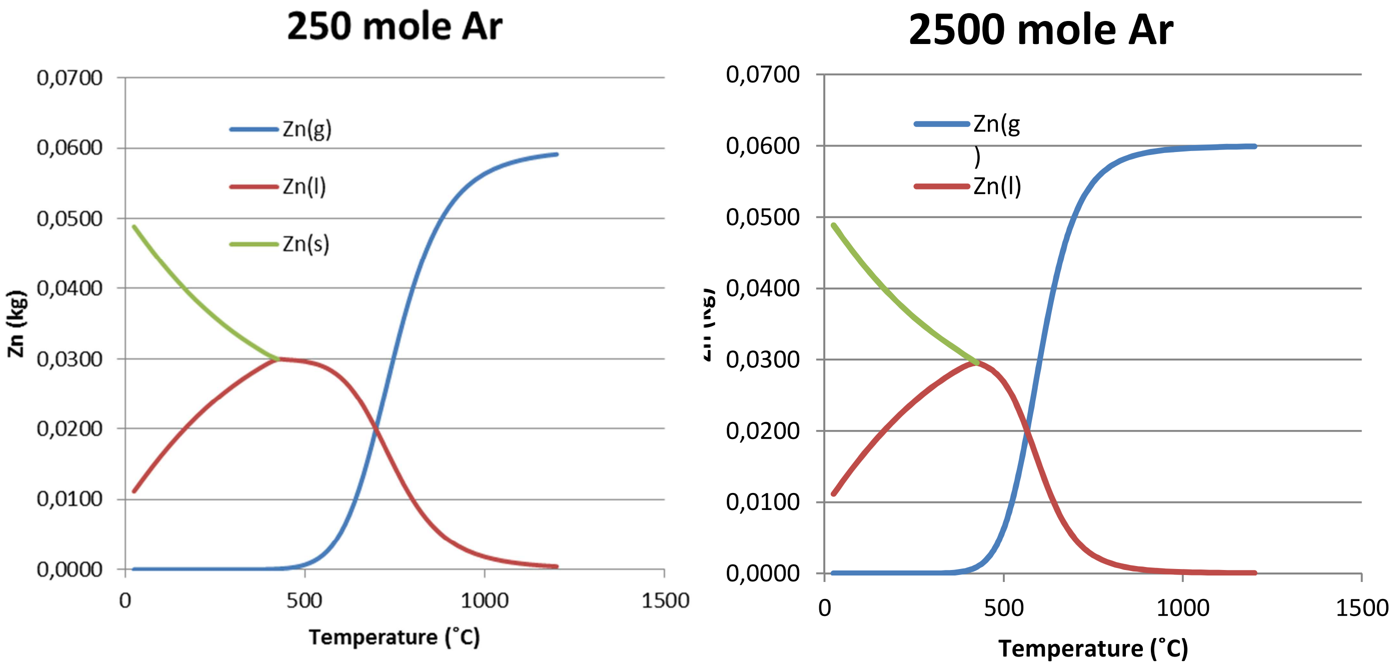


Figure 2.5.2: Equilibrium compositions as a function of temperature for different amounts of argon

The graphs in figure 2.5 show that a higher amount of argon gas in the system results into a higher partial pressure of zinc at a certain temperature. In practice this will translate into a larger reactor, since the pressure is still atmospheric, so a higher amount of argon gas will need more space.

Argon (mole)	**Zn(g) at 1000 ˚C**	**% of total [Zn(g)/0,06]**
2,5	0,0081	13,5
25	0,0365	60,8
250	0,0564	94,0
2500	0,0596	99,3

Table 2.3: Amount of Zn(g) in equilibrium at 1000 ˚C.

Looking at a temperature of 1000 ˚C, the percentage of Zn(g) in the equilibrium composition increases the most between 0,1 and 1,0 kg of argon. Between 10 and 100 kg of argon, this percentage hardly increases. In practice it will not be efficient to use a very high gas flow, since this will only increase the removal of Zn(g) slightly.

2.5.4 Pressure dependency

Also the pressure in the system influences the evaporation of zinc. According to the ideal gas law ($pV = nRT$), the number of gas molecules reduces when the pressure is reduced. Therefore a vacuum can be applied to increase the ratio Zn(g)/Zn(l) in the equilibrium. To study these effects, HSC is used to calculate the equilibrium compositions at a temperature of 1000 ˚C and with 2,5 and 25 moles of argon gas in the system. The alloy compositions are the same as in sections 2.4.3 and 2.4.4.

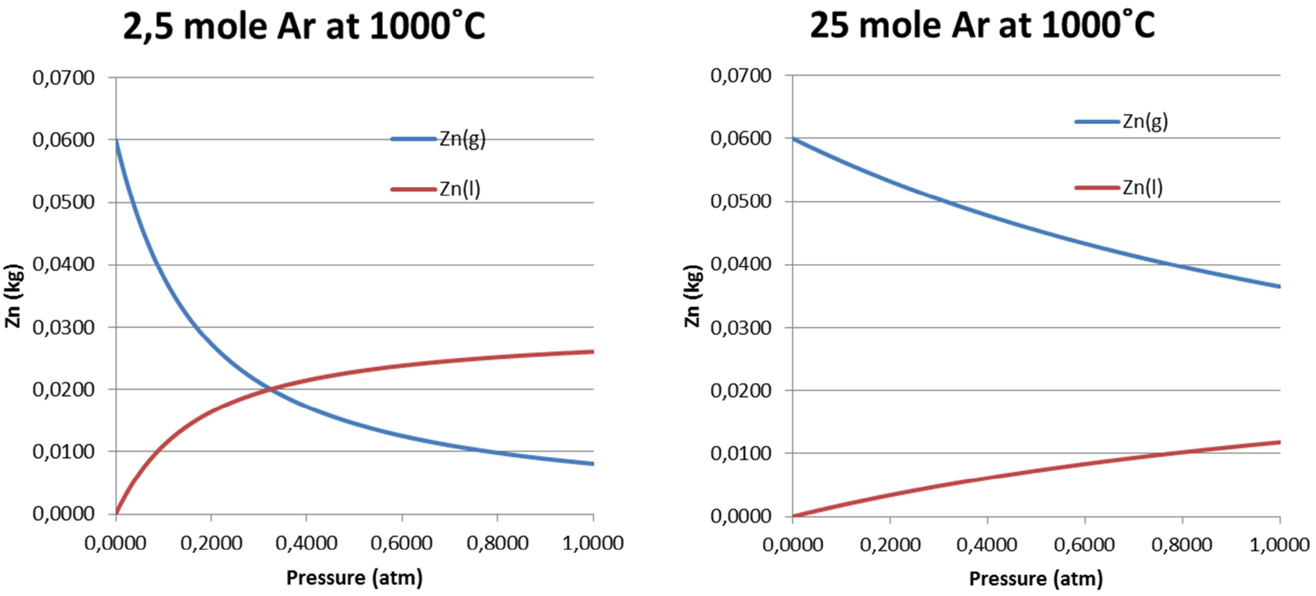


Figure 2.6: Equilibrium compositions as a function of pressure at different amounts of argon in the system.

If it is mechanically possible to create a good vacuum, there is no need for a higher argon flow since the percentage of Zn(g) out of the total Zn is already very good for a low amount of argon gas in the system.

2.6 Removal of other contaminants

In table 2.2 the melting and boiling points of several metals that are used in Al-alloys are shown. The alloying metals in the 2000 and 7000 series are mainly Cu, Zn and Mg, but also Si, Fe, Mn, Cr and Ti are included in smaller amounts. The table shows that most metals have very high boiling points compared to Zn, and therefore cannot be removed with the proposed method of lowering the gas phase partial pressure.

On the other hand, the boiling point of Mg is relatively low, resulting in volatile behavior in the reactor, and its concentration in the alloy melt can be decreased. Moreover, Mg will react with cryolite and end up in the slag when cryolite is used in the salt flux. However, magnesium fluoride instead of cryolite can avoid the Mg loss caused by interaction between Mg and salts flux. The possibilities of this method are tested in section 3.3. If the process of argon blowing removes the magnesium from the melt, the use of MgF_2 in the flux would be meaningless.

In HSC a graph is made for the equilibrium $Mg(l) \leftrightarrow Mg(g)$ at 1000 ˚C and 25 moles of argon gas in the system. The alloy weight is 1 kg and the composition is 0,90 kg Al, 0,06 kg Zn, 0,02 kg Cu and 0,02 kg Mg.

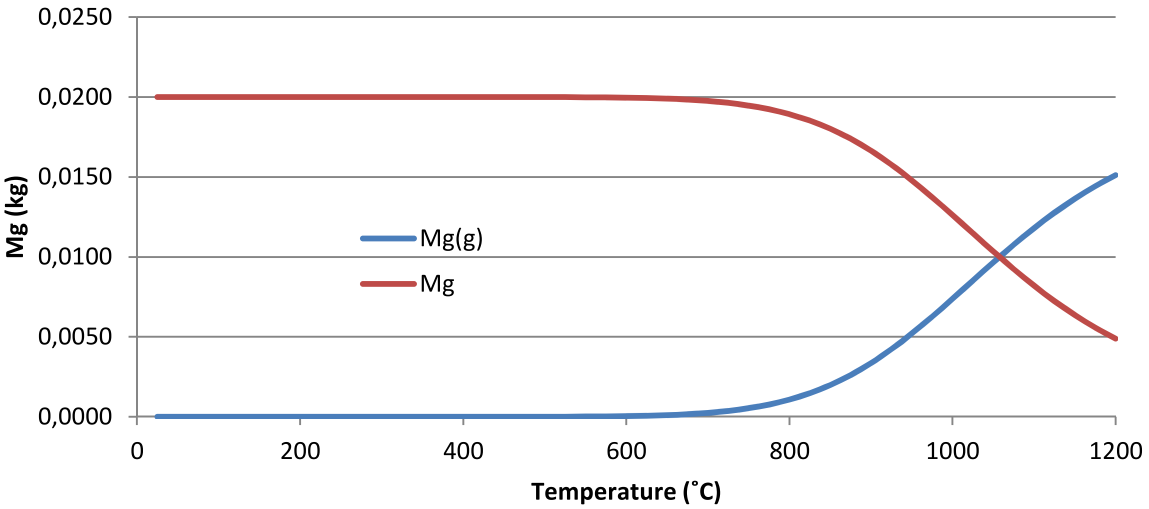


Figure 2.7: Equilibrium compositions of Mg as a function of temperature.

Note: Mg stands for the sum of Mg(s) and Mg(l). From this graph one can conclude that some Mg will evaporate, but on a smaller scale than Zn since Mg is less volatile and is less abundant in the scrap. Around 800 ˚C some Mg starts to evaporate, but on a very small scale. Around 1050 ˚C the ratio Mg(g)/Mg is 1 in an equilibrium.

Of course this method will not totally remove the Mg from the alloy. Also the flue dust in the off-gas will contain magnesium, this could be detrimental if the off-gas dust is destined for zinc production.

3. Experiments

Chapter 3 describes the experiments in this research. The results of these experiments are shown and explained in chapter 4. Section 3.8 shows a brief overview of the experiments.

For the following experiments the aircraft scrap was provided the company Aircraft End-of-Life Solutions (AELS) from Delft, the Netherlands. The scrap origins from a small type of aircraft for commercial purposes. A photo of the scrap is shown below in figure 3.1. The scrap pieces vary from several millimeters to centimeters in length, as can be seen on the picture. XRF analysis is used to estimate the composition of the scrap.

Figure 3.1: Aircraft scrap.

3.1 Equipment

The equipment for the experiments includes 3 types of furnaces, which are used for high temperature de-coating, scrap melting and metal refining tests. For the chemical analysis of the alloys an X-Ray Fluorescence Analyzer (XRF) is used. An X-Ray Diffraction Analyzer (XRD) is used for the analysis of different phases and compounds.

3.1.1 Furnaces

The furnaces used for this research are shown in figures 3.2, 3.3 and 3.4. In the furnace shown in figure 3.2 the de-coating and small scale pre-melting experiments are performed. The furnace in figure 3.3 is used for the experiments with argon gas blowing, which will be described in section 3.4. The larger melting tests are conducted in the furnace shown in figure 3.4. On the inside, this furnace has a quartz tube. A crucible with the alloy can be placed inside the quartz tube. The bottom and top of the quartz tube are cooled with water. In this way any evaporating zinc will cool down and precipitate on the tube, and it can be collected. On the top, the furnace has a thin lance, which is connected to an argon gas inlet. The lance can be pulled up to remove it from the alloy melt. Figure 3.5 shows the top of the tube furnace with the argon blowing lance.

Figure 3.2: Pre-melting and de-coating furnace for small samples.

Figure 3.3: Tube furnace with an argon gas lance on top.

Figure 3.4: Furnace for larger melting tests.

Figure 3.5: Top of the tube furnace.
Op the top, the beige colored lance can be moved up and down. The top right corner shows the valves for argon gas inlet. The grey tube to its right is the outlet for off-gas. The quartz tube is grey-colored from the condensation of presumably zinc.

3.1.2 XRF

To analyze the chemical composition of the samples, an X-Ray Fluorescence Analyzer is used. This device is able to measure the weight percentage of the elements that are present in the sample. In this research it is used for the Al-alloys to measure their content of Al, Zn and several other important elements. The device uses the emission of X-rays from the material after it has been bombarded with high-energy X-rays. The emitted 'secondary' X-rays are characteristic for the types of elements in the sample.

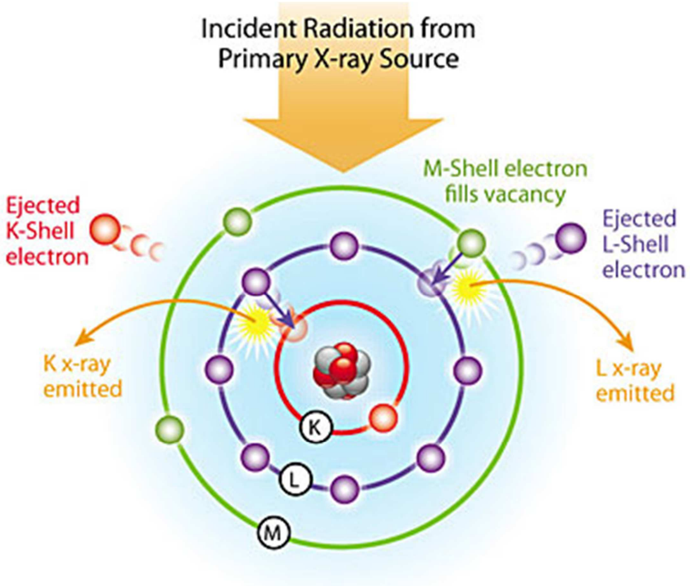


Figure 3.6: Principles of X-ray fluorescence.
http://www.azom.com/article.aspx?ArticleID=525

3.1.3 XRD

The XRD is used to analyze the compounds included in the salt slag. After melting, the slag dross will include several compounds that might be important to understand the reactions occurred during the melting process. The XRD will detect these compounds and their abundance at different wavelengths of the X-ray. A great advantage of XRD and XRF is that these methods are non-destructive.

3.2 Effects of coating on aluminium alloy melting

In order to study the effect of a coating on the aluminium scrap in the melting process, experiments are done to compare the compositions of Al-alloy melt of normal scrap with scrap that has undergone a de-coating process. Presumably the major part of this coating is aircraft paint. De-coating can remove a large amount of contaminants before the melting process.

3.2.1 Weight of the coating

First, a small amount of scrap has been treated to remove the major part of the coating. By heating the scrap at a given temperature which is below the Al alloy melting point, the coating is oxidized and can be easily removed.

Experimental conditions test A1:

- *Air atmosphere*
- *Heating rate:* *15 ^{o}C/min*
- *Temperature:* *480 ^{o}C*
- *Time:* *2 hours*
- *No salt flux*
- *Furnace:* *Small melting and de-coating furnace (Figure 3.2)*

After the thermal treatment, most of the coating is removed by flushing with water. All the coating residues are removed by hand. By measuring the weight loss, the weight of the coating can be estimated. The exact same test has also been done on a large amount of scrap (> 1 kg) in preparation of the argon blowing tests. This preparation is described in section 3.5.1. Later on an amount of around 200 g of scrap was de-coated to measure the weight loss during this process.

3.2.2 Melting tests with de-coated and not de-coated scrap on a small scale

Next, the de-coated scrap is melted in a salt flux of NaCl-KCl-10%Na_3AlF_6 and a salts-to-alloy ratio of 2:1. A similar test is done with not de-coated fresh scrap. The compositions of these tests are shown in table 3.1.

Experiment	**A1 (fresh scrap)**	**A2 (de-coated scrap)**
Salts-to-alloy ratio	2:1	2:1
Initial scrap weight	20,64 g	27,38 g
Amount of KCl	23,12 g	30,67 g
Amount of NaCl	18,16 g	24,09 g
Amount of Na_3AlF_6	4,13 g	5,48 g

Table 3.1: Salt compositions for tests A1 and A2.

Experimental conditions test A2:

- *Air atmosphere*
- *Heating rate:* *20 ^oC/min*
- *Temperature:* *800 ^oC*
- *Holding time:* *3 hours*
- *Flux:* *44 wt% NaCl, 56 wt % KCl, 10 wt% Na_3AlF_6*
- *Salts-to-alloy ratio* *2:1*
- *Furnace:* *Small melting and de-coating furnace (Figure 3.2)*

After melting and cooling down the salts in the crucible are removed with hot water, and the slag and Al-alloy particles are examined with respectively XRD and XRF.

3.2.3 Melting of not de-coated scrap on a larger scale

The melting tests from the previous section showed a bad coalescence for the not de-coated scrap compared to the de-coated scrap. However, these tests have been performed on a very small scale. To see if the coalescence is better on a larger scale, a melting test is performed with not de-coated scrap. The weight of the scrap was 700,38 g. The compositions are shown in table 3.2.

Experiment	**A3**
Salts-to-alloy ratio	1,76 : 1
Initial scrap weight	700,38 g
Amount of KCl	627 g
Amount of NaCl	493 g
Amount of Na_3AlF_6	112 g

Table 3.2: Salt compositions for test A3.

Experimental conditions test A3:

- *Air atmosphere*
- *Heating rate:* *7 ^oC/min*
- *Temperature:* *860 ^oC*
- *Holding time:* *4 hours*
- *Flux:* *44 wt% NaCl, 56 wt % KCl, 10 wt% Na_3AlF_6*
- *Salts-to-alloy ratio* *1,76 : 1*
- *Furnace:* *Large melting furnace (Figure 3.4)*

The coalescence is important for the metal recovery in the melting process. The results of this test will give information on the necessity of de-coating.

3.2.4 Melting of de-coated scrap on a larger scale

The results of the melting test with not de-coated scrap in the previous section can be compared with a similar test with the use of de-coated scrap. Because it is desirable to use the obtained alloy from this test for the later argon blowing tests, the holding time is shorter than in experiment A3 to maintain a certain grade of zinc in the alloy. If the zinc content of the pre-melted alloy is too low, it becomes harder to understand the effect argon blowing has on zinc removal.

The main aspect of this test is to compare the difference in coalescence of the alloy and the separation of slag and alloy in the melting test between de-coated and not de-coated scrap. Because the holding time is different from the previous test, it is not a goal to compare the zinc contents in both tests.

Experiments A4 and A5 (preliminary tests)

First, two separate melting tests are done with de-coated scrap. The original goal of these tests was to prepare a master alloy for the argon blowing experiments. Because this pre-melting test was done in two separate crucibles, it did not result into one uniform alloy, and the alloy from one crucible was not sufficient for all the argon blowing tests. Therefore the decision was made to create a new large and uniform master alloy, which is explained in experiment A6. However, the results of these melting tests can be studied to provide a better view on the melting process of de-coated scrap. The compositions are shown in table 3.3.

Experiment	**A4 and A5**
Salts-to-alloy ratio	2:1
Initial scrap weight	250 g
Amount of KCl	280 g
Amount of NaCl	220 g
Amount of Na_3AlF_6	50 g

Table 3.3: Salt compositions for tests A4 and A5.

A4 and A5 melting test conditions:

- *Air atmosphere*
- *Heating rate:* *20^oC/min*
- *Temperature:* *850^oC*
- *Holding time:* *3 hours*
- *Flux:* *NaCl-KCl-10%Na_3AlF_6*
- *Salts-to-alloy ratio:* *2:1*
- *Furnace:* *Small melting and de-coating furnace (Figure 3.2)*

For the XRF analysis, the alloys from these tests are named respectively *Al-alloy 1* and *Al-alloy 2*.

Experiment A6: creating an alloy for argon blowing tests

The metal that was molten in this test consisted of de-coated scrap, and a smaller amount of already pre-melted alloy from experiments A4 and A5. This pre-melted alloy originates from an earlier attempt to create a suitable master alloy for the argon blowing tests, and was also created with de-coated scrap. The composition of the total metal in this melting test is:

Weight of de-coated scrap	547,87 g
Weight of pre-melted alloy	316,90 g
Total metal weight	864,77 g

The 2 pre-melted alloys from experiments A4 and A5 had zinc contents of 2,77 % and 2,41% (see section 4.1.4), thus the average is 2,6 %. Since the initial zinc content of the scrap is approximately 5,5 %, the initial zinc content of the metal feed can be calculated as below:

$$\frac{547{,}87 * 5{,}5 + 316{,}90 * 2{,}6}{864{,}77} = 4{,}44\ \%$$

The initial zinc content in this experiment is 4,44 %.

The composition of test A6 is shown in table 3.4.

Experiment	**A6**
Salts-to-alloy ratio	1 : 1
Initial metal weight	864,77 g
Amount of KCl	484 g
Amount of NaCl	380 g
Amount of Na_3AlF_6	86,5 g

Table 3.4: Salt compositions for test A6.

Experimental conditions test A6:

- *Air atmosphere*	
- *Heating time:*	*2 hours*
- *Temperature:*	*860^{o}C*
- *Holding time:*	*2 hours*
- *Flux:*	*44 wt% NaCl, 56 wt % KCl, 10 wt% Na_3AlF_6*
- *Salts-to-alloy ratio:*	*1 : 1*
- *Furnace:*	*Large melting furnace (Figure 3.4)*

Because the metal in this melting test is relatively clean, a salts-to-alloy ratio of 1:1 is sufficient.

3.3 Effects of MgF_2 versus Na_3AlF_6 in melting tests

The fresh, not de-coated scrap is melted in the presence of a salt flux of NaCl-KCl-MgF_2 with a salts-to-alloy ratio of 2:1. The reason why MgF_2 is used instead of the more commonly used cryolite (Na_3AlF_6) is because it might not be desirable to lose Mg from the alloy. Since magnesium is a common alloying element for aluminium, in some cases it is better to keep the magnesium in the alloy. This way the option to study the effects of Mg removal by lowering the partial pressure is remained open. Obviously, when one wants to maintain the magnesium in the alloy, and it is removed in the process of argon blowing, the use of MgF_2 would be futile. The compositions of tests B1 and B2 are shown in table 3.5.

Experimental conditions test B1:

- *Air atmosphere*
- *Not de-coated scrap*
- *Heating rate:* *20^{o}C/min*
- *Temperature:* *800^{o}C*
- *Time:* *3 hours*
- *Flux:* *44 wt% NaCl, 56 wt % KCl, 10 wt% MgF_2*
- *Salts-to-alloy ratio* *2:1*
- *Furnace:* *Small melting and de-coating furnace (Figure 3.2)*

In addition to this, a same test is done with the use of cryolite instead of magnesium fluoride to compare the results of the melting process.

Experimental conditions test B2:

- *Air atmosphere*
- *Not de-coated scrap*
- *Heating rate:* *20^{o}C/min*
- *Temperature:* *800^{o}C*
- *Time:* *3 hours*
- *Flux:* *44 wt% NaCl, 56 wt % KCl, 10 wt% Na_3AlF_6*
- *Salts-to-alloy ratio* *2:1*
- *Furnace:* *Small melting and de-coating furnace (Figure 3.2)*

Experiment	**B1**	**B2**
Salts-to-alloy ratio	2:1	2:1
Initial scrap weight	20,51 g	20,64 g
Amount of NaCl	18,05 g	23,12 g
Amount of KCl	22,97 g	18,16 g
Amount of MgF_2	4,10 g	-
Amount of Na_3AlF_6	-	4,13 g

Table 3.5: Salt compositions for tests B1 and B2

After the melting process Al-alloy particles and the slag dross are examined with XRF- and XRD analysis.

3.4 Effects of variable salts-to-alloy ratio in melting tests

To study the effects of a variable ratio of salts to alloy, two experiments were done with different amounts of flux at the same weight of not de-coated alloy. This is done with both MgF_2 and Na_3AlF_6 as an additive. For the first and third experiment (C1 and C3), salt flux was added in the same weight as the alloy, so with a ratio of 1:1. In the second and fourth experiment (C2 and C4) the amount of flux was doubled.

Experimental conditions tests C1-4:

- *Air atmosphere*
- *Not de-coated scrap*
- *Heating rate:* *20°C/min*
- *Temperature:* *800°C*
- *Time:* *3 hours*
- *Flux:* *C1 and C2: 44 wt% NaCl, 56 wt % KCl, 10 wt% MgF_2*
  C3 and C4: 44 wt% NaCl, 56 wt % KCl, 10 wt% Na_3AlF_6
- *Salts-to-alloy ratio* *1:1 or 2:1, dependent on the test*
- *Furnace:* *Small melting and de-coating furnace (Figure 3.2)*

The salt compositions for these tests are shown in table 3.6.

Experiment	**C1**	**C2**	**C3**	**C4**
Salts-to-alloy ratio	1:1	2:1	1:1	2:1
Initial scrap weight	20,51 g	20,51 g	20,72 g	20,64 g
Amount of NaCl	9,03 g	18,05 g	11,60 g	23,12 g
Amount of KCl	11,48 g	22,97 g	9,12 g	18,16 g
Amount of MgF_2	2,06 g	4,10 g	-	-
Amount of Na_3AlF_6	-	-	2,07 g	4,13 g

Table 3.6: Salt compositions for experiments C1-4.

Afterwards the Al-alloy and slag are examined with XRF- and XRD analysis.

3.5 Zinc-removal by argon gas blowing

For the experiments of argon blowing, two different master alloys are used. The first test (D1) was performed with the so-called 'Al-alloy 1' from test A4 and was meant as a try-out test for the furnace. The Al-alloy 1 had an initial zinc content of 2,77 %. The second test and third test (D2 and D3) were performed with the alloy from experiment A6, which had an initial zinc content of 2,42 %. As explained in section 3.2.4, the decision was made to re-melt the Al-alloy 1 into a larger master alloy, because the alloy amount was not sufficient for all the tests.

3.5.1 Preparation of the alloy

The obtained metal from the pre-melting stage is cut into smaller pieces (figure 3.7, left), so that these will fit into the crucibles that are suitable for the tube furnace. These crucibles have an inner diameter of 3,6 cm. The surfaces of the metal are polished, so that all oxides and contaminants are removed from the surface. Because of little dents on the surface, some small spots may remain unpolished. These dark spots are visible in the left picture of figure 3.7.

For each test an alloy weight of about 80 grams is used. This results into a melt height of about 3 cm in the crucible. This is sufficient to perform the argon blowing tests, while it prevents the flow of the melt over the edge of the crucible.

Figure 3.7: Sawed and polished alloy (left), 4 cm diameter Alsint crucible (middle) and alloys in the crucible (right).

The crucibles are placed in the tube furnace and the Al-alloy is heated up to the selected temperature in 2 ½ hours. The lance is lowered into the melt for a stated period of time. The lance has a controlled flow rate of argon gas of 11,6 liters per hour. This is equal to 3,2 cm^3/s. After the stated period of time, the lance is removed from the melt. Afterwards the furnace is switched off to cool down to room temperature, which takes about 2 hours.

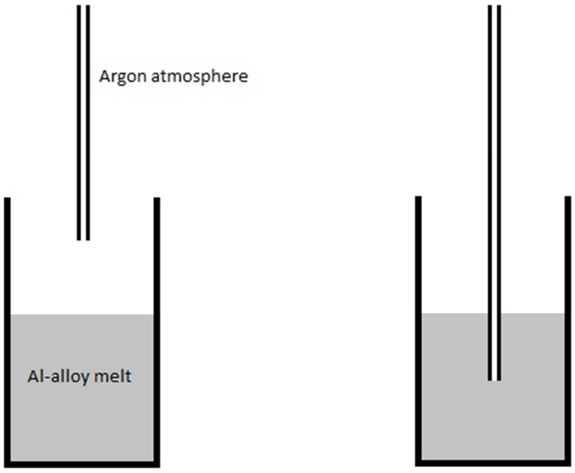


Figure 3.8: In the first phase (left), the lance is placed above the metal and no gas is flowing. In the second phase (right) when the metal is molten, the lance is lowered into the melt and blows argon gas with a fixed flow rate. After the stated time, the lance is pulled out of the melt.

3.5.2 Argon blowing

The next step is to study the effect of argon blowing in the melt on the zinc content of the alloy.

Test with master alloy from experiment A4 (preliminary test)

The first argon blowing tests is performed with the master alloy from experiment A4, which is named 'Al-alloy 1' in the XRF tests. The initial zinc content of the alloy was 2,77 %. This experiment was mainly done to test the working of the furnace as a preliminary test.

D1 test conditions:

- *Argon atmosphere*
- *Alloy from de-coated scrap*
- *Temperature: 860 °C*
- *Time: 2 ½ hours heating up*
  30 min argon gas blowing
  around 2 hours cooling to room temperature
- *No flux*
- *Furnace: Tube furnace (Figure 3.3)*

Test with master alloy from experiment A6

A test is conducted on 900 °C for a holding time of 1 ½ hours during which argon is blown into the melt for 30 minutes. Before and after the argon blowing, the melt is kept on holding temperature for 30 minutes to let it stabilize. The alloy for this test comes from experiment A6 and had an initial zinc content of 2,42 %.

D2 test conditions:

- *Argon atmosphere*
- *Alloy from de-coated scrap*
- *Temperature:* *900 ^oC*
- *Time:* *2 ½ hours heating up*
  30 minutes to stabilize the melt
  30 minutes of argon blowing
  30 minutes to stabilize the melt
  around 2 hours cooling to room temperature
- *No flux*
- *Furnace:* *Tube furnace (Figure 3.3)*

3.5.3 Identical test without argon blowing

To see if the method of argon blowing has any effects, one test is done without lowering the lance into the melt. This test can easily be compared to test D2 in which the same alloy is used (from A6) and argon is blown into the melt under the same conditions and for the same holding time.

D3 test conditions:

- *Argon atmosphere*
- *Alloy from de-coated scrap*
- *Temperature:* *900 ^oC*
- *Time:* *2 ½ hours heating up*
  90 minutes on holding temperature
  around 2 hours cooling to room temperature
- *No flux*
- *Furnace:* *Tube furnace (Figure 3.3)*
- ***No argon blowing into the melt***

3.6 Mechanisms behind zinc removal

Up until now, it is not clear what the most important mechanism is behind the removal of zinc from the molten alloy; evaporation or entrapment in the slag phase. To obtain a better insight in this, two experiments are performed. In the first experiment de-coated scrap is molten in the presence of a salt flux. In the second experiment also de-coated scrap is molten, but without the protection of a salt flux. To protect the melt from oxidation, the second test is performed in an argon atmosphere. The salt composition for test E1 is shown in table 3.7.

E1 melting test conditions:	***E2 melting test conditions:***
- *Air atmosphere* - *Use of de-coated scrap* - *Temperature: 800 ^{o}C* - *Heating time: 40 min* - *Holding time: 3 hours* - *Flux: 44 wt% NaCl, 56 wt % KCl, 10 wt% Na_3AlF_6* - *Salts-to-alloy ratio 2:1* - *Furnace: Small melting and de-coating furnace (Figure 3.2)*	- *Argon atmosphere* - *Use of de-coated scrap* - *Temperature: 800 ^{o}C* - *Heating time: 40 min* - *Holding time: 3 hours* - *No salt flux* - *Furnace: Tube furnace (Figure 3.3)*

Experiment	**E1**
Salts-to-alloy ratio	2:1
Initial scrap weight	27,38 g
Amount of KCl	30,67 g
Amount of NaCl	24,09 g
Amount of Na_3AlF_6	5,48 g

Table 3.7: Salt compositions for test E1.

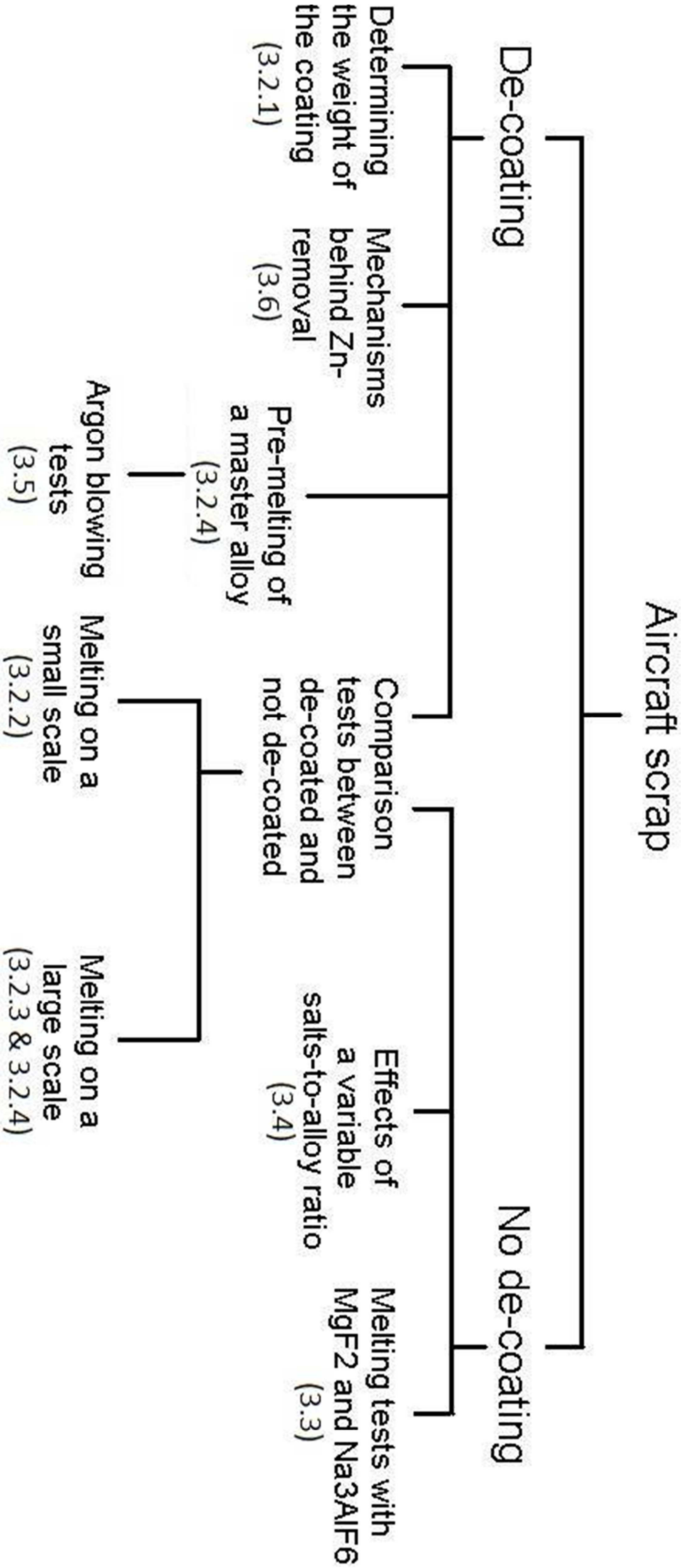
The results will show if during melting the zinc is transferred to the slag phase (test E1) or if the zinc is evaporated (test E2). An XRD analysis on the salt slag will possibly not work because the XRD analysis only detects compounds with a concentration of more than 5 wt%.

3.7 XRD test on furnace dust

The tube furnace, in which all of the argon blowing tests (D1-3) and melting test E2 are performed, has a water cooling system on top of the furnace. This cooling system drastically lowers the temperature in the top of the furnace, cooling down the off-gas and flue dust. When zinc vapor is evaporated and reaches this cooler area, theoretically speaking the zinc should condensate and solidify on the side of the tube. To test this hypothesis, the dust on the tube wall is collected and analyzed with XRD to determine the composition.

3.8 Process overview

Below, a schematic overview is given of the tests in this research.



4. Results

This chapter describes the experimental results. The appendix shows the XRF analysis results for the experiments in this chapter.

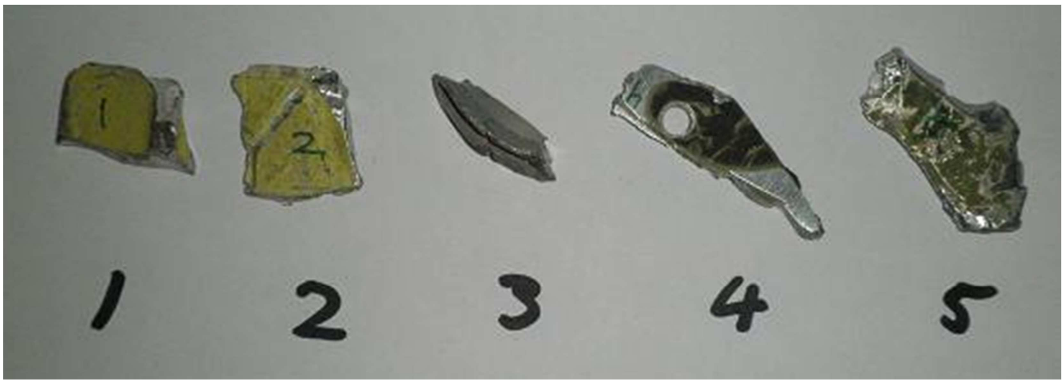


Figure 4.0: The 5 XRF-tested pieces of scrap.

Figure 4.0 shows the 5 pieces of scrap on which an XRF analysis has been done. The results of the XRF analysis are shown in table 4.1. The ratios of the alloying metals to Al are shown in table 4.2.

Sample #	*1*	*2*	*3*	*4*	*5*	*Average*	*Std. dev.*
Al	89,69 %	89,98 %	95,63 %	89,22 %	90,70 %	91,04 %	2,62 %
Zn	5,70 %	5,67 %	0,0891 %	5,84 %	5,44 %	4,55 %	2,50 %
Cu	1,61 %	2,07 %	0,353 %	2,00 %	1,45 %	1,50 %	0,69 %
Mg	2,15 %	1,91 %	0,747 %	2,11 %	1,96 %	1,78 %	0,58 %
Si	<0,005 %	<0,005 %	1,16 %	0,078 %	<0,005%	0,25%	0,51 %

Table 4.1: XRF analysis results for 5 scrap pieces.

Sample #	*1*	*2*	*3*	*4*	*5*	*Average*	*Std. dev.*
Zn/Al ratio	6,36 %	6,30 %	0,09 %	6,55 %	6,00 %	5,06 %	2,78 %
Mg/Al ratio	1,80 %	2,30 %	0,37 %	2,24 %	1,60 %	1,66 %	0,78 %
Cu/Al ratio	2,40 %	2,12 %	0,78 %	2,36 %	2,16 %	1,97 %	0,67 %

Table 4.2: Element ratios with respect to Al.

The average zinc content from these samples is 4,55 %. Because of the high standard deviation, this can vary greatly from sample to sample. The major outlier is sample number 3, which has a much higher Al-content than the other samples, and has a negligible zinc content. All other samples are suspected to be of the 7000-series Al-alloy. Sample 3 contains relatively more silicon. Also the shape of sample 3 is different; it is a part of a ring structure while the other pieces presumably are parts of the plate work. However, the major part of the scrap consists of the plate work aluminium. Therefore it is more realistic to give an estimation of the zinc content of around 5,5 %, slightly higher than the average from samples 1, 2, 4 and 5.

4.1 Effects of coating

4.1.1 Weight of the coating

To calculate the amount of coating on the aircraft scrap, de-coating tests on 3 different weights of scrap were done at 480˚C for 2 hours. The medium sized test (~200 g scrap) is also split into oxidation of the coating, sieving and washing of the scrap.

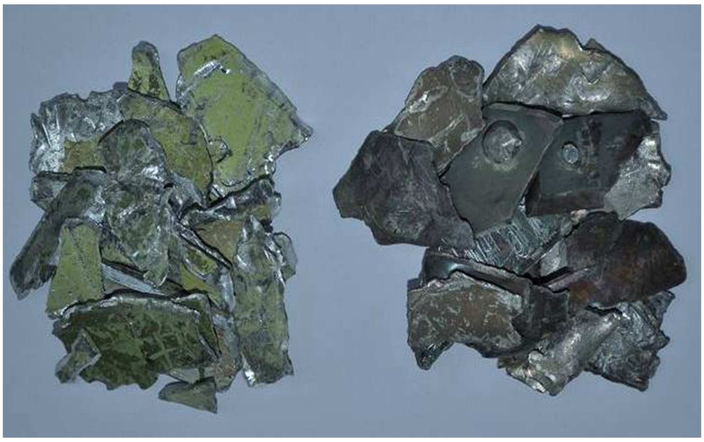


Figure 4.1: The fresh scrap (left) and de-coated scrap (right).

Small scale de-coating test

The weight difference after de-coating is regarded to be the weight of the coating. For the small scale test the results are shown in table 4.3. The coating is approximately 1,6% of the mass of the scrap.

	Small scale	**Medium scale**	**Large scale**
Initial weight:	27,77 g	200,51 g	1065,43 g
Weight after de-coating	27,32 g	198,27 g	1048,63 g
Weight of (coating) loss	0,45 g	2,24 g	16,8 g
Weight loss %	1,62 %	1,12 %	1,58 %

Table 4.3: De-coating results for the 3 sizes of tests.

Medium scale de-coating test

For the medium scale test, also the weight loss to gases during thermal treatment in the furnace is calculated. This is purely the weight before and after the oxidation process, so including the coating. The results are shown in table 4.4, and in table 4.3 for comparison to the other 2 tests.

	Initial weight	**Weight after**	**Weight loss**	**Weight loss %**
Oxidation in furnace	200,51 g	199,39 g	1,12 g	0,56 %
Sieving of scrap	199,39 g	198,52 g	0,87 g	0,43 %
Water washing	198,52 g	198,27 g	0,25 g	0,13 %
Total	200,51 g	198,27 g	2,24 g	1,12 %

Table 4.4: Different stages in the de-coating process of the medium scale test.

After the oxidation, the coating that freely releases from the scrap is sieved out by shaking the sieve. The powder from the sieving is shown in figure 4.2. The weight loss from sieving the scrap after oxidation is also shown in table 4.3. Next, the scrap is washed with water to remove the remainder of the coating from the scrap. Figure 4.3 shows the green-colored water after washing of the scrap.

Figure 4.2: Powder from sieving the de-coated scrap.

The weight loss to gases is already relatively large. This means a substantial part of the coating consists as organic material. The coating loss in the water washing step is a lot smaller than the loss from sieving the scrap after the de-coating process. The waste water contains no solid particles that are visible with the eye, and the remaining coating has dissolved in the water. The total weight loss in the de-coating process is 1,12 %, including the gas loss, losses in sieving and in water washing.

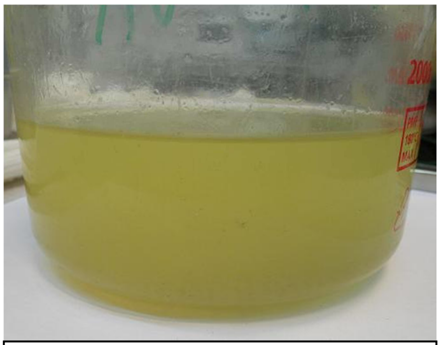


Figure 4.3: Water after washing the de-coated scrap.

Large scale de-coating test

In section 3.4, a larger amount of scrap is de-coated, the same way as in the small scale de-coating test. In the furnace a part of the coating was released from the scrap, the rest was removed by water washing. The results are shown in table 4.3.

The de-coating process on a larger scale has approximately the same weight loss as the small scale de-coating test. The reason why the medium scale test gave a different result is unclear. It is possible that the weight ratios of coating to the aluminum alloy in the scrap are different, and coating in the selected scrap for medium scale experiment has a lower weight ratio.

4.1.2 Melting tests with not de-coated and de-coated scrap on a small scale

Two melting tests on a small scale were executed, one with not de-coated scrap and one with de-coated scrap. The results are shown below in figures 4.4 and 4.5. The objective is to remove the contaminants and inclusions from the melt and form a good coalescent alloy with less entrapped salts.

Figure 4.4: Experiment A1, not de-coated scrap with a salts-to-alloy ratio of 2:1, in crucible after melting (left), obtained alloy (middle) and non metallic contaminants

Figure 4.5: Experiment A2, de-coated scrap with a salts-to-alloy ratio of 2:1, in crucible after melting (left), obtained alloy (middle) and non metallic contaminants (right).

On the bottom of the crucible the Al-alloy formed several beads in test A1, and one large bead in test A2. On top of the alloy was the salt slag with non metallic inclusions (NMI's). The salts are removed by leaching with hot water, and the non metallic inclusions and Al-alloy are separated manually by picking out the alloy beads. The weight of the alloy is measured to calculate the yield, shown in table 4.5. The NMI's are dried and prepared for XRD analysis.

Experiment	**De-coated: yes/no**	**Salts-to-alloy ratio**	**Initial weight of metal**	**Weight after melting**	**Yield**
A1	No	2:1	20,64 g	20,02 g	97,0 %
A2	Yes	2:1	27,38 g	27,09 g	98,9 %

Table 4.5: Yields for experiments A1 and A2.

From the pictures it is clear that the coalescence of Al droplets is much better when the de-coated scrap were used. The recycled Al alloy with not de-coated scrap is consists of about 11 metal beads, while the recycled Al alloy with de-coated scrap consists of 1 major metal bead. In practice, coalescence is very important for the recovery of alloy from the melting process. A bad coalescence will result in a bad recovery, because the small size metal beads will be harder to separately from the salts slag, moreover, more oxides are generated due to the increased specific surface area of metal beads. The non metallic inclusions from the not de-coated scrap contain more black particles, which is an indication that the slag includes more contaminants.

The yield in experiment A2 is almost 2% higher than in A1. A higher yield for experiment A2 was expected, because the weight of the coating, which is approximately 1,6%, has already been removed.

The XRF analysis on the Al-alloy gave the results shown in table 4.6 below.

	Test A1	**Test A2**	**Test A1**	**Test A2**
Element	**Content in wt%**	**Content in wt%**	**Me/Al ratio**	**Me/Al ratio**
Al	92,33	91,21	-	
Zn	4,66	3,28	5,05 %	3,60 %
Mg	<0,005	0,259	0 %	0,3 %
Cu	2,28	2,53	2,47 %	2,71 %

Table 4.6: XRF analysis results for tests A1 and A2

The content of zinc in test A2 is 1,38 % lower than in test A1. Xiao et al. [12] observed that the viscosity of slag is increased with the increase of non metallic contaminants. The higher viscosity decreases the ability of the alloy to flow, and this results in an inability of the zinc to be transported to the top of the melt, where it can evaporate. This way the de-coating process, which led to a much better coalescence, not only turned out to be important for the recovery rate in the melting process, it also improved the ability of evaporation for zinc during the melting process. It is clear that the low magnesium content in both cases is a result of its reaction with cryolite.

The XRD analysis on the non metallic inclusions shows the presence of mainly K_2NaAlF_6 and $(K,Na)MgF_3$. The presence of K_2NaAlF_6 is the result of exchange of elements between the salt flux of $NaCl\text{-}KCl\text{-}Na_3AlF_6$. Also MgF_2 is detected, which is a residue on the crucible wall from previous experiments. The next page shows the results of the XRD analysis in figure 4.6 for test A1 and figure 4.7 for test A2 on the non metallic inclusions.

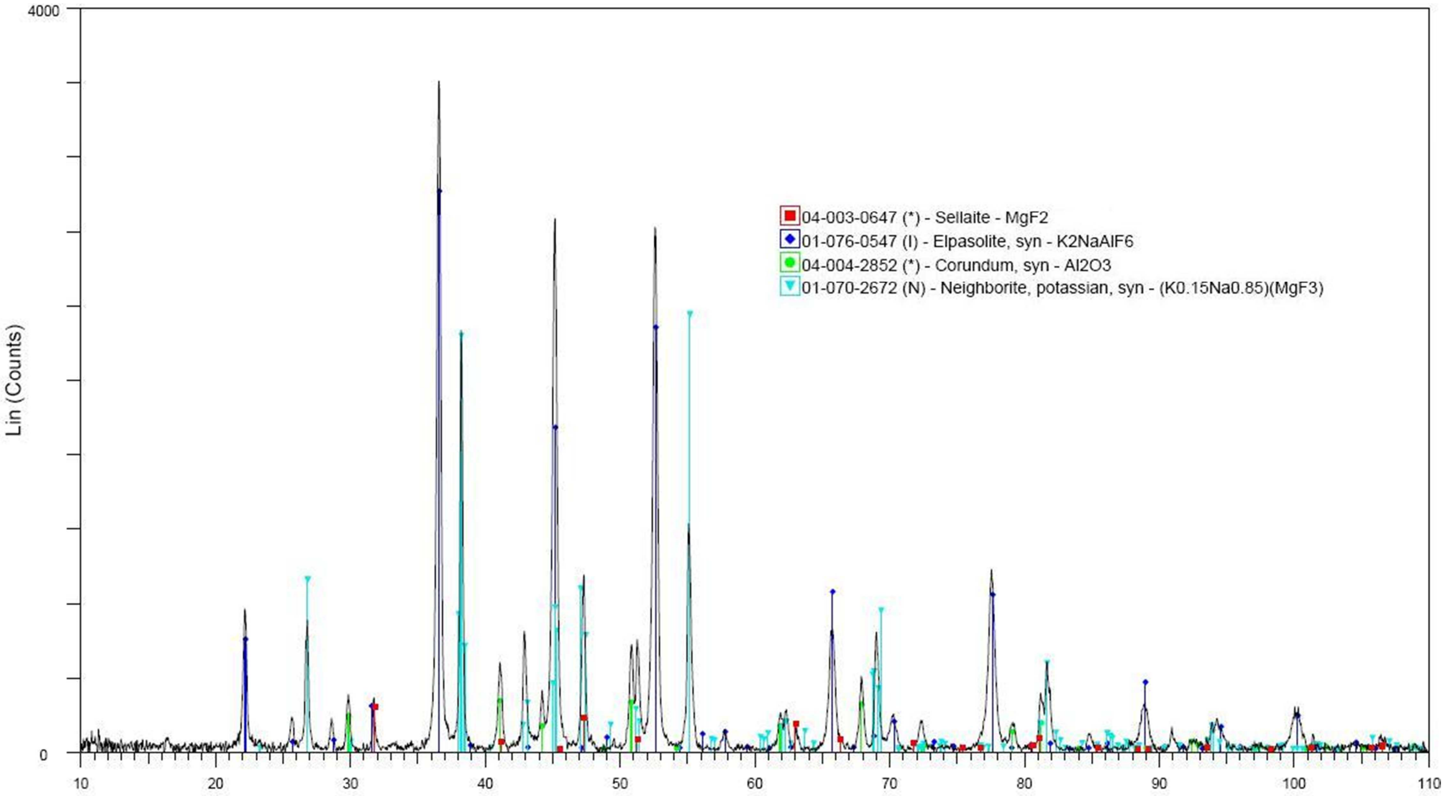


Figure 4.6: XRD analysis results on the non metallic inclusions of experiment A1.

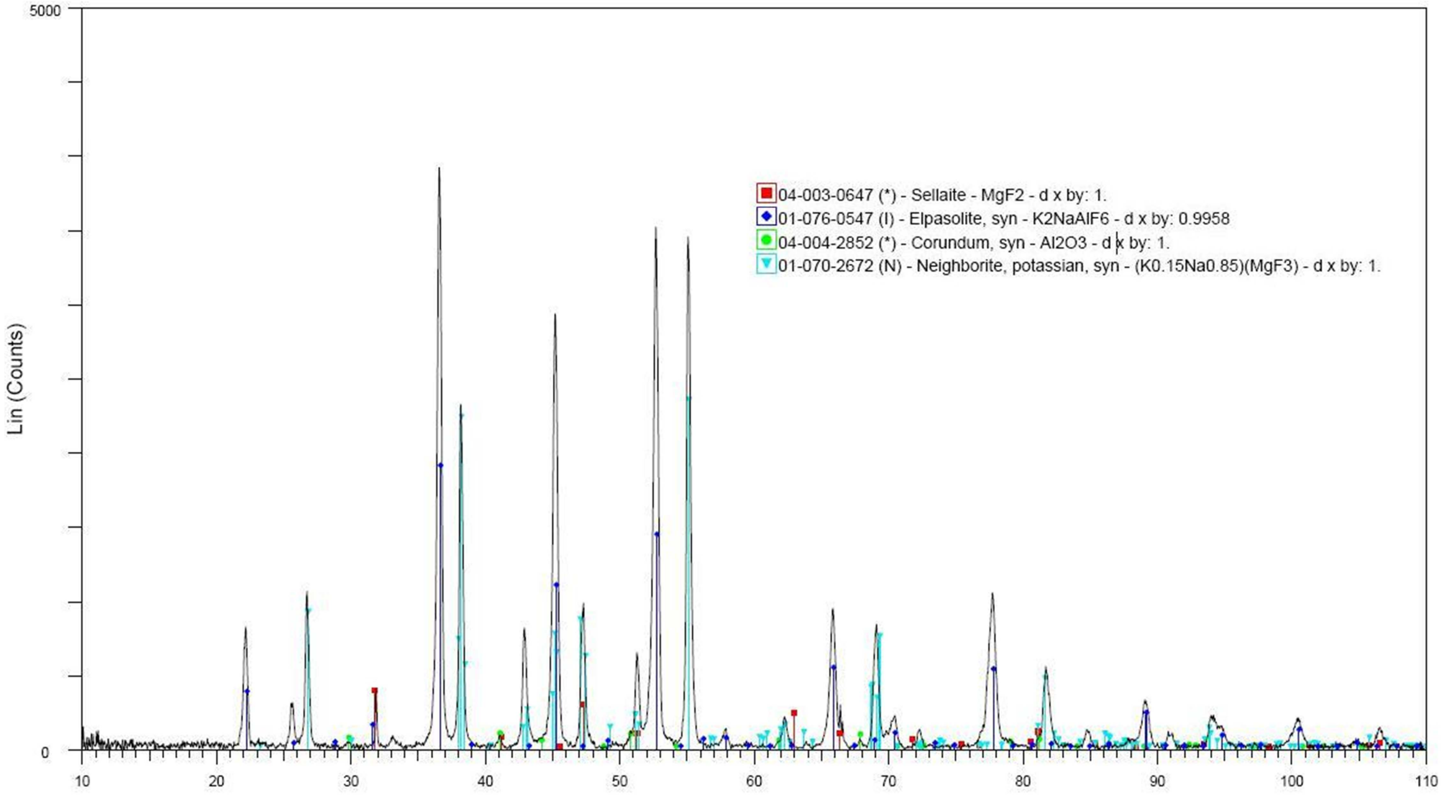


Figure 4.7: XRD analysis results on the non metallic inclusions of experiment A2.

4.1.3 Melting tests with not de-coated scrap on a larger scale

After a large amount of not de-coated scrap was melted at a holding temperature of 860 ˚C for 4 hours, the alloy and the salt were removed from the crucible. The alloy was stuck on the bottom of the crucible, which had to be broken to remove the alloy (figure 4.8). The results are shown in table 4.7. The initial crucible weight was 2357 g.

Experiment A3	**Total weight (inc. crucible)**	**Weight of the metal (scrap)**	**Weight of the salt flux**
Before melting	4290 g	700,38 g	1232,51 g
After melting	4270 g	658,70 g	740,00 g
Difference	*- 20 g*	*- 41,68 g (94,0% yield)*	*- 492,51 g*

Table 4.7: Weights before and after melting.

A large mass of alloy has been formed in the bottom of the crucible (figure 4.8). The salt contained a couple dozens of small alloy particles with diameters of several millimeters each. A part of these particles are shown in figure 4.11. The top surface of the obtained alloy piece was very clean, as shown in figure 4.9. Adversely, the sides and the bottom surface contained large black spots, which look like a remainder of the coating (figure 4.10). Even the green color of the coating can be recognized on the bottom side of the alloy. Due to evaporation, at least 20 g of the salt flux has been lost in the melting process. However, the weight loss within the salt flux (almost 0,5 kg) is much larger than the total weight loss. A part of the salt slag was captured as inclusions in the alloy, the major part is stuck on the wall of the crucible.

Figure 4.8: Mass of alloy in the bottom of the crucible.

Figure 4.9: Top surface of the recovered metal alloy.

Figure 4.10: Bottom side of the recovered metal alloy.

Figure 4.11: The small alloy particles from within the salt flux.

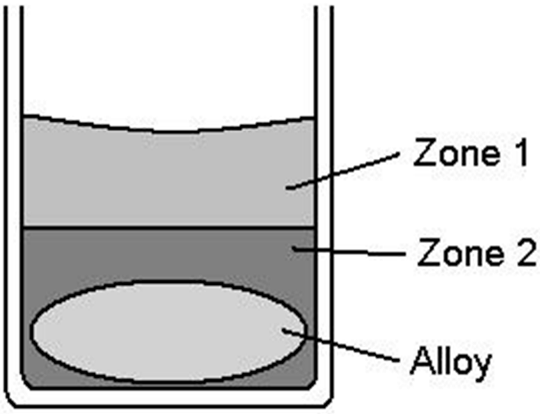
Upon cutting the alloy, the inside shows black inclusions within the alloy (figure 4.12, left). Presumably these are parts of the slag that ended up trapped in the metal.

Figure 4.12:
Left: Inside of the alloy with black inclusions.
Right: Black contaminations of the sides of the alloy from the not de-coated scrap.

Figure 4.13: Salt slag after melting of not de-coated scrap.

The salt slag had a prominent dark grey color (figure 4.13). After the melting process, the salt flux contains non metallic inclusions (NMI's). By washing the salt flux with hot water, the salts dissolve into water and the NMI's are filtered out. A part of the salt slag also was stuck on the crucible wall, which made it hard to recover. This explains the large weight loss of salt flux, while there is only a small total weight change.

The salt slag seemed to have formed 2 layers within the crucible, in which the lower part was dirtier (figure 4.14). The lower zone (zone 2) was very dark compared to the upper zone (zone 1), and contained small alloy drops.



In practice the furnaces are stirred, so this phenomenon will not occur.

Figure 4.14: Illustration of a cross-section of the crucible.

The XRF analysis results for test A3 are shown in table 4.8:

Test A3		
Element	**Content in wt%**	**Me/Al ratio**
Al	92,82	-
Zn	2,74	2,95 %
Mg	0,071	0,076%
Cu	3,38	3.64 %

Table 4.8: XRF results for test A3.

Although the results of the melting test are poor, the zinc content has reduced with a fair amount from around 5,5 % in the scrap to 2,74 %. The melting of de-coated scrap in the next section will give a comparison to this result, since the test on small scale resulted into a lower zinc content for de-coated scrap.

Also up scaling of the melting process shows to improve the removal of zinc, since the small scale test with not de-coated scrap resulted into a zinc content of 4,66 %, whereas test A3 results into a zinc content of 2,95 %.

4.1.4 Melting tests with de-coated scrap on a larger scale

Experiments A4 and A5


Figure 4.15: Obtained metals after melting experiments A4 and A5.

The initial goal of melting tests A4 and A5 was to obtain a suitable alloy for the argon blowing tests. However, the total amount of alloy was not sufficient and the 2 resulting pieces of alloy did not have a uniform composition, which was desirable. After the melting tests A4 and A5 of de-coated scrap, a large piece of alloy has formed in the bottom of each crucible. Both alloys are shown in figure 4.15. The surfaces of the alloys is dark colored, which is an indication that oxides have formed on the surface.

By weighting the two metal pieces the yield is calculated as shown in table 4.9.

Experiment	**Initial weight**	**Resulting weight**	**Yield**
A4	250,24 g	245,96 g	98,29 %
A5	250,63 g	246,75 g	98,45 %

Table 4.9: Yield of melting experiments A4 and A5.

The XRF analysis results for these tests are shown in table 4.10:

	Test A4	**Test A5**	**Test A4**	**Test A5**
Element	**Content in wt%**	**Content in wt%**	**Me/Al ratio**	**Me/Al ratio**
Al	90,34	92,17	-	-
Zn	2,77	2,41	3,07 %	2,61 %
Mg	<0,005	<0,005	0 %	0 %
Na	1,18	0,637	1,31 %	0,69 %
Cl	1,00	0,254	1,11 %	0,28 %
K	0,618	0,370	0,68 %	0,40 %
Cu	3,05	2,95	3,38 %	3,20 %

Table 4.10: XRF analysis results for experiments A4 and A5.

The XRF analysis results show zinc contents of 2,77 % for test A4 and 2,41 % for test A5. Assuming that the initial zinc content in the scrap was around 5,5 %, the zinc contents were decreased by 2,73 and 3,09 % respectively, resulting in zinc removal efficiencies of 49,6 % and 56,2 %. Also the cryolite caused the magnesium to be removed from the alloy. Furthermore the concentrations of Na, K and Cl are relatively high. These are remainders of the NaCl-KCl salt flux and were trapped as inclusions in the metal.

Experiment A6

In experiment A6 de-coated scrap and relatively clean alloy from experiments A4 and A5 is melted to form a suitable alloy for the argon blowing tests (section 4.4), which was not managed in tests A4 and A5. A weight balance for the melting test of de-coated scrap is given in table 4.11:

Experiment A6	Weight of the metal (scrap)	Weight of the salt flux
Before melting	864,77 g	864,7 g
After melting	848,18 g	783,62
Metal yield	98,08 %	

Table 4.11: Weights before and after melting.

Figure 4.16 shows the metal alloy obtained from experiment A6. The surface of this alloy is clearly cleaner than the alloy from the melting test with not de-coated scrap (figure 4.10), and also cleaning than the surfaces of alloys A4 and A5 (figure 4.15), which were black from oxidation. Furthermore, there are no small alloy beads like in experiment A3, i.e. the coalescence is better.

Figure 4.16: Alloy from experiment A6.

Figure 4.17: Salt slag after experiment A6.

As expected the salt slag from experiment A6 is much cleaner than the slag from experiment A3. Figure 4.18 shows both salt slags next to each other.

The results of the XRF analysis on the master alloy from test A6 are shown in table 4.12.

Figure 4.18: Salt slags from experiments A3 for not de-coated alloy (left) and A6 for de-coated alloy (right).

Experiment A6		
Element	**Content in wt%**	**Me/Al ratio**
Al	93,19	-
Zn	2,42	2,60 %
Mg	0,133	0,143 %
Cu	2,71	2,91 %
Si	0,331	0,355 %

Table 4.12: XRF analysis results for experiment A6.

The zinc content in the master alloy from test A6 is 2,42 %. Taking into account that the initial zinc content was around 4,44 % as shown in section 3.2.4, this means that the zinc content is already reduced by around 45 %, just by the melting process.

The melting test with not de-coated scrap (A3) resulted into a final zinc content of 2,95 %, compared to 2,42 % for the test with de-coated scrap. As concluded in section 4.1.2, the presence of non metallic inclusions leads to a higher viscosity in the melt, which counteracts the flow of zinc to the top of the melt. However, test A3 was done with scrap and no pre-melted alloy like in test A6, so the initial zinc content was higher. Also the holding time of this test was longer, which normally leads to a lower final zinc content. Therefore it is not meaningful to directly compare these tests.

4.2 Effects of MgF_2 versus Na_3AlF_6 in melting tests

The following tests were done to study the effects of MgF_2 as an additive to the salt flux instead of the more common cryolite. The use of MgF_2 will keep Mg in the alloy melt, in case this is desirable. The tests were done with not de-coated scrap at 800 ˚C for 3 hours. After the melting tests B1 (with MgF_2) and B2 (with cryolite), the following results were obtained as shown in figures 4.19 and 4.20. The salts were leached with hot water and the alloy was separated manually from the non metallic inclusions. The NMI's were dried and prepared for XRD analysis.

Figure 4.19: Experiment B1: salts-to-alloy ratio 2:1 with 10% MgF_2 in crucible after melting (left), obtained alloy (middle) and non metallic inclusions (right).

Figure 4.20: Experiment B2: salts-to-alloy ratio 2:1 with 10% Na_3AlF_6 in crucible after melting (left), obtained alloy (middle) and non metallic inclusions (right).

After melting scrap with KCl-NaCl-MgF_2 flux the obtained non metallic inclusions and alloy particles had a prominent dark color. The recycled Al alloy were very irregularly shaped, and had formed several small pieces.

In both cases the coalescence of alloy is poor, probably due to the use of not de-coated scrap. Though, the test with cryolite seems more promising. The Al-alloy pieces from experiment B1 have a very irregular shape and are fragile, while the alloy from B2 is round shaped. The surface of the grains is very dark in B1, which could mean that the surface is covered with oxides. Also the non metallic inclusions from test B1 are much darker, and the separation of alloy and slag does not look good. From this point it is clear that the coalescence is better when cryolite is used, regarding the round particles obtained in test B2. The results from the XRF analysis are shown in table 4.13:

	Test B1	**Test B2**	**Test B1**	**Test B2**
Element	**Content in wt%**	**Content in wt%**	**Me/Al ratio**	**Me/Al ratio**
Al	87,11	92,33	-	-
Zn	6,19	4,66	7,10 %	5,05 %
Mg	2,64	<0,005	3,03 %	0 %
Cu	2,22	2,28	2,55 %	2,47 %

Table 4.13: XRF analysis results for tests B1 and B2.

As expected the cryolite removes Mg from the melt, regarding the Mg/Al ratios for both tests. In test B1 the Mg/Zn ratio is 3,03 %, while in test B2 the magnesium content is negligible. Comparison between the XRD analysis results (figures 4.21 and 4.22) of both tests also shows that cryolite removes the Mg from the melt. The XRD analysis shows high quantities of MgF_2 and some MgO in the non metallic contaminants from test B1, while test B2 has MgF_2 in the non metallic contaminants as a residue in the crucible from earlier experiments.

Experiment	**De-coated: yes/no**	**Salts-to-alloy ratio**	**Initial weight**	**Weight after melting**	**Yield**
B1	No	2:1	20,51 g	20,22 g	98,6 %
B2	No	2:1	20,64 g	20,02 g	97,0 %

Table 4.14: Yields for experiments B1 and B2.

The metal yields of experiments B1 and B2 are shown in table 4.14. The yield in experiment B1 is higher than the yield in experiment B2. However, table 4.13 shows that the weight percentage aluminium in test B1 is about 5% lower. The higher metal yield does not have value if the amount of valuable product is low, and the contamination (zinc) remains.

During the melting process, a part of the relatively volatile Zn will evaporate. The addition of cryolite or MgF_2 increases the viscosity of the salt flux, because these salts both have high melting points (respectively 1020 °C and 1263 °C [6]) compared to equimolar NaCl and KCl. The hypothesis is that because of the higher viscosity of a melt with MgF_2, it will be harder for zinc to move to the surface of the melt, where it can evaporate. Also oxide layers can prevent the evaporation of zinc. This leads to a higher final zinc content for test B1.
The much lower aluminium content in test B1 is probably a result of oxidation.

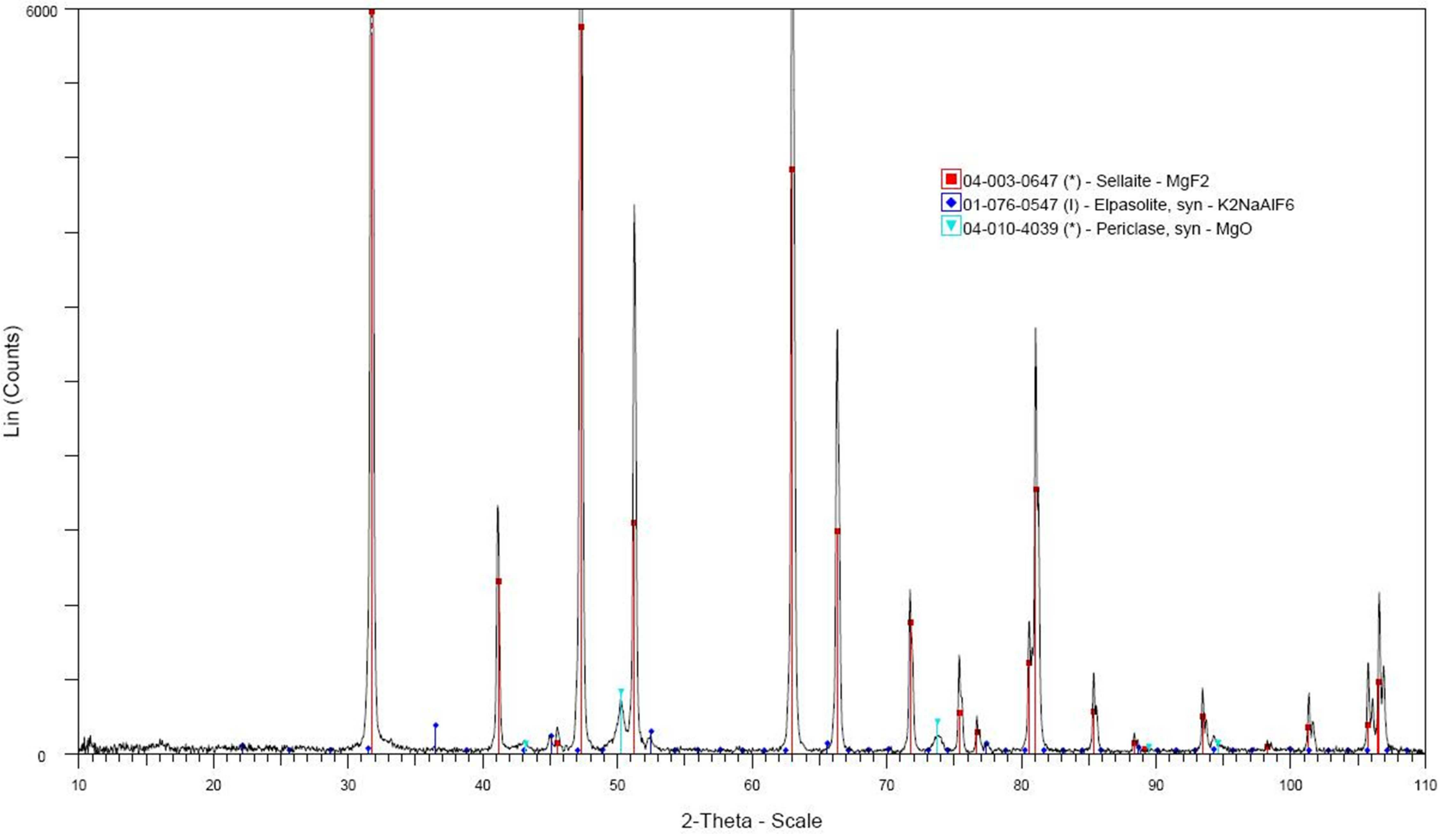


Figure 4.21: XRD analysis results of the non metallic inclusions for experiment B1.

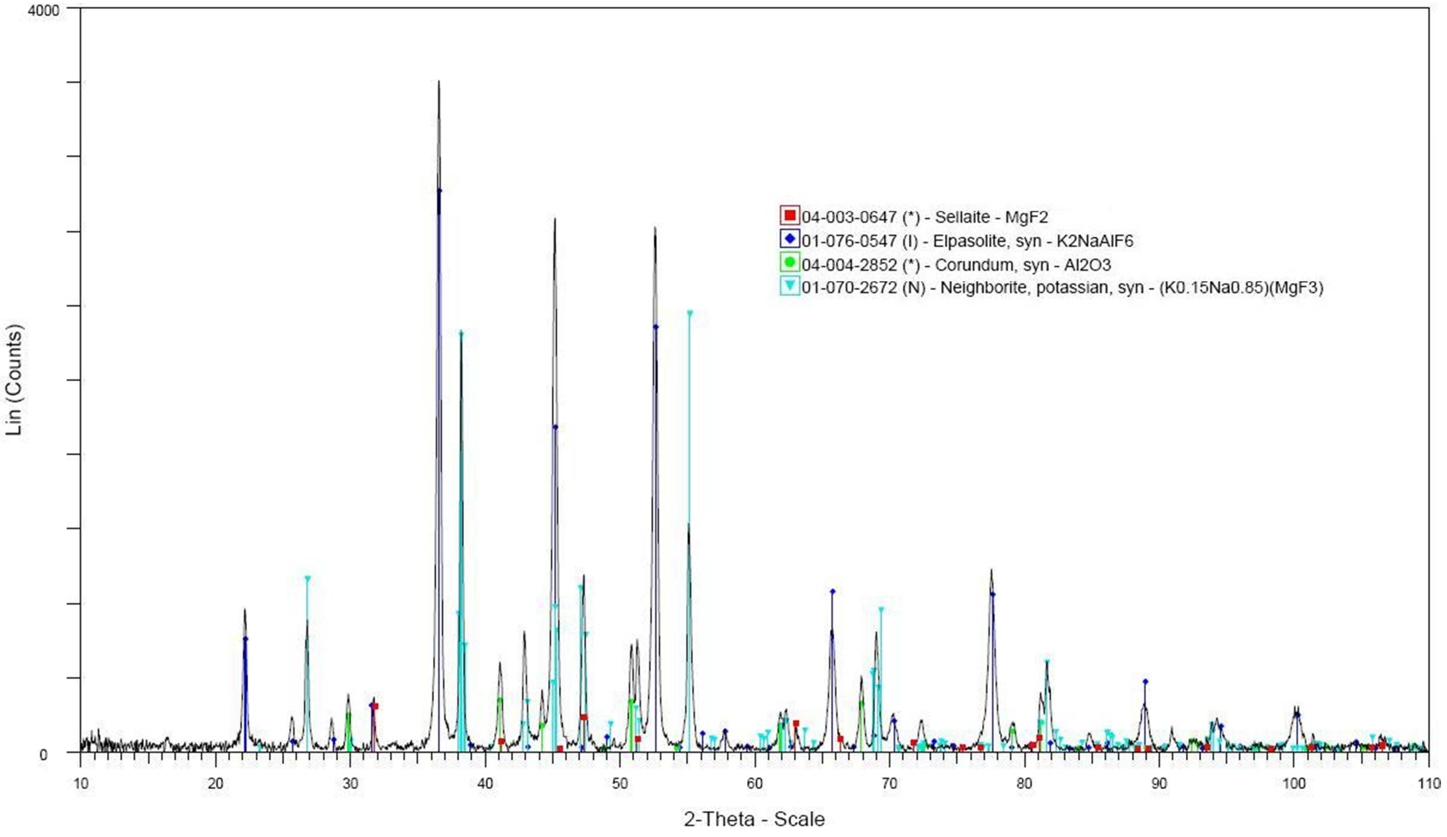


Figure 4.22: XRD analysis results of the non metallic inclusions for experiment B2.

4.3 Effects of a variable salts-to-alloy ratio in melting tests

The following tests are done to study the effects of the amount of salt used in the melting process. The first two tests (C1 and C2) are done with MgF_2 as additive to the salt flux, the second two (C3 and C4) with cryolite as additive.

4.3.1 Melting with MgF_2

The tests are done on not de-coated scrap on 800 ˚C for 3 hours. The scale of the tests is relatively small, with around 20 g of scrap per test. After melting the salts are leached with hot water and the NMI's dried for XRD analysis. In figures 4.23 and 4.24 below the results of scrap melting with an addition of 10% MgF_2 are shown.

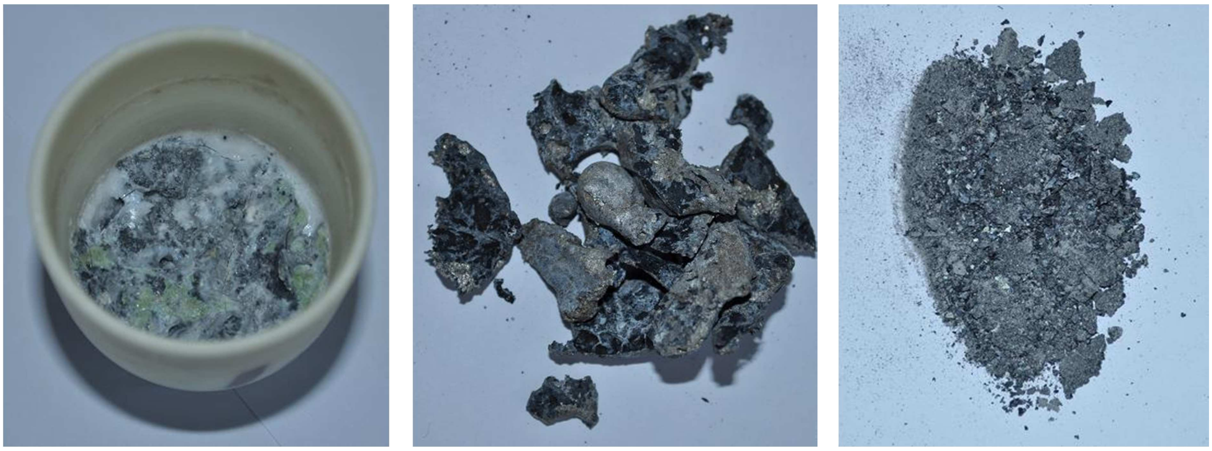


Figure 4.23: Experiment C1: salts-to-alloy ratio 1:1 with MgF_2 in crucible after melting (left), obtained alloy (middle) and non metallic contaminants (right).

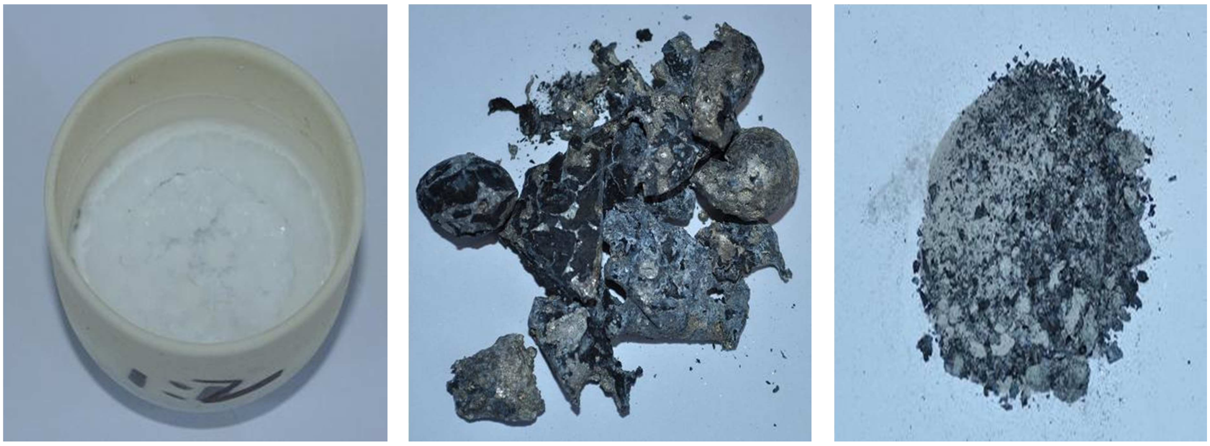


Figure 4.24: Experiment C2: salts-to-alloy ratio 2:1 with MgF_2 in crucible after melting (left), obtained alloy (middle) and non metallic contaminants (right).

On the first look there are not many differences between the two alloys, as shown in figure 4.25. A closer look shows that the alloy particles in C1 are smaller and more irregularly shaped than the ones in C2. Also the non metallic contaminants are darker for C1.

Figure 4.25: The aluminium alloy particles from experiment C1 (right) and C2 (left) with a scale.

The results from the XRF analysis for the recovered alloys of tests C1 and C2 are shown in table 4.15.

	Test C1	**Test C2**	**Test C1**	**Test C2**
Element	**Content in wt%**	**Me/Al ratio**	**Content in wt%**	**Me/Al ratio**
Al	91,05	-	87,11	-
Zn	5,54	6,08 %	6,19	7,10 %
Mg	0,970	1,07 %	2,64	3,03 %
Cu	1,99	2,19 %	2,22	2,55 %

Table 4.15: XRF analysis results for tests C1 and C2.

Since test C2 had a higher Zn/Al ratio than test C1, in this case the addition of more salts does not result in a better removal of contaminants. The thicker salt layer possibly even counteracted the flow of zinc to the top of the melt, reducing the evaporation of zinc. Since the initial zinc content was around 5,5 %, practically no zinc was removed from the melt. Also the coalescence of the alloy and the separation of slag and alloy did not improve with the use of more salts.

The XRD analysis in figures 4.26 and 4.27 show the presence of mainly MgF_2 in the non metallic contaminants, and smaller amounts of K_2NaAlF_6 and MgO. The presence of MgF_2 was expected, since this salt does not react with any impurities. K_2NaAlF_6 must be a residue of previous tests in the crucible, since no cryolite was added in this test and therefore it can not be the result of metal ion exchange.

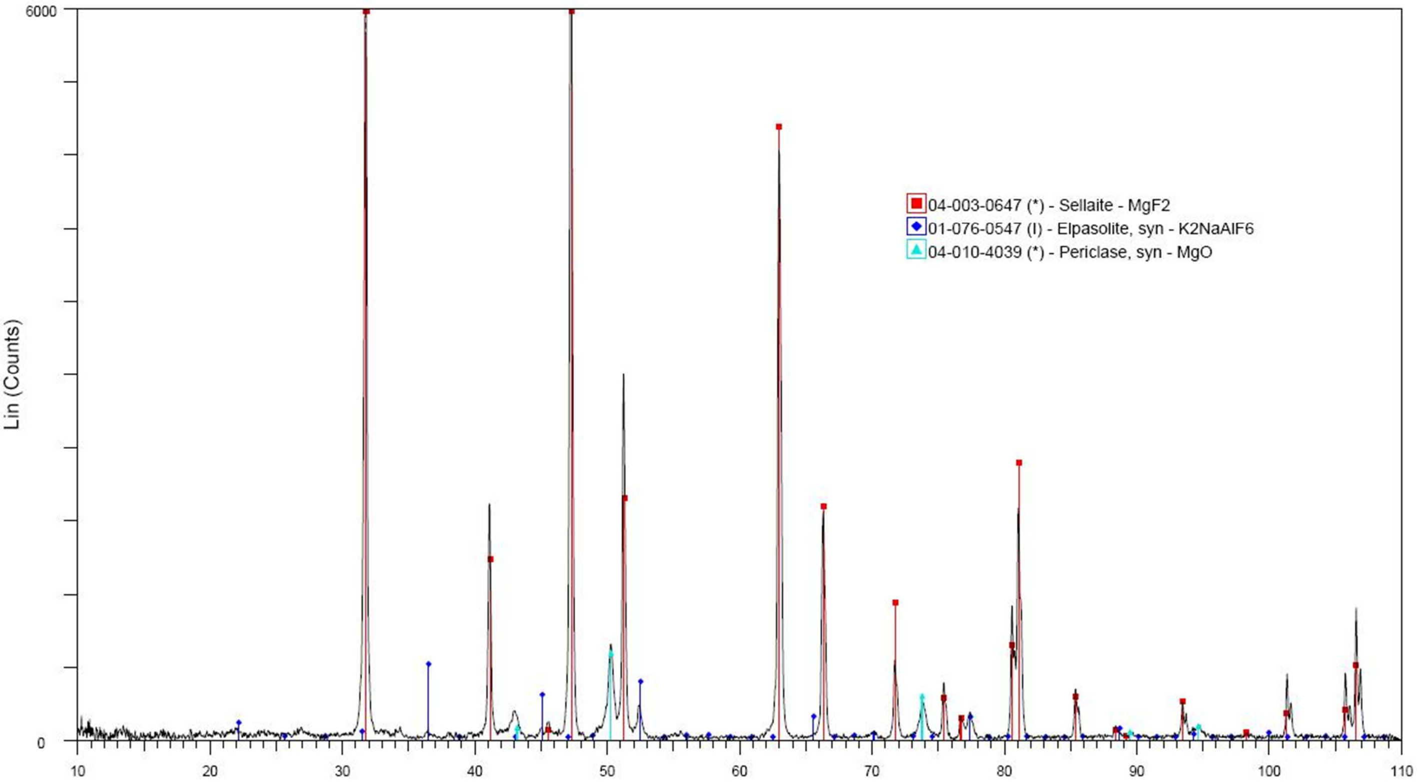


Figure 4.26: XRD analysis results on the non metallic inclusions for experiment C1.

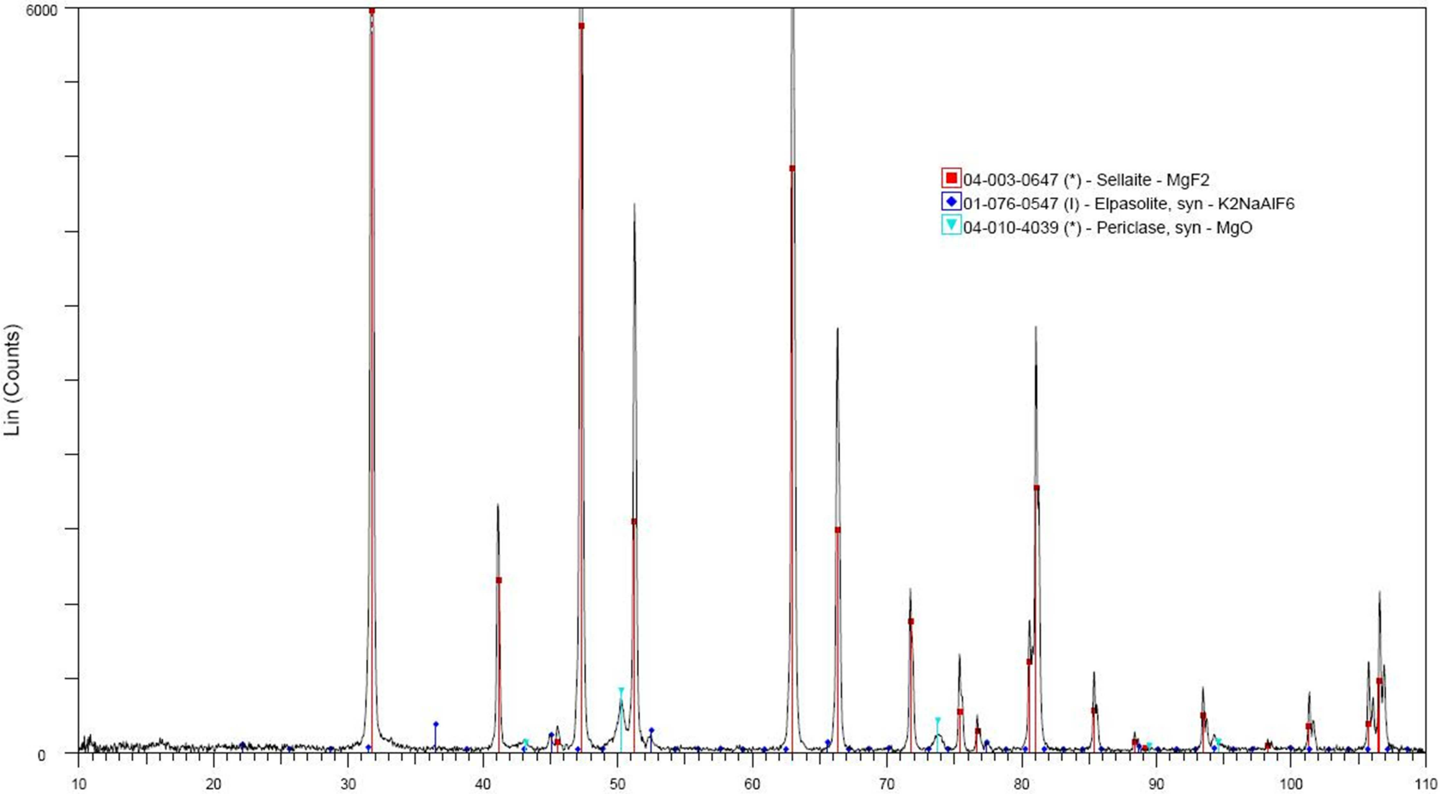


Figure 4.27: XRD analysis results on the non metallic inclusions for experiment C2.

4.3.2: Melting with Na_3AlF_6

The tests are done on not de-coated scrap on 800 ˚C for 3 hours. The scale of the tests is relatively small, with around 20 g of scrap per test. After melting the salts are leached with hot water and the NMI's dried for XRD analysis. In figures 4.28 and 4.29 below the results of scrap melting with an addition of 10% Na_3AlF_6 are shown.

Figure 4.28: Experiment C3: salts-to-alloy ratio of 1:1 and 10%Na_3AlF_6 in crucible after melting (left), obtained alloy (middle) and slag (right).

Figure 4.29: Experiment C4: salts-to-alloy ratio 2:1 and 10%Na_3AlF_6 in crucible after melting (left), obtained alloy (middle) and slag (right).

Experiment C3 produced a large amount of small beads, while in experiment C4 the number of beads was smaller and the bead sizes were larger. This is a logical result of the smaller amount cryolite used in experiment C3, since cryolite improves the cohesion between Al droplets. The alloy beads are shown in figure 4.30.

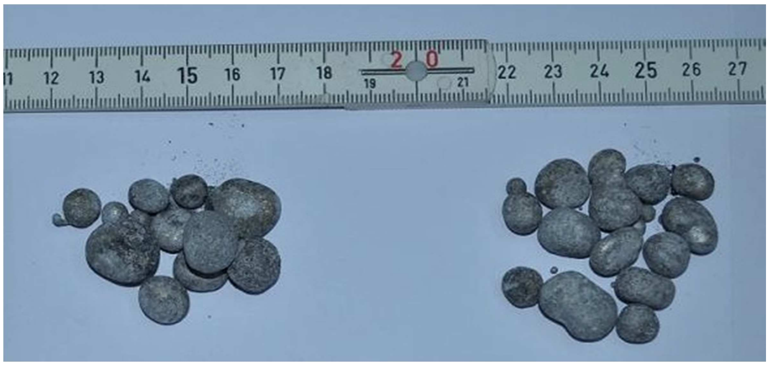


Figure 4.30: The aluminium alloy particles from experiments C3 (right) and C4 (left) with a scale.

The results from the XRF-test are shown below in table 4.16.

	Test C3	**Test C4**	**Test C3**	**Test C4**
Element	**Content in wt%**	**Me/Al ratio**	**Content in wt%**	**Me/Al ratio**
Al	91,83	-	92,33	-
Zn	4,10	4,46 %	4,66	5,05 %
Mg	0,641	0,70 %	<0,005	0 %
Cu	2,59	2,82 %	2,28	2,47 %

Table 4.16: XRF analysis results for tests C3 and C4.

The XRF analysis shows that the use of more cryolite increased the amount of Mg loss in the alloy, as was expected since cryolite reacts with magnesium. Besides this, no other element content seems to deviate. The slightly higher Zn/Al ratio can be explained by the thicker layer of salt, which counteracts the flow of Zn to the top of the melt, thereby reducing evaporation. Table 4.17 shows lower a lower Zn wt% for the two tests with cryolite.

	Test C1	**Test C2**	**Test C3**	**Test C4**
Al wt%	91,05	87,11	91,83	92,33
Zn wt%	5,54	6,19	4,10	4,66

Table 4.17: Summary of Al and Zn weight percentages in recovered metal alloys C1-4.

The results of the XRD analysis are shown in figure 4.31 for test C3 and figure 4.32 for test C4. The XRD shows the presence of K_2NaAlF_6 and $(K,Na)MgF_3$, and in smaller amounts MgF_2 and Al_2O_3 in the non metallic contaminants. The first compound is the result of exchange of elements between the salt flux. $(K,Na)MgF_3$ is a product of the reaction of cryolite with the Mg in the alloy, and MgF_2 is present as a residue on the surface of the crucible.

Table 4.18 shows the yield of the recovered metal from tests C1-4.

Experiment	**De-coated: yes/no**	**Salts-to-alloy ratio**	**Initial weight**	**Weight after melting**	**Yield**
C1	No	1:1	20,51 g	21,71 g	105,9%
C2	No	2:1	20,51 g	20,22 g	98,6 %
C3	No	1:1	20,72 g	20,05 g	96,8 %
C4	No	2:1	20,64 g	20,02 g	97,0 %

Table 4.18: Yields for experiments C1-4.

The yield in experiment C1 clearly is incorrect. The weight of the alloy after the melting process is 5,9% higher than the initial weight. The metal will have reacted with other elements like oxygen to form compounds, causing the extra weight. The separation of slag and alloy is very poor in tests C1 and C2, as also can been seen from the dark color of the alloy. This resulted into the large yield for experiment C1. *Because of the disappointing results for the tests with MgF_2, like bad coalescence and poor slag-alloy separation, all the following tests are performed with the use of cryolite in the salt flux.*

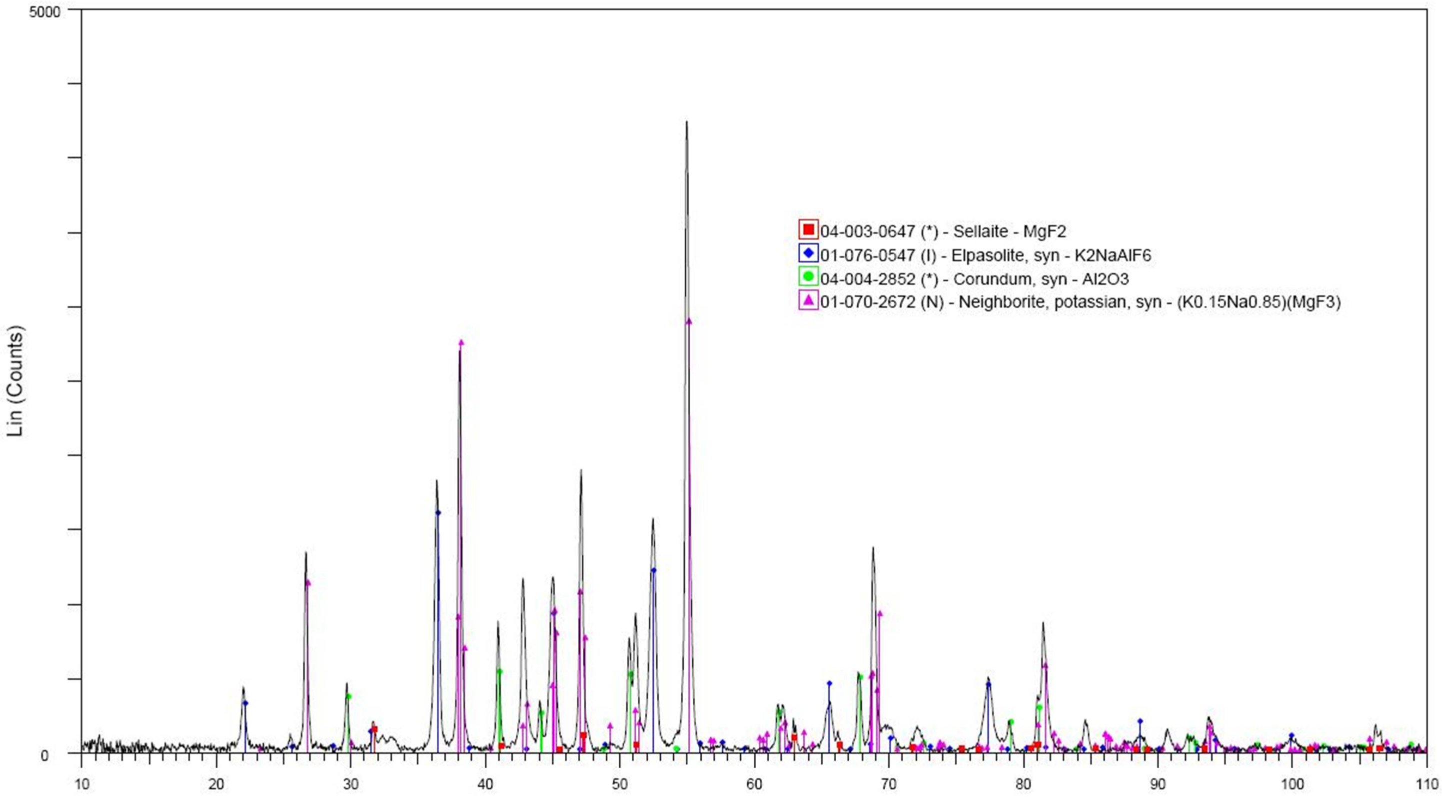


Figure 4.31: XRD analysis results on the non metallic inclusions for experiment C3.

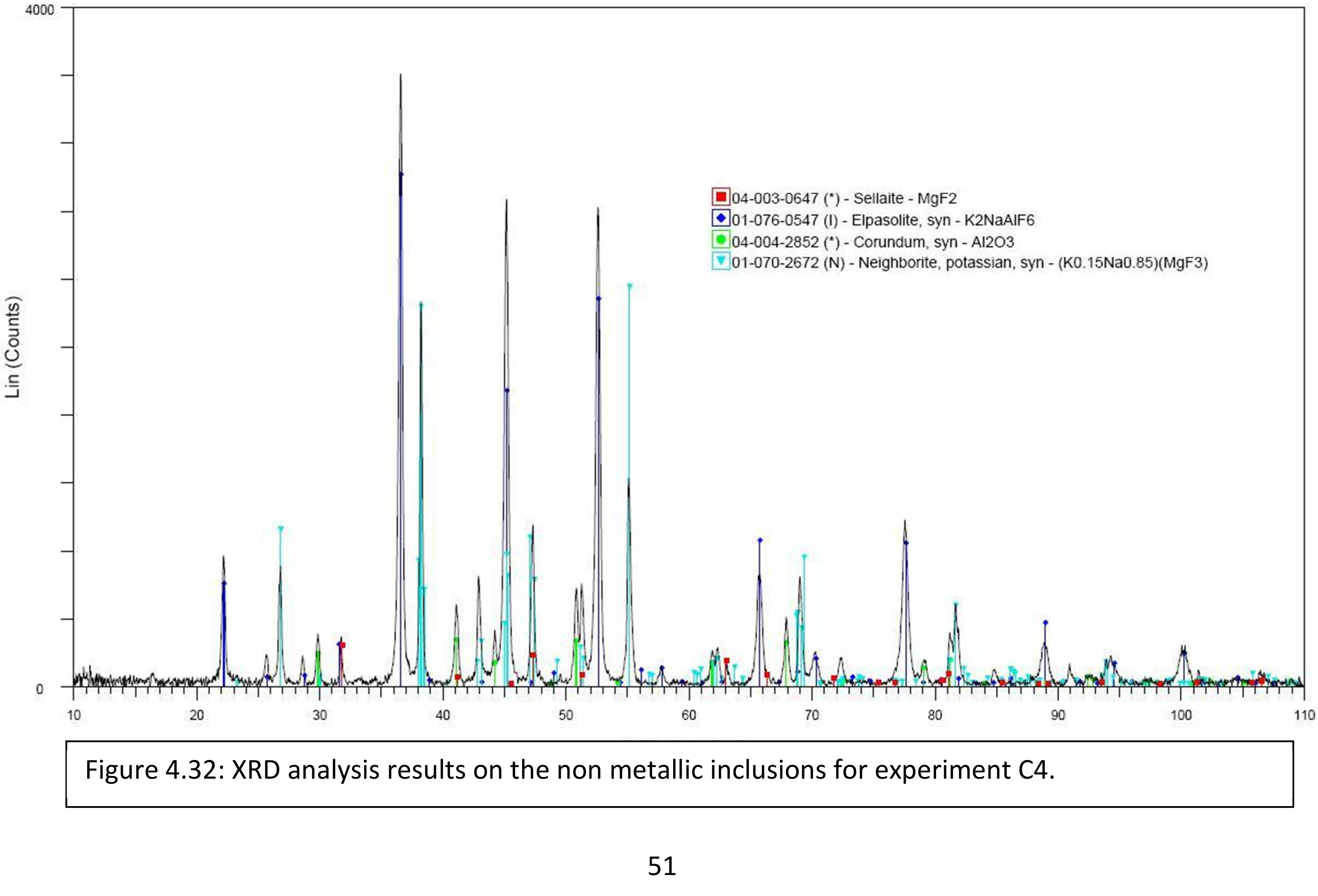


Figure 4.32: XRD analysis results on the non metallic inclusions for experiment C4.

4.4 Zinc-removal by argon gas blowing

The following tests are done to study the effect of argon blowing into the molten Al-alloy for removing zinc. First, the alloy has to be prepared for these tests.

4.4.1 Preparation of the alloy

The alloy from experiments A4 and A6 was polished and sawed into pieces, as explained in section 3.5.1. During the sawing of the metal into small pieces for the argon blowing tests, one of the samples showed a small piece of hard metal (figure 4.33) with a different color than the Al-alloy. This metal piece was only several millimeters wide and presumably is titanium, regarding its color and hardness while sawing. Because of its high melting point (1668 ˚C) the titanium did not dissolve into the melt.

Figure 4.33: Small piece of titanium in the Al-alloy.

4.4.2 Argon blowing tests

Test with master alloy from experiment A4 (preliminary test)

This test was mainly done to test the working of the tube furnace as a preliminary test. After the argon blowing test, the sample shows some oxidation on the top side of the alloy (figure 4.34) This is a logical result, since the argon atmosphere never is fully oxygen-free. The initial zinc content of the alloy from experiment A4 was 2,77 %. Note: this is a preliminary experiment to test the procedure.

Figure 4.34: Sample after test D1.

The weight balance from the test is given in table 4.19.

Experiment	*D1*
Temperature	860 °C
Starting weight	79,82 g
Final weight	79,16 g
Weight difference	- 0,66 g

Table 4.19: Weight balance for test D1.

The XRF analysis results for the alloy before and after the argon blowing test are shown in table 4.20.

	Test A4	**Test D1**
Element	**Content in wt%**	**Content in wt%**
Al	90,34	94,16
Zn	2,77	2,15
Mg	<0,005	0,0650
Na	1,18	0,041
Cl	1,00	0,0144
K	0,618	0,0113
Cu	3,05	2,73

Table 4.20: XRF analysis results for the alloy before and after argon blowing.

The argon blowing test has reduced the zinc content by 0,62 %. The relatively high amounts of Na, K and Cl have been removed. The salts NaCl and KCl were trapped as inclusions in the alloy and have evaporated during re-melting of the alloy for argon blowing.

Test with master alloy from experiment A6

Test D2 with argon blowing into the melt was performed at a temperature of 900 °C. The master alloy for this test origins from experiment A6. This is the first result in the argon blowing test that is significant, since the objective of test D1 mainly was to test the tube furnace. Table 4.21 shows a weight balance for this argon blowing test.

Experiment	*D2*
Temperature	900 °C
Starting weight	81,78 g
Final weight	83,21 g
Weight difference	+ 1,43 g

Table 4.21: Weight balance for test D2.

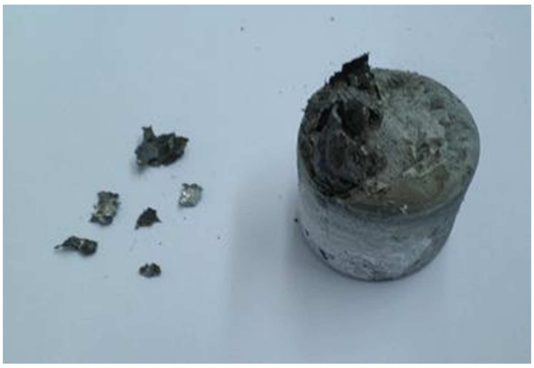


Figure 4.35: Sample after test D2.

These results show that the weight of the sample actually increased, unlike test D1 in which the weight decreased. A possible explanation is the oxidation of the aluminium because of oxygen in the system, as shown in figure 4.35. On top of the melt loose flakes of oxidized metal are visible. The reaction of the metal and oxygen will increase the alloy's weight. The bubbling of argon gas in test D2 may have functioned as a stirring mechanism, promoting the reaction of aluminium with any oxygen that leaked into the system. This is also based on figure 4.35, where irregular shapes, dark colors and loose particles are visible on the top of the sample after argon gas blowing.

The XRF analysis result for experiment D2 is shown in table 4.22.

Test D2		
Element	**Content in wt%**	**Me/Al ratio**
Al	94,12	-
Zn	1,88	2,00 %
Mg	0,113	0,12 %
Cu	2,59	2,75 %
Si	0,208	0,22 %

Table 4.22: XRF analysis results for experiment D2.

The zinc content after test D2 is 1,88 %. Since the initial zinc content was 2,42 %, this means a reduction of the zinc content by 0,54 %. In the next experiment a similar test is done, but without any argon blowing.

4.4.3 Test without argon blowing

The purpose of this test is to obtain the efficiency of argon blowing, since at this point it is unclear what the net effect of argon blowing in test D2 is. A weight balance of the test in which no argon is blown into the melt are shown in table 4.23.

Experiment	*D3*
Temperature	900 °C
Starting weight	83,12 g
Final weight	82,53
Weight difference	- 0,59 g

Table 4.23: Weight balance for test D3.

Figure 4.36: Alloy after test D7.

The alloy in figure 4.36 shows less oxidation than the alloy from test D2. Since the weight in this test also decreased, unlike the weight in test D2, the assumption that oxidation increases the weight of the previous test seems verified.

The results of the XRF analysis on the recovered alloy from test D3 are shown in table 4.24.

Test D3		
Element	**Content in wt%**	**Me/Al ratio**
Al	94,01	-
Zn	2,11	2,24 %
Mg	0,157	0,16 %
Cu	2,69	2,86 %
Si	0,105	0,11%

Table 4.24: XRF analysis results for experiment D3.

Table 4.25 shows the net effect of argon blowing for the 5 main elements.

	Initial (alloy test A6)	**Without argon blowing (D3)**	**With argon blowing (D2)**	**Total difference**	**Net effect Ar blowing**
Element	**Content in wt%**	**Content in wt%**	**Content in wt%**		
Al	93,19	94,01	94,12	+0,93 wt%	+0,11 %
Zn	2,42	2,11	1,88	-0,54 wt%	-0,23 %
Mg	0,133	0,157	0,113	-0,02 wt%	-0,044 %
Cu	2,71	2,69	2,59	-0,12 wt%	-0,10 %
Si	0,331	0,105	0,208	-0,12 wt%	+0,103 %

Table 4.25: Net effect of argon blowing for the 5 main elements.

The zinc content in the resulting alloy is 2,11 wt%. This is 0,31 % lower than the zinc content in the master alloy, which was 2,42 wt%. The similar test in which argon was blown into the melt for 30 minutes resulted into a zinc content of 1,88 wt%. This means that the process of argon blowing lowered the zinc content by 0,23 wt% in 30 minutes. Thus the efficiency of argon blowing is:

0,23 / 2,42 = 9,5 %.

This is only a small reduction of the zinc content compared to the melting process in the presence of salt flux, which reduced the zinc content with over 2 wt%.

Of course the zinc is easier to remove when its concentration is higher, but even then the argon blowing did not greatly reduce the zinc content. It is also possible the argon gas bubbles functioned as a stirring mechanism, which promoted the transport of zinc to the top of the melt. A stirring test can provide more information about this suggestion.

4.5 Mechanisms behind zinc removal

To get a better view on the question if zinc is removed from the melt by evaporation or by the salt flux, one melting test of de-coated scrap is done in the presence of a salt flux and a similar test in absence of a salt flux at 800 ˚C for 3 hours. The test without salt flux is done in an argon atmosphere to prevent major oxidation of the metal. The melting test results for experiments E1 and E2 are shown in figures 4.37 and 4.38.

Figure 4.37: Experiment E1, de-coated scrap with a salts-to-alloy ratio of 2:1, in crucible after melting (left), obtained alloy (middle) and non metallic inclusions (right).

Figure 4.38: Experiment E2, not de-coated scrap without a salt flux, in crucible after melting (left), obtained alloy (middle) and after sawing (right).

Experiment E2 results into a very black and brittle alloy on the top side. The black parts are a result of oxidation. Even in the argon gas protected atmosphere, oxygen leaked in and oxidized the melt. During sawing, the loose parts in the top fell off. Because of the oxidation, the upper parts seem not to have fully been molten. The lower part of the alloy did melt and formed a solid alloy, which is visible by making a cross-cut.

Table 4.26 gives a weight balance and the metal yields for experiments E1 and E2.

Experiment	De-coated: yes/no	Salts-to-alloy ratio	Initial weight of metal	Weight after melting	Yield
E1	Yes	2:1	27,38 g	27,09 g	98,9 %
E2	Yes	No salts	54,16 g	53,99 g	99,7 %

Table 4.26: Yields for experiments E1 and E2.

The yield is higher in experiment E2, but this is likely to be the result of the oxidation, which increased the weight of the alloy. Also the solid contaminants are not transferred to a salt flux. Table 4.27 shows the results of the XRF analysis of the recovered alloy from tests E1 and E2.

	Test E1	**Test E2**	**Test E1**	**Test E2**
Element	**Content in wt%**	**Content in wt%**	**Me/Al ratio**	**Me/Al ratio**
Al	91,21	92,20		
Zn	3,28	2,48	3,60 %	2,69 %
Mg	0,259	1,31	0,3 %	1,42 %
Cu	2,53	2,99	2,71 %	3,24 %

Table 4.27: XRF analysis results for tests E1 and E2

The XRF analysis results show that the second melting test, in which no salt flux was added to the melt, results into a lower zinc content. The presence of salt flux possibly counteracts the evaporation of zinc from the melt, because zinc first has to travel through the salt layer before it can evaporate. In test E2 magnesium is still present in the alloy, because there was no cryolite to react with. These results clarify that evaporation is the most important mechanism behind the removal of zinc, and that zinc is not, or hardly, transferred to the salt flux. Furthermore, the XRD analysis results also do not show any compound of zinc.

4.6 XRD analysis on furnace dust

The results of the XRD analysis for the dust from the wall of the tube furnace is given in figure 4.39. This dust was collected from all tests that were done in the tube furnace, i.e. tests D1-3 and test E2.

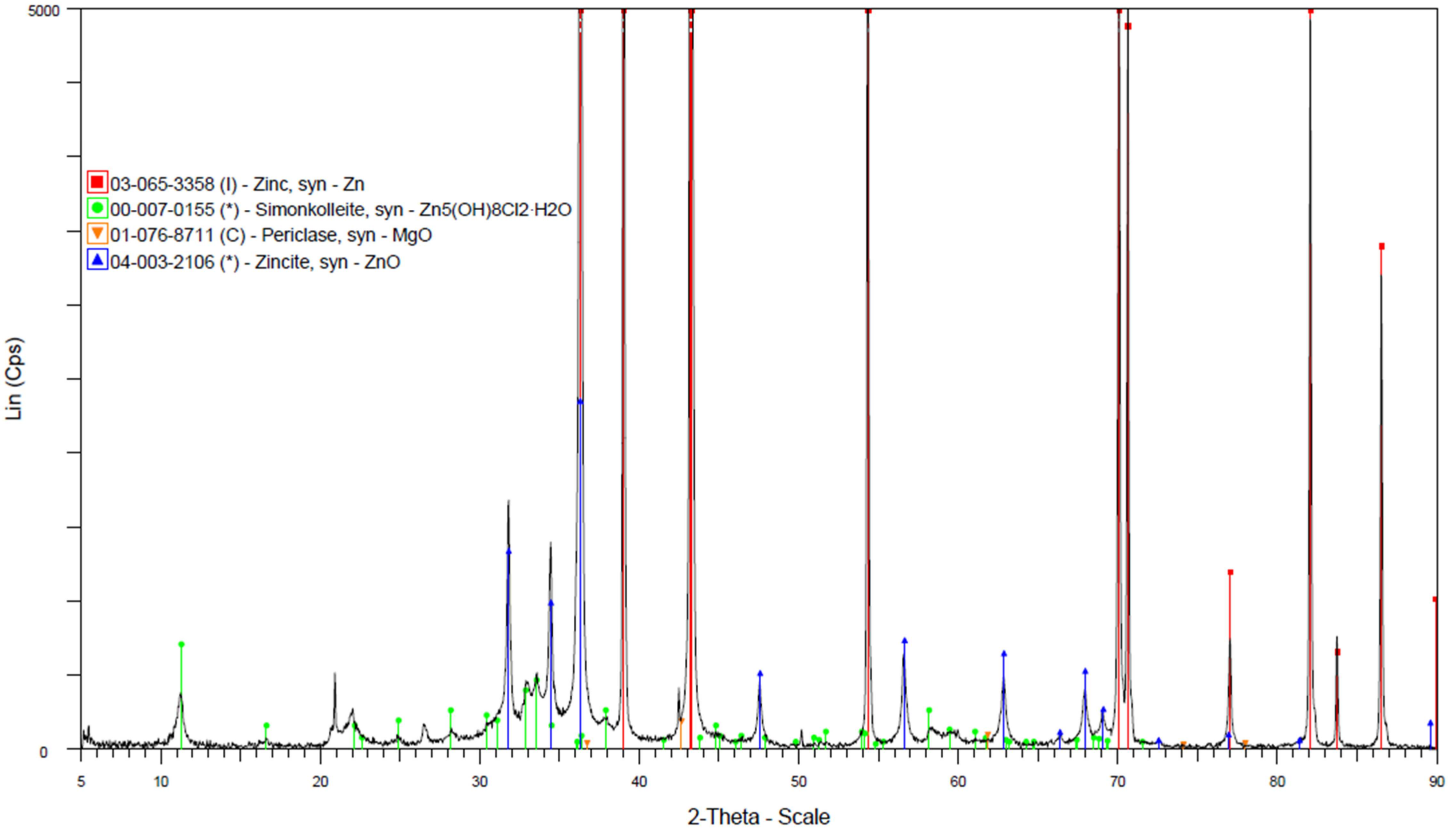


Figure 4.39: XRD analysis results on the dust from the wall of the tube furnace.

The analysis shows that the major part of the dust consists of pure zinc. As was shown in section 4.6, this indicates that the zinc is evaporating from the alloy. The second major phase in the dust is ZnO, which shows that a part of the evaporated zinc is oxidized, even though the tests are performed in an argon atmosphere. Furthermore MgO is also found in the dust, which means magnesium has been evaporating from the alloy during the tests. The alloy used in the argon blowing tests was pre-molten in the presence of cryolite, so the initial magnesium content was very low. This means that magnesium is evaporated even at a low concentration and a low partial pressure. The fourth compound in the dust is Simonkolleite, which is a result of the reaction of zinc-chlorine, zinc-oxide and moisture that is left in the furnace:

$$ZnCl_2 + 4ZnO + 5H_2O \rightarrow Zn_5(OH)_8Cl_2\cdot(H_2O)$$

The chloride was left in the master alloy, as a remainder from the salt flux.

5. Conclusions

5.1 Initial scrap composition

The composition of the scrap is very variable, since the aircraft not only consists out of different metals, but also out of different kinds of metal alloys. The major part of the scrap consists of 7000-series Al-alloy, which has a Zn-content of 5,5 to 6 wt%. The presence of other alloys reduces the average Zn-content to an estimated 5 wt%. The used samples origin from one aircraft, and it is likely that the alloy composition will also differ between different types of aircraft.

Some of the other solid metals, like Fe and Ti, are heavier than Al and have a much higher melting point. When these metals are not dissolved they can settle in the bottom of the furnace [14]. Electro refining could be used to further purify the metal, but this involves addition installations and a very high energy consumption.

5.2 De-coating

The results from the melting tests on a small scale showed that the coalescence of aluminium is much better for de-coated scrap than for the not de-coated scrap. Also the yield turned out higher for de-coated scrap, which is logical since the weight of the coating is no longer included. Also on a larger scale the coalescence of de-coated scrap was better, since one large piece of alloy did form without several smaller beads. In the melting of not de-coated scrap, the weight of the other alloy beads was only a fraction of the large alloy piece. On an industrial scale the coalescence might even be further improved.

In practice the coalescence of alloy is very important for the recovery rate. In the melting process, the slag and alloy are separated and the slag forms the top layer. Thus the alloy can easily be removed by tapping, and the operator can stop tapping when the slag layer is reached. If the coalescence is not good, the alloy and slag phase will be mixed up and slag will be entrapped in the alloy during the tapping.

The separation of alloy and slag was very bad for the melting of not de-coated scrap on the small scale. Also on the large scale the separation was poor. Pieces of slag ended up on the surface of the alloy, captured between the alloy and the crucible wall, and even as inclusions within the alloy. In an industrial process this would cause that during the tapping of the metal, this part of the slag phase will come along. Before solidifying of the metal, this contamination is trapped inside the metal.

Furthermore, the de-coated scrap is expected to have a better fluidity because of the absence of a large amount of contaminants. This improves the transport of zinc through the melt upwards, where it can evaporate.

Finally de-coating will reduce the amount of salts required in the melting process, since few contaminations will be captured in the slag phase. This also greatly reduces the cleaning treatment for salt slags.

In total, the de-coating of scrap gives:

- better coalescence of the metal droplets during the melting process.
- cleaner slag --> less salt flux is needed in the melting process --> and less salt treatment.
- a higher yield.
- lower viscosity of the melt, leading to better zinc evaporation efficiency.

5.3 Use of salt fluxes

The use of cryolite is more preferred compared to magnesium fluoride, since the tests with cryolite showed a much better coalescence of Al droplets and separation of the slag and metal. Also the cryolite can react with magnesium and remove this element from the alloy into the flux layer, in case this is desirable. However, when magnesium must be kept in the alloy, cryolite cannot be used. Also a smaller cryolite addition has a lower efficiency, since the residues on the Al scrap surfaces were entrapped in the salt flux during the re-melting, and increase the viscosity of molten salt flux which baffles the coalescence of Al alloy small beads. For this same reason the use of both cryolite and magnesium fluoride together will not give better results. If one wants to maintain the magnesium in the melt, more research with the use MgF_2 should be done. A higher temperature could improve the fluidity and coalescence of the alloy.

In total, the use of cryolite:

- gives a better coalescence of the metal.
- leads to a much better separation of the alloy and slag phases.
- removes magnesium from the alloy, depending on the situation this can be seen as an advantage or a disadvantage.
- results into an eutectic point at lower temperature than with the use of MgF_2, thus lower temperature is required in the melting process.

Furthermore the use of too much salt flux turned out to reduce the evaporation of Zn, because the salts counteracted the flow of Zn to the top of the melt. Obviously the use of more salts is more expensive. The right salt composition must give a good coalescence of the alloy and a good separation of the alloy and the slag phase. The main aspect of pre-melting is not the removal of Zn from the melt, although this is an advantage. The last part of the Zn-removal has to occur with argon blowing, also since Zn gets harder to remove when its concentration in the melt is lowered, because the partial pressure gets lower. To find the optimal composition of salt flux, more research on this subject is required.

5.4 Zinc removal by argon gas blowing

Since the partial pressure of Zn decreased with Zn concentration, the removal of Zn gets harder during the process. This means that the zinc is more easily removed during the melting process where the zinc content is still high, and becomes harder during the process of argon blowing.

Assuming that the initial zinc content of the scrap is around 5,5 %, the zinc content in the master alloy was reduced with over 3 % to 2,42 %, just by melting the scrap in the presence of a salt flux. Test D2 showed that once the zinc content is lower than 2.5 %, it is much harder to remove even more zinc; a 1 ½ hour melting test (without argon blowing) lowered the zinc content by 0,31 %. An identical test including 30 minutes of argon blowing lowered the zinc content by 0,54 %. This means the argon blowing removes 0,23 % more zinc.

Consider the following model: a secondary aluminium producer has 3 types of Al-alloy available:

- Type 1 is pure scrap with a zinc content of 5,5 %.
- Type 2 is pre-melted alloy with a zinc content of 2,5 %.
- Type 3 is argon blown alloy melt with a zinc content of 1,8 %.

When type 1 is directly loaded into a smelter which contains other types of Al-alloy melts without zinc, the average zinc content in the alloy is lowered. Suppose the mixing ratio is 1:1, this means the average zinc content in the alloy becomes 5,5 / 2 = 2,75 %. At this point is already is much harder to remove zinc from the alloy, because of its low concentration, leading to a lower partial pressure of zinc. If one wants to compose an alloy with a maximum of 0,5% zinc, at least 10 times as much Al-alloy without any zinc has to be mixed. Eventually this means primary aluminium has to be mixed, otherwise the zinc content will keep rising.

When type 2 is loaded into a smelter, only 4 times as much Al(-alloy) without zinc has to be mixed. The alloy is already molten from the pre-melting process, so no extra energy has to be consumed to melt this.

When type 3 is loaded into a smelter, 2,6 times as much Al(-alloy) without zinc has to be mixed. This looks like an improvement over type 2, but the process of argon blowing requires treatment in an extra reactor. Lances for blowing inert gas into the melt are very expensive equipment, and also very sensitive for maintenance. Furthermore there are operational costs like extra personnel and costs for the gas. Because argon is too expensive for practical operations, nitrogen could be used. This can lead to the forming of nitrides in the alloy, which can be harmful, even in small concentrations.

In total, the process of argon blowing efficiency of the argon blowing process is too low, because of the small decrease in the zinc content compared to a pre-melting operation and the capital and operational expenses that come with a installation for inert gas blowing.

5.5 Mechanisms behind Zn removal and the influence of salt flux

The results of test E1 and E2 show that the absence of a salt flux results into a lower zinc content than in the presence of a salt flux. A disadvantage of this test is that the upper side of the alloy showed oxidation. In practice the concentration of oxygen in the reactor will be even higher than in laboratory test, which will lead to a higher grade of oxidation. Therefore the presence of a protectoral salt flux is always required in the melting process. However, the results indicate that the presence of a salt flux counteracts the evaporation of zinc from the alloy. This is also shown in the results of melting with a variable salts-to-alloy ratio (section 4.3). Because of this it is desirable to melt the aircraft scrap in the lowest possible amount of salt. The XRD test on the dust from the furnace confirms that the zinc has evaporated from the alloy melt, and that zinc will be a major part of the furnace flue dust.

Modern furnaces have a holding capacity of 15 to 25 tons per cycle, this is salt plus scrap together [2]. A higher amount of salts will lead to a lower capacity for the scrap, leading to a less metal being refined. A higher amount of salts also counteracts the evaporation of zinc from the melt, thereby reducing the efficiency of the pre-melting process.

In total, an increase of the amount of salts will:

- reduce the capacity of the melting furnace, leading to a higher cost per ton of metal.
- reduce the evaporation of zinc from the alloy melt during the pre-melting process.
- increase the costs for salt flux treatment.
- lead to a higher loss of metal in the salt flux [2].

This leads back to the importance of de-coating, which is shown to greatly reduce the required amount of salt flux in the melting process, as concluded in section 5.2.

6. Recommendations

6.1 Scrap pre-treatment

The fresh scrap seemed to contain some other metals like iron, copper and titanium. Because these occur in very small amounts, they will not have a major impact on the Al-alloy melt. Before melting the scrap, a magnetic separator can be used to remove the iron parts from the scrap. This is a very simple and relatively cheap method to remove these contaminants from the scrap. The use of gravity separation is not recommended, because of the very low amount of heavy metals in the scrap. The investment would be too large compared to the proportion of heavy metal. In the melting process these relatively heavy metals will sink to the bottom of the smelter, where they can be separated. Their high melting point prevents dissolving into the melt. The dissolved metals could be removed by electro refining, but as mentioned before this involves high capital and operational costs.

6.2 Refining process

The recommendation for the refining process to remove Zn from the Al-alloy consists out of 3 stages. In the first stage the scrap is de-coated, to remove the major part of the coating. In the second part, the scrap is pre-melted to remove a certain grade of zinc from the alloy. Finally, the alloy melt is mixed with other aluminium alloys, primary aluminium or other alloying metals to form the right alloy composition. Figure 6.1 gives a schematic overview of the process.

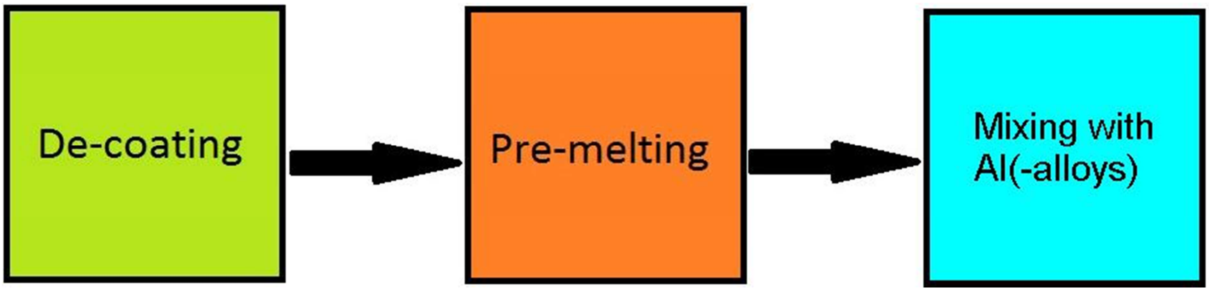


Figure 6.1: Schematic process overview.

6.2.1 De-coating

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Heat Balance

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6.2.2 Pre-melting

The experiments showed that the pre-melting process had an important role in the reduction of the zinc concentration in the aluminium alloy. The pre-melting experiment A6 had a reduction in zinc content from around 4,5 % to 2,42 % in the pre-melted alloy. However, experiment D2 showed that the reduction in zinc content is not that large when the initial zinc content is already decreased. Therefore it is important to set up a pre-melting process in which only the aircraft scrap is molten. If the aircraft scrap would be directly mixed into a melt of other alloys, the average zinc content is relatively low and it becomes much harder to remove zinc.

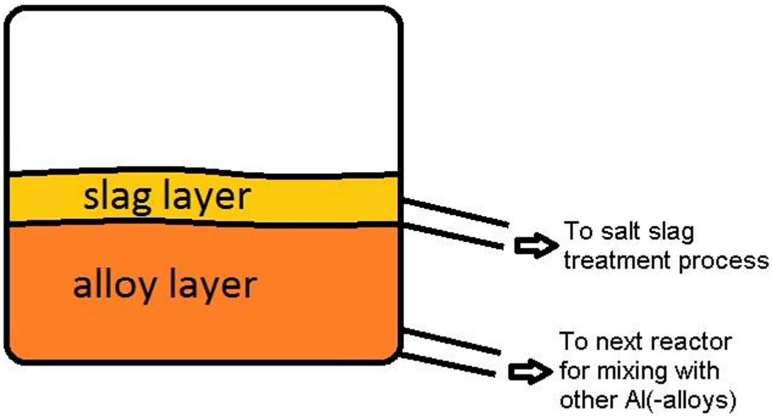

Figure 6.3: Melting process.

The pre-melting process is practically identical to the standard melting processes for aluminium alloys. Because the salt slag layer has a lower weight, it will float on top of the metal, and aluminium can easily be tapped as shown in figure 6.3. The molten alloy can be transported to a next reactor, where it can be mixed with other aluminium alloys, primary aluminium and/or alloying elements. If the scrap contains any heavier metal contaminants, like titanium, iron, lead or copper, these will sink to the bottom of the melt and can be separated as a thin layer of impurities. Like proposed in the previous section, the off-gases can be used in the de-coating process.

6.2.3 Argon blowing

As argued in chapter 5, the use of an inert gas blowing installation is not recommended for practical use. The investment and operational costs are too high and the effect of gas blowing is too low. The pre-melting process offers a much cheaper alternative for lowering the zinc content in the aluminium alloy.

6.3 Composition of salt flux

As mentioned in section 5.3, the optimal composition of the salt flux requires further investigation. The major part of the salt flux used in pre-melting will consist out of KCl and NaCl. These are relatively cheap salts and because of the low eutectic point (sec. 2.1.2) the metal will be covered with molten salt at a relatively low temperature.

It is not recommended to use MgF_2 in the salt flux, as the results for this addition were not good. The use of cryolite delivered a much better coalescence and metal-slag separation, but cryolite reacts with Mg to remove it from the alloy, which is undesirable if the final product is an Al-alloy with magnesium.

As shown in section 5.5, the amount of salt flux used in the melting process has be minimized for various reasons. This is not only important for economic reasons, also the use of more salt flux reduced the evaporation of zinc from the alloy melt. More experiments with aircraft scrap can indicate what the optimal amount of salts in a furnace is.

6.4 Future research

To continue the research on this subject, several options are available:

1) Although there is an indication of the composition of the scrap used in this research, the airplane from which the scrap origins is not one of the widely-used aircraft in the world, so the major part of the scrap will not consist of this kind of scrap. Each manufacturer will have its own metal composition. This will lead to a range of compositions for the metals that end up in the smelter. To expand the current research, analogical tests can be done on scrap from different aircraft.
2) As described in section 2.4.4, the equilibrium of $Zn(l) \leftrightarrow Zn(g)$ is moved to the right when the pressure is lowered. If the equipment is available, the current method can be expanded by applying a vacuum.

7. Acknowledgements

This research has been done in the scope of my bachelor thesis for the bachelor study of Applied Earth Sciences at the Delft University of Technology, faculty of Civil Engineering and Geosciences.

The research was conducted at the Materials Science and Engineering (MSE) department of the faculty of 3ME of the Delft University of Technology.

Special thanks for supervision and guidance during the research:

- Dr. Y. Yang, TU Delft, Faculty of 3ME, department of MSE, group Metals Production, Refining and Recycling.
- Dr. Y. Xiao, TU Delft, Faculty of 3ME, department of MSE, group Metals Production, Refining and Recycling.
- G. Zhu, TU Delft, Faculty of 3ME, department of MSE, group Metals Production, Refining and Recycling.

Thanks to the company Aircraft End-of-Life Solutions from Delft for their interest, support and discussions, and the supply of aircraft scrap.

Ruud Hendrikx at the Department of Materials Science and Engineering of the Delft University of Technology is acknowledged for the X-ray analysis.

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Appendix: XRF analysis results

Index for XRF analysis results:

Number of the XRF:	Page	Title:	Used in experiments:	Section:
1	74	Scrap 1	-	4.0
2	75	Scrap 2	-	4.0
3	76	Scrap 3	-	4.0
4	77	Scrap 4	-	4.0
5	78	Scrap 5	-	4.0
6	79	2:1 Salts-to-alloy ratio 10% cryolite not de-coated	A1, B2, C4	4.1.2, 4.2, 4.3.2
7	80	2:1 Salts-to-alloy ratio 10% cryolite de-coated	A2, E1	4.1.2 4.5
8	81	Alloy non-decoated-scrap	A3	4.1.3
9	82	Al-alloy-1	A4, D1	4.1.4, 4.4.2
10	83	Al-alloy-2	A5	4.1.4
11	84	Master alloy from de-coated scrap	A6, D2, D3	4.1.4, 4.4.2, 4.4.3
12	85	Extratest MgF2 2:1 *Note: this is '2:1 Salts-to-alloy ratio 10% MgF2 not de-coated'. The original test was incorrect.*	B1, C2	4.2, 4.3.1
13	86	1:1 Salts-to-alloy ratio 10% MgF2 not de-coated	C1	4.3.1
14	87	1:1 Salts-to-alloy ratio 10% cryolite not de-coated	C3	4.3.2
15	88	Al-alloy 1st Ar test	D1	4.4.2
16	89	900C Ar blowing	D2	4.4.2
17	90	900C no Argon blowing	D3	4.4.3
18	91	Molten scrap without salt flux	E2	4.5

```
******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change       * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                 *                 *
* 2628 CD Delft         * Fax  015-2786730                 *                 *
***************Semi-Quantitative XRF analysis ********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.131    2011-05-23
Scrap piece 1    23may11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     =  2 PProp 13
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0       29+Cu      1.61    0.14    52+Te      <
11 Na      <                       30+Zn      5.70    0.12    53+I       <
12+Mg      2.15    0.16    31+Ga      0.0130  0.0009  55+Cs      0.0093  0.0028
13+Al     89.69    0.20    32 Ge      <                       56+Ba      0.0104  0.0039
14 Si      <                       33 As      <                       SumLa..Lu  0.118   0.063
15+Px      0.0245  0.0020  34 Se      <                       72+Hf      0.0108  0.0029
15 P                               35 Br      <                       73 Ta      <
16 Sx                              37 Rb      <                       74+W       <
16+S       0.0421  0.0032  38+Sr      0.0060  0.0007  75 Re      <
17+Cl      0.0779  0.0086  39 Y       <                       76 Os      <
18+Ar      0.0304  0.0059  40+Zr      0.0062  0.0006  77+Ir      0.0056  0.0017
19+K       0.0264  0.0029  41 Nb      <                       78 Pt      <
20+Ca      0.0227  0.0025  42+Mo      0.0081  0.0014  79+Au      <
21 Sc      <                       44+Ru      <                       80 Hg      <
22+Ti      0.0268  0.0030  45+Rh      <                       81 Tl      <
23+V       0.0054  0.0010  46 Pd      <                       82 Pb      <
24+Cr      0.206   0.023   47 Ag      <                       83 Bi      <
25+Mn      0.0223  0.0017  48 Cd      <                       90 Th      <
26+Fe      0.177   0.020   49 In      <                       92 U       <
27 Co      <                       50 Sn      <                       94 Pu
28 Ni      <                       51 Sb      <                       95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0       44+Ru      <                       57+La      0.0066  0.0017
 4 Be   *                  45+Rh      <                       58 Ce      <
 5 B    *                  46 Pd      <                       59 Pr      <
 6 C    *                  47 Ag      <                       60 Nd      <
 7 N    *                  75 Re      <                       62+Sm      0.0516  0.0076
 8 O    *                  76 Os      <                       63 Eu      <2e     0.0045
 9 F    *                  77+Ir      0.0056  0.0017  64+Gd      0.0245  0.0046
                           78 Pt      <                       65+Tb      0.0266  0.0043
                           79+Au      <                       66 Dy      <
                                                      67 Ho      <
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :   53.9 %
```

```
******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change       * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                 *                 *
* 2628 CD Delft         * Fax  015-2786730                 *                 *
***************Semi-Quantitative XRF analysis ********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.132    2011-05-23
Scrap piece 2   23may11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     =  2 PProp 13
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0       29+Cu      2.07    0.15    52 Te      <
11+Na      <               30+Zn      5.67    0.12    53 I       <
12+Mg      1.91    0.15    31+Ga      0.0113  0.0007  55+Cs      0.0054  0.0020
13+Al     89.98    0.19    32 Ge      <               56 Ba      <
14 Si      <               33 As      <               SumLa..Lu  0.002   0.051
15+Px      0.0125  0.0013  34 Se      <               72 Hf      <2e     0.0032
15 P                       35 Br      <               73 Ta      <
16 Sx                      37 Rb      <               74+W       <
16+S       0.0115  0.0020  38+Sr      <               75 Re      <
17+Cl      0.0226  0.0025  39 Y       <               76 Os      <
18+Ar      <               40+Zr      0.110   0.006   77+Ir      0.0070  0.0014
19+K       0.0117  0.0014  41 Nb      <               78 Pt      <
20+Ca      0.0094  0.0011  42+Mo      <               79+Au      <
21 Sc      <               44 Ru      <               80+Hg      <
22+Ti      0.0307  0.0034  45 Rh      <               81 Tl      <
23+V       <               46 Pd      <               82 Pb      <
24+Cr      0.0203  0.0023  47 Ag      <               83 Bi      <
25+Mn      0.0056  0.0012  48 Cd      <               90 Th      <
26+Fe      0.094   0.010   49 In      <               92 U       <
27 Co      <               50 Sn      <               94 Pu
28 Ni      <               51 Sb      <               95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0       44 Ru      <               57 La      <
 4 Be   *                  45 Rh      <               58 Ce      <
 5 B    *                  46 Pd      <               59 Pr      <
 6 C    *                  47 Ag      <               60 Nd      <
 7 N    *                  75 Re      <               62 Sm      <
 8 O    *                  76 Os      <               63 Eu      <
 9 F    *                  77+Ir      0.0070  0.0014  64 Gd      <
                           78 Pt      <               65 Tb      <
                           79+Au      <               66 Dy      <
                                                      67 Ho      <
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :   77.3 %
```

```
*******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change       * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                 *                 *
* 2628 CD Delft         * Fax  015-2786730                 *                 *
***************Semi-Quantitative XRF analysis *********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.133    2011-05-23
Scrap piece 3    23may11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     =  2 PProp 13
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0       29+Cu      0.353   0.038   52 Te      <
11 Na      <               30+Zn      0.0891  0.0045  53 I       <
12+Mg      0.747   0.083   31+Ga      0.0126  0.0008  55+Cs      0.0070  0.0025
13+Al     95.63    0.13    32 Ge      <               56+Ba      0.0074  0.0034
14+Si      1.16    0.12    33 As      <               SumLa..Lu  0.014   0.061
15+Px      0.0199  0.0020  34 Se      <               72 Hf      <
15 P                       35 Br      <               73 Ta      <
16+Sx      0.0536  0.0060  37+Rb      <               74 W       <
16 S                       38 Sr      <               75 Re      <
17+Cl      0.0537  0.0060  39 Y       <               76 Os      <
18+Ar      0.0484  0.0062  40+Zr      <               77+Ir      <
19+K       0.0244  0.0027  41 Nb      <               78+Pt      <
20+Ca      0.0184  0.0020  42+Mo      0.0058  0.0011  79 Au      <
21 Sc      <               44 Ru      <               80 Hg      <
22+Ti      0.0287  0.0032  45 Rh      <               81+Tl      <
23+V       <               46 Pd      <               82+Pb      0.463   0.011
24+Cr      0.120   0.013   47 Ag      <               83+Bi      0.437   0.022
25+Mn      0.147   0.007   48 Cd      <               90 Th      <
26+Fe      0.525   0.058   49 In      <               92 U       <
27 Co      <               50 Sn      <               94 Pu
28+Ni      0.0160  0.0018  51+Sb      0.0116  0.0011  95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0       44 Ru      <               57 La      <
 4 Be   *                  45 Rh      <               58 Ce      <2e     0.0040
 5 B    *                  46 Pd      <               59 Pr      <
 6 C    *                  47 Ag      <               60+Nd      0.0077  0.0032
 7 N    *                  75 Re      <               62 Sm      <
 8 O    *                  76 Os      <               63 Eu      <
 9 F    *                  77+Ir      <               64 Gd      <
                           78+Pt      <               65 Tb      <
                           79 Au      <               66 Dy      <
                                                      67 Ho      <
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :   54.0 %
```

```
*******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change       * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                 *                 *
* 2628 CD Delft         * Fax  015-2786730                 *                 *
***************Semi-Quantitative XRF analysis *********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.134    2011-05-23
Scrap piece 4    23may11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     = No supporting film
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0.018   29+Cu      2.00    0.15    52 Te      <
11 Na      <2e     0.051   30+Zn      5.84    0.12    53 I       <
12+Mg      2.11    0.16    31+Ga      0.0090  0.0008  55+Cs      <
13+Al     89.22    0.20    32 Ge      <               56+Ba      0.0061  0.0029
14+Si      0.0780  0.0098  33 As      <               SumLa..Lu  0.018   0.050
15+Px      0.0155  0.0011  34 Se      <               72 Hf      <2e     0.0030
15 P                       35 Br      <               73 Ta      <
16 Sx                      37 Rb      <               74 W       <
16+S       0.330   0.016   38 Sr      <               75 Re      <
17+Cl      0.0246  0.0027  39 Y       <               76 Os      <
18+Ar      <               40+Zr      0.0884  0.0044  77+Ir      0.0074  0.0014
19+K       0.0161  0.0018  41 Nb      <               78 Pt      <
20+Ca      0.0624  0.0069  42+Mo      <               79+Au      <
21 Sc      <               44 Ru      <               80+Hg      <
22+Ti      0.0271  0.0030  45 Rh      <               81 Tl      <
23 V       <               46 Pd      <               82 Pb      <
24+Cr      0.0310  0.0034  47 Ag      <               83 Bi      <
25+Mn      0.0099  0.0012  48 Cd      <               90 Th      <
26+Fe      0.091   0.010   49 In      <               92 U       <
27 Co      <               50 Sn      <               94 Pu
28 Ni      <               51 Sb      <               95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0.018   44 Ru      <               57 La      <
 4 Be                      45 Rh      <               58+Ce      0.0081  0.0030
 5 B                       46 Pd      <               59 Pr      <
 6 C                       47 Ag      <               60 Nd      <
 7 N                       75 Re      <               62 Sm      <
 8 O                       76 Os      <               63 Eu      <
 9 F       <               77+Ir      0.0074  0.0014  64 Gd      <
                           78 Pt      <               65 Tb      <
                           79+Au      <               66 Dy      <
                                                      67 Ho      <
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :   67.4 %
```

```
******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change       * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                 *                 *
* 2628 CD Delft         * Fax  015-2786730                 *                 *
***************Semi-Quantitative XRF analysis ********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.135    2011-05-23
Scrap piece 5    23may11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     = No supporting film
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0.017   29+Cu      1.45    0.13    52 Te      <
11 Na      <2e     0.048   30+Zn      5.44    0.11    53 I       <
12+Mg      1.96    0.15    31+Ga      0.0094  0.0006  55+Cs      0.0072  0.0023
13+Al     90.70    0.19    32+Ge      <               56+Ba      0.0094  0.0032
14 Si      <               33 As      <               SumLa..Lu  0.007   0.043
15+Px      0.0091  0.0008  34 Se      <               72+Hf      0.0064  0.0024
15 P                       35 Br      <               73 Ta      <
16+Sx      0.0065  0.0010  37 Rb      <               74+W       <
16 S                       38 Sr      <               75 Re      <
17+Cl      0.0274  0.0030  39 Y       <               76 Os      <
18+Ar      <               40+Zr      0.0052  0.0005  77+Ir      0.0062  0.0012
19+K       0.0172  0.0019  41 Nb      <               78 Pt      <
20+Ca      0.0109  0.0012  42+Mo      <               79+Au      <
21 Sc      <               44 Ru      <               80 Hg      <
22+Ti      0.0368  0.0041  45 Rh      <               81 Tl      <
23+V       <               46 Pd      <               82 Pb      <
24+Cr      0.202   0.022   47 Ag      <               83 Bi      <
25+Mn      0.0134  0.0011  48 Cd      <               90 Th      <
26+Fe      0.0757  0.0084  49 In      <               92 U       <
27 Co      <               50 Sn      <               94 Pu
28 Ni      <               51 Sb      <               95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0.017   44 Ru      <               57 La      <
 4 Be                      45 Rh      <               58 Ce      <
 5 B                       46 Pd      <               59 Pr      <
 6 C                       47 Ag      <               60 Nd      <
 7 N                       75 Re      <               62 Sm      <
 8 O                       76 Os      <               63 Eu      <
 9 F       <               77+Ir      0.0062  0.0012  64 Gd      <
                           78 Pt      <               65 Tb      <
                           79+Au      <               66 Dy      <
                                                      67 Ho      <
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :   87.4 %
```

```
******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change       * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                 *                 *
* 2628 CD Delft         * Fax  015-2786730                 *                 *
***************Semi-Quantitative XRF analysis ********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.112    2011-05-11
Salts-to-alloy ratio 2:1  10% cryolite not de-coated 11may11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     =  2 PProp 13
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0       29+Cu      2.28    0.16    52 Te      <
11 Na      <2e     0.040   30+Zn      4.66    0.11    53 I       <
12 Mg      <               31+Ga      0.0124  0.0009  55+Cs      0.0144  0.0027
13+Al     92.33    0.17    32 Ge      <               56+Ba      0.0177  0.0037
14 Si      <               33 As      <               SumLa..Lu  0.029   0.058
15+Px      0.0131  0.0016  34 Se      <               72+Hf      <
15 P                       35 Br      <               73 Ta      <
16+Sx      0.0212  0.0028  37 Rb      <               74+W       <
16 S                       38 Sr      <               75 Re      <
17+Cl      0.120   0.013   39 Y       <               76 Os      <
18+Ar      <               40+Zr      0.0490  0.0025  77+Ir      <
19+K       0.0516  0.0057  41 Nb      <               78 Pt      <
20+Ca      0.0167  0.0019  42+Mo      0.0051  0.0013  79+Au      <
21 Sc      <               44 Ru      <               80 Hg      <
22+Ti      0.0233  0.0026  45 Rh      <               81 Tl      <
23+V       <               46 Pd      <               82+Pb      0.0084  0.0015
24+Cr      0.111   0.012   47 Ag      <               83 Bi      <
25+Mn      0.126   0.006   48 Cd      <               90 Th      <
26+Fe      0.116   0.013   49 In      <               92 U       <
27 Co      <               50 Sn      <               94 Pu
28 Ni      <               51 Sb      <               95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0       44 Ru      <               57 La      <
 4 Be   *                  45 Rh      <               58 Ce      <2e     0.0035
 5 B    *                  46 Pd      <               59+Pr      0.0151  0.0062
 6 C    *                  47 Ag      <               60 Nd      <
 7 N    *                  75 Re      <               62 Sm      <
 8 O    *                  76 Os      <               63 Eu      <
 9 F    *                  77+Ir      <               64 Gd      <
                           78 Pt      <               65 Tb      <
                           79+Au      <               66 Dy      <
                                                      67 Ho      <
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :   62.4 %
```

```
******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change       * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                 *                 *
* 2628 CD Delft         * Fax  015-2786730                 *                 *
***************Semi-Quantitative XRF analysis ********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.111    2011-05-11
Salts-to-alloy ratio 2:1  10% cryolite de-coated 11may11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     = No supporting film
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0.018   29+Cu      2.53    0.17    52 Te      <
11+Na      0.424   0.047   30+Zn      3.28    0.09    53 I       <
12+Mg      0.259   0.029   31+Ga      0.0111  0.0006  55+Cs      0.0109  0.0027
13+Al     91.21    0.18    32 Ge      <               56+Ba      0.0133  0.0038
14 Si      <               33 As      <               SumLa..Lu  0.009   0.041
15+Px      <               34 Se      <               72+Hf      <
15 P                       35 Br      <               73+Ta      <
16+Sx      0.0299  0.0033  37 Rb      <               74 W       <
16 S                       38 Sr      <               75+Re      <
17+Cl      1.31    0.13    39 Y       <               76 Os      <
18+Ar      <               40+Zr      0.0369  0.0018  77+Ir      0.0055  0.0011
19+K       0.342   0.038   41 Nb      <               78 Pt      <
20+Ca      0.0198  0.0022  42+Mo      0.0095  0.0011  79+Au      <
21 Sc      <               44 Ru      <               80 Hg      <
22+Ti      0.0273  0.0030  45 Rh      <               81 Tl      <
23+V       0.0059  0.0006  46 Pd      <               82 Pb      <
24+Cr      0.0686  0.0076  47 Ag      <               83 Bi      <
25+Mn      0.240   0.012   48 Cd      <               90 Th      <
26+Fe      0.157   0.017   49 In      <               92 U       <
27 Co      <               50 Sn      <               94 Pu
28 Ni      <               51 Sb      <               95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0.018   44 Ru      <               57 La      <
 4 Be                      45 Rh      <               58+Ce      <
 5 B                       46 Pd      <               59 Pr      <
 6 C                       47 Ag      <               60 Nd      <
 7 N                       75+Re      <               62 Sm      <
 8 O                       76 Os      <               63 Eu      <
 9 F       <               77+Ir      0.0055  0.0011  64 Gd      <
                           78 Pt      <               65 Tb      <
                           79+Au      <               66 Dy      <
                                                      67 Ho      <
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :   96.9 %
```

```
******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change       * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                 *                 *
* 2628 CD Delft         * Fax  015-2786730                 *                 *
***************Semi-Quantitative XRF analysis ********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.152    2011-06-09
alloy not-decoated-scrap Zhu  09jun11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     = No supporting film
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0.015   29+Cu      3.38    0.20    52 Te      <
11+Na      0.060   0.025   30+Zn      2.74    0.08    53 I       <
12+Mg      0.0708  0.0079  31+Ga      0.0119  0.0007  55+Cs      0.0106  0.0027
13+Al     92.82    0.17    32 Ge      <               56+Ba      0.0124  0.0038
14+Si      0.0771  0.0086  33 As      <               SumLa..Lu  0.024   0.043
15+Px      0.0226  0.0011  34 Se      <               72+Hf      <
15 P                       35 Br      <               73+Ta      <
16 Sx                      37 Rb      <               74 W       <
16+S       0.0051  0.0010  38 Sr      <               75 Re      <
17+Cl      0.0324  0.0036  39 Y       <               76 Os      <
18+Ar      <               40+Zr      0.0385  0.0019  77+Ir      <
19+K       0.0662  0.0073  41 Nb      <               78 Pt      <
20+Ca      0.0076  0.0008  42+Mo      0.0065  0.0010  79 Au      <
21 Sc      <               44 Ru      <               80 Hg      <
22+Ti      0.0181  0.0020  45+Rh      <               81 Tl      <
23+V       <               46 Pd      <               82+Pb      0.0051  0.0012
24+Cr      0.0362  0.0040  47 Ag      <               83 Bi      <
25+Mn      0.308   0.015   48 Cd      <               90 Th      <
26+Fe      0.183   0.020   49 In      <               92 U       <
27 Co      <               50+Sn      <               94 Pu
28+Ni      0.0519  0.0058  51 Sb      <               95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0.015   44 Ru      <               57+La      0.0089  0.0012
 4 Be                      45+Rh      <               58+Ce      0.0082  0.0025
 5 B                       46 Pd      <               59 Pr      <
 6 C                       47 Ag      <               60+Nd      0.0057  0.0020
 7 N                       75 Re      <               62 Sm      <
 8 O                       76 Os      <               63 Eu      <
 9 F       <               77+Ir      <               64 Gd      <
                           78 Pt      <               65 Tb      <
                           79 Au      <               66 Dy      <
                                                      67 Ho      <
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :   95.9 %
```

```
******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change       * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                 *                 *
* 2628 CD Delft         * Fax  015-2786730                 *                 *
***************Semi-Quantitative XRF analysis ********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.116    2011-05-12
Al-alloy-1 12may11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     =  2 PProp 13
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0       29+Cu      3.05    0.19    52 Te      <
11+Na      1.18    0.12    30+Zn      2.77    0.08    53 I       <
12 Mg      <               31+Ga      0.0121  0.0007  55+Cs      0.0068  0.0030
13+Al     90.34    0.19    32 Ge      <               56+Ba      0.0120  0.0042
14+Si      0.124   0.014   33 As      <               SumLa..Lu  0.005   0.045
15+Px      0.0193  0.0013  34 Se      <               72+Hf      <
15 P                       35 Br      <               73+Ta      <
16+Sx      0.0055  0.0017  37 Rb      <               74 W       <
16 S                       38 Sr      <               75 Re      <
17+Cl      1.00    0.11    39 Y       <               76 Os      <
18+Ar      <               40+Zr      0.0391  0.0020  77+Ir      <
19+K       0.618   0.068   41 Nb      <               78 Pt      <
20+Ca      0.0297  0.0033  42+Mo      0.0074  0.0010  79+Au      <
21 Sc      <               44+Ru      <               80 Hg      <
22+Ti      0.157   0.017   45 Rh      <               81 Tl      <
23+V       0.0124  0.0008  46 Pd      <               82 Pb      <
24+Cr      0.0338  0.0038  47 Ag      <               83 Bi      <
25+Mn      0.315   0.016   48 Cd      <               90 Th      <
26+Fe      0.193   0.021   49 In      <               92 U       <
27 Co      <               50+Sn      0.0112  0.0009  94 Pu
28+Ni      0.0483  0.0054  51 Sb      <               95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0       44+Ru      <               57+La      <
 4 Be   *                  45 Rh      <               58 Ce      <
 5 B    *                  46 Pd      <               59 Pr      <
 6 C    *                  47 Ag      <               60 Nd      <
 7 N    *                  75 Re      <               62 Sm      <
 8 O    *                  76 Os      <               63 Eu      <
 9 F    *                  77+Ir      <               64 Gd      <
                           78 Pt      <               65 Tb      <
                           79+Au      <               66 Dy      <
                                                      67 Ho      <
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :  101.3 %
```

```
*******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change        * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                  *                 *
* 2628 CD Delft         * Fax  015-2786730                  *                 *
***************Semi-Quantitative XRF analysis *********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.117    2011-05-12
Al-alloy-2 12may11

Spectrometer's configuration:  PW2400 Rh 60kV        Method    : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     =  2 PProp 13
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0       29+Cu      2.95    0.18    52 Te      <
11+Na      0.637   0.071   30+Zn      2.41    0.08    53 I       <
12 Mg      <               31+Ga      0.0118  0.0007  55+Cs      0.0082  0.0028
13+Al     92.17    0.17    32 Ge      <               56+Ba      0.0134  0.0039
14+Si      0.513   0.057   33 As      <               SumLa..Lu  0.004   0.045
15+Px      0.0221  0.0016  34 Se      <               72+Hf      <
15 P                       35 Br      <               73+Ta      <
16+Sx      0.0141  0.0021  37 Rb      <               74 W       <
16 S                       38 Sr      <               75 Re      <
17+Cl      0.254   0.028   39 Y       <               76 Os      <
18+Ar      <               40+Zr      0.0346  0.0017  77+Ir      <
19+K       0.370   0.041   41 Nb      <               78 Pt      <
20+Ca      0.0236  0.0026  42+Mo      0.0086  0.0011  79+Au      <
21 Sc      <               44 Ru      <               80+Hg      <
22+Ti      0.0173  0.0019  45 Rh      <               81 Tl      <
23+V       0.0060  0.0007  46 Pd      <               82+Pb      0.0054  0.0011
24+Cr      0.0329  0.0037  47 Ag      <               83 Bi      <
25+Mn      0.297   0.015   48 Cd      <               90 Th      <
26+Fe      0.190   0.021   49 In      <               92 U       <
27 Co      <               50 Sn      <               94 Pu
28+Ni      0.0109  0.0012  51 Sb      <               95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0       44 Ru      <               57 La      <
 4 Be   *                  45 Rh      <               58 Ce      <
 5 B    *                  46 Pd      <               59 Pr      <
 6 C    *                  47 Ag      <               60 Nd      <
 7 N    *                  75 Re      <               62 Sm      <
 8 O    *                  76 Os      <               63 Eu      <
 9 F    *                  77+Ir      <               64 Gd      <
                           78 Pt      <               65 Tb      <
                           79+Au      <               66 Dy      <
                                                      67 Ho      <
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :   86.0 %
```

```
******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change       * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                  *                 *
* 2628 CD Delft         * Fax  015-2786730                  *                 *
***************Semi-Quantitative XRF analysis ********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.145    2011-06-01
master alloy from de-coated scrap   01jun11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     = No supporting film
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0.015   29+Cu      2.71    0.18    52 Te      <
11+Na      0.171   0.022   30+Zn      2.42    0.08    53 I       <
12+Mg      0.133   0.015   31+Ga      0.0100  0.0007  55+Cs      0.0093  0.0025
13+Al     93.19    0.16    32 Ge      <               56+Ba      0.0136  0.0035
14+Si      0.331   0.037   33 As      <               SumLa..Lu  0.003   0.042
15+Px      0.0079  0.0007  34 Se      <               72 Hf      <
15 P                       35 Br      <               73+Ta      <
16+Sx      0.0311  0.0035  37 Rb      <               74 W       <
16 S                       38 Sr      <               75 Re      <
17+Cl      0.188   0.021   39 Y       <               76 Os      <
18+Ar      <               40+Zr      0.0341  0.0017  77+Ir      <
19+K       0.0760  0.0084  41 Nb      <               78 Pt      <
20+Ca      0.0149  0.0017  42+Mo      0.0066  0.0010  79+Au      <
21 Sc      <               44+Ru      <               80 Hg      <
22+Ti      0.0435  0.0048  45 Rh      <               81 Tl      <
23+V       0.0062  0.0007  46 Pd      <               82 Pb      <
24+Cr      0.0485  0.0054  47 Ag      <               83 Bi      <
25+Mn      0.300   0.015   48 Cd      <               90 Th      <
26+Fe      0.212   0.023   49 In      <               92 U       <
27 Co      <               50 Sn      <               94 Pu
28+Ni      0.0351  0.0039  51 Sb      <               95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0.015   44+Ru      <               57 La      <
 4 Be                      45 Rh      <               58 Ce      <
 5 B                       46 Pd      <               59 Pr      <
 6 C                       47 Ag      <               60 Nd      <
 7 N                       75 Re      <               62 Sm      <
 8 O                       76 Os      <               63 Eu      <
 9 F       <               77+Ir      <               64 Gd      <
                           78 Pt      <               65 Tb      <
                           79+Au      <               66 Dy      <
                                                      67 Ho      <
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :   89.0 %
```

```
******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change       * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                 *                 *
* 2628 CD Delft         * Fax  015-2786730                 *                 *
***************Semi-Quantitative XRF analysis ********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.128    2011-05-19
extratest MgF2 2:1 19may11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     =  2 PProp 13
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z          m/m%   StdErr    Z          m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0       29+Cu      2.22    0.16    52 Te      <
11+Na      <               30+Zn      6.19    0.12    53 I       <
12+Mg      2.64    0.18    31+Ga      0.0125  0.0010  55+Cs      0.0059  0.0025
13+Al     87.11    0.22    32 Ge      <               56+Ba      0.0101  0.0034
14+Si      0.474   0.053   33 As      <               SumLa..Lu  0.013   0.061
15+Px      0.0258  0.0022  34 Se      <               72 Hf      <
15 P                       35 Br      <               73 Ta      <
16+Sx      0.0598  0.0066  37 Rb      <               74 W       <
16 S                       38+Sr      <               75 Re      <
17+Cl      0.161   0.018   39 Y       <               76 Os      <
18 Ar      <               40+Zr      0.135   0.007   77+Ir      0.0062  0.0017
19+K       0.0529  0.0059  41 Nb      <               78 Pt      <
20+Ca      0.091   0.010   42+Mo      0.0063  0.0014  79+Au      <
21 Sc      <               44 Ru      <               80 Hg      <
22+Ti      0.270   0.030   45 Rh      <               81 Tl      <
23+V       0.0054  0.0009  46 Pd      <               82 Pb      <
24+Cr      0.369   0.041   47 Ag      <               83 Bi      <
25+Mn      <               48 Cd      <               90 Th      <
26+Fe      0.143   0.016   49 In      <               92 U       <
27 Co      <               50 Sn      <               94 Pu
28 Ni      <               51 Sb      <               95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0       44 Ru      <               57 La      <
 4 Be   *                  45 Rh      <               58 Ce      <
 5 B    *                  46 Pd      <               59 Pr      <
 6 C    *                  47 Ag      <               60 Nd      <
 7 N    *                  75 Re      <               62 Sm      <
 8 O    *                  76 Os      <               63 Eu      <
 9 F    *                  77+Ir      0.0062  0.0017  64 Gd      <
                           78 Pt      <               65 Tb      <
                           79+Au      <               66 Dy      <
                                                      67 Ho      <
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <2e     0.0039
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :   56.2 %
```

```
******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change       * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                 *                 *
* 2628 CD Delft         * Fax  015-2786730                 *                 *
***************Semi-Quantitative XRF analysis ********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.115    2011-05-11
Salts-to-alloy ratio 1:1 10% MgF2 not de-coated 11may11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     =  2 PProp 13
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0       29+Cu      1.99    0.15    52 Te      <
11+Na      <               30+Zn      5.54    0.11    53 I       <
12+Mg      0.97    0.11    31+Ga      0.0057  0.0012  55+Cs      0.0082  0.0029
13+Al     91.05    0.19    32 Ge      <               56+Ba      0.0130  0.0041
14 Si      <               33 As      <               SumLa..Lu  0.032   0.078
15+Px      0.0118  0.0023  34 Se      <               72 Hf      <
15 P                       35 Br      <               73 Ta      <
16 Sx                      37 Rb      <               74 W       <
16 S       <               38 Sr      <               75 Re      <
17+Cl      0.0464  0.0052  39 Y       <               76 Os      <
18+Ar      0.0403  0.0080  40+Zr      0.120   0.006   77 Ir      <
19+K       0.0196  0.0022  41 Nb      <               78+Pt      <
20+Ca      0.0442  0.0049  42+Mo      <               79+Au      <
21 Sc      <               44 Ru      <               80 Hg      <
22+Ti      0.0330  0.0037  45 Rh      <               81 Tl      <
23+V       0.0055  0.0011  46 Pd      <               82 Pb      <
24+Cr      0.0135  0.0019  47 Ag      <               83 Bi      <
25+Mn      0.0129  0.0017  48 Cd      <               90 Th      <
26+Fe      0.0741  0.0082  49 In      <               92 U       <
27 Co      <               50 Sn      <               94 Pu
28 Ni      <               51 Sb      <               95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0       44 Ru      <               57 La      <
 4 Be   *                  45 Rh      <               58 Ce      <2e     0.0049
 5 B    *                  46 Pd      <               59 Pr      <
 6 C    *                  47 Ag      <               60 Nd      <
 7 N    *                  75 Re      <               62 Sm      <
 8 O    *                  76 Os      <               63 Eu      <
 9 F    *                  77 Ir      <               64 Gd      <
                           78+Pt      <               65 Tb      <
                           79+Au      <               66 Dy      <2e     0.0084
                                                      67 Ho      <2e     0.0089
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <2e     0.0051
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :   39.7 %
```

```
******************************************************************************
* TU-Delft*Faculty 3mE    * Section Structure & Change     * R.W.A. Hendrikx *
* Mekelweg 2              * Tel. 015-2782255               *                 *
* 2628 CD Delft           * Fax  015-2786730               *                 *
***************Semi-Quantitative XRF analysis ********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.114    2011-05-11
Salts-to-alloy ratio 1:1 10% cryolite not de-coated 11may11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     =  2 PProp 13
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0       29+Cu      2.59    0.17    52 Te      <
11 Na      <2e     0.035   30+Zn      4.10    0.10    53 I       <
12+Mg      0.641   0.071   31+Ga      0.0125  0.0010  55+Cs      0.0087  0.0028
13+Al     91.83    0.18    32+Ge      <               56+Ba      0.0108  0.0039
14+Si      0.093   0.010   33 As      <               SumLa..Lu  0.025   0.064
15+Px      0.0132  0.0018  34 Se      <               72 Hf      <
15 P                       35 Br      <               73+Ta      <
16+Sx      0.0077  0.0028  37 Rb      <               74 W       <
16 S                       38+Sr      <               75 Re      <
17+Cl      0.156   0.017   39 Y       <               76 Os      <
18 Ar      <               40+Zr      0.0777  0.0039  77+Ir      0.0053  0.0018
19+K       0.0741  0.0082  41 Nb      <               78 Pt      <
20+Ca      0.0163  0.0018  42+Mo      0.0059  0.0014  79 Au      <
21 Sc      <               44 Ru      <               80 Hg      <
22+Ti      0.0325  0.0036  45 Rh      <               81 Tl      <
23+V       0.0065  0.0010  46 Pd      <               82 Pb      <
24+Cr      <               47 Ag      <               83 Bi      <
25+Mn      0.180   0.009   48 Cd      <               90 Th      <
26+Fe      0.114   0.013   49 In      <               92 U       <
27 Co      <               50 Sn      <               94 Pu
28 Ni      <               51 Sb      <               95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0       44 Ru      <               57+La      0.0081  0.0020
 4 Be   *                  45 Rh      <               58 Ce      <
 5 B    *                  46 Pd      <               59 Pr      <
 6 C    *                  47 Ag      <               60 Nd      <
 7 N    *                  75 Re      <               62 Sm      <
 8 O    *                  76 Os      <               63 Eu      <
 9 F    *                  77+Ir      0.0053  0.0018  64 Gd      <
                           78 Pt      <               65+Tb      0.0090  0.0042
                           79 Au      <               66 Dy      <
                                                      67 Ho      <
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :   52.9 %
```

```
******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change       * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                 *                 *
* 2628 CD Delft         * Fax  015-2786730                 *                 *
***************Semi-Quantitative XRF analysis ********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.120    2011-05-16
Al-alloy 1st Ar  test 16may11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     = No supporting film
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0.015   29+Cu      2.73    0.18    52 Te      <
11+Na      0.041   0.020   30+Zn      2.15    0.07    53 I       <
12+Mg      0.0650  0.0072  31+Ga      0.0095  0.0006  55+Cs      0.0088  0.0026
13+Al     94.16    0.15    32 Ge      <               56+Ba      0.0098  0.0037
14+Si      0.093   0.010   33 As      <               SumLa..Lu  0.009   0.038
15 Px                      34 Se      <               72 Hf      <
15+P       <               35 Br      <               73+Ta      <
16+Sx      0.0050  0.0008  37 Rb      <               74 W       <
16 S                       38 Sr      <               75 Re      <
17+Cl      0.0144  0.0016  39 Y       <               76 Os      <
18 Ar      <               40+Zr      0.0340  0.0017  77+Ir      <
19+K       0.0113  0.0013  41 Nb      <               78 Pt      <
20+Ca      <               42+Mo      <               79+Au      <
21 Sc      <               44 Ru      <               80 Hg      <
22+Ti      0.100   0.011   45 Rh      <               81 Tl      <
23+V       0.0099  0.0007  46 Pd      <               82+Pb      <
24+Cr      0.0314  0.0035  47 Ag      <               83 Bi      <
25+Mn      0.292   0.015   48 Cd      <               90 Th      <
26+Fe      0.186   0.021   49 In      <               92 U       <
27 Co      <               50+Sn      0.0061  0.0007  94 Pu
28+Ni      0.0346  0.0038  51 Sb      <               95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0.015   44 Ru      <               57 La      <
 4 Be                      45 Rh      <               58 Ce      <
 5 B                       46 Pd      <               59 Pr      <
 6 C                       47 Ag      <               60 Nd      <
 7 N                       75 Re      <               62 Sm      <
 8 O                       76 Os      <               63 Eu      <
 9 F       <               77+Ir      <               64 Gd      <
                           78 Pt      <               65 Tb      <
                           79+Au      <               66 Dy      <
                                                      67 Ho      <
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :  110.6 %
```

```
******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change       * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                 *                 *
* 2628 CD Delft         * Fax  015-2786730                 *                 *
***************Semi-Quantitative XRF analysis ********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.144    2011-06-01
900C Ar blowing   01jun11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     = No supporting film
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0.013   29+Cu      2.59    0.17    52 Te      <
11+Na      0.163   0.018   30+Zn      1.88    0.07    53 I       <
12+Mg      0.113   0.013   31+Ga      0.0066  0.0006  55+Cs      0.0091  0.0027
13+Al     94.12    0.15    32 Ge      <               56+Ba      0.0116  0.0038
14+Si      0.208   0.023   33 As      <               SumLa..Lu  0.006   0.037
15+Px      0.0126  0.0008  34 Se      <               72 Hf      <
15 P                       35 Br      <               73+Ta      <
16+Sx      0.0441  0.0049  37 Rb      <               74 W       <
16 S                       38 Sr      <               75 Re      <
17+Cl      0.124   0.014   39 Y       <               76 Os      <
18+Ar      <               40+Zr      0.0333  0.0017  77 Ir      <
19+K       0.0363  0.0040  41 Nb      <               78+Pt      <
20+Ca      0.0153  0.0017  42+Mo      0.0064  0.0009  79 Au      <
21 Sc      <               44 Ru      <               80 Hg      <
22+Ti      0.0384  0.0043  45+Rh      <               81 Tl      <
23+V       0.0063  0.0006  46 Pd      <               82+Pb      <
24+Cr      0.0484  0.0054  47 Ag      <               83 Bi      <
25+Mn      0.294   0.015   48 Cd      <               90 Th      <
26+Fe      0.203   0.023   49 In      <               92 U       <
27 Co      <               50 Sn      <               94 Pu
28+Ni      0.0279  0.0031  51 Sb      <               95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0.013   44 Ru      <               57 La      <
 4 Be                      45+Rh      <               58 Ce      <
 5 B                       46 Pd      <               59 Pr      <
 6 C                       47 Ag      <               60 Nd      <
 7 N                       75 Re      <               62 Sm      <
 8 O                       76 Os      <               63 Eu      <
 9 F       <               77 Ir      <               64 Gd      <
                           78+Pt      <               65 Tb      <
                           79 Au      <               66 Dy      <
                                                      67 Ho      <
                                                      68 Er      <
                                                      69 Tm      <
                                                      70 Yb      <
                                                      71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :  109.6 %
```

```
*******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change        * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                  *                 *
* 2628 CD Delft         * Fax  015-2786730                  *                 *
***************Semi-Quantitative XRF analysis *********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.147    2011-06-01
900C no Argon blowing  01jun11

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     = No supporting film
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0.014    29+Cu      2.69    0.17      52 Te      <
11+Na      0.076   0.019    30+Zn      2.11    0.07      53 I       <
12+Mg      0.157   0.017    31+Ga      0.0096  0.0006    55+Cs      0.0080  0.0027
13+Al     94.01    0.15     32 Ge      <                 56+Ba      0.0109  0.0037
14+Si      0.105   0.012    33 As      <                 SumLa..Lu  0.005   0.037
15+Px      0.0225  0.0010   34 Se      <                 72+Hf      <
15 P                        35 Br      <                 73+Ta      <
16+Sx      0.0117  0.0013   37 Rb      <                 74 W       <
16 S                        38 Sr      <                 75 Re      <
17+Cl      0.0265  0.0029   39 Y       <                 76 Os      <
18+Ar      <                40+Zr      0.0334  0.0017    77 Ir      <
19+K       0.0181  0.0020   41 Nb      <                 78 Pt      <
20+Ca      0.0257  0.0029   42+Mo      0.0058  0.0009    79+Au      <
21 Sc      <                44+Ru      <                 80 Hg      <
22+Ti      0.0524  0.0058   45 Rh      <                 81 Tl      <
23+V       0.0070  0.0006   46 Pd      <                 82 Pb      <
24+Cr      0.0478  0.0053   47 Ag      <                 83 Bi      <
25+Mn      0.297   0.015    48 Cd      <                 90 Th      <
26+Fe      0.229   0.025    49 In      <                 92 U       <
27 Co      <                50 Sn      <                 94 Pu
28+Ni      0.0361  0.0040   51 Sb      <                 95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0.014    44+Ru      <                 57+La      <
 4 Be                       45 Rh      <                 58 Ce      <
 5 B                        46 Pd      <                 59 Pr      <
 6 C                        47 Ag      <                 60 Nd      <
 7 N                        75 Re      <                 62 Sm      <
 8 O                        76 Os      <                 63 Eu      <
 9 F       <                77 Ir      <                 64 Gd      <
                            78 Pt      <                 65 Tb      <
                            79+Au      <                 66 Dy      <
                                                         67 Ho      <
                                                         68 Er      <
                                                         69 Tm      <
                                                         70 Yb      <
                                                         71 Lu      <

KnownConc= 0                    REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :  108.6 %
```

```
******************************************************************************
* TU-Delft*Faculty 3mE  * Section Structure & Change       * R.W.A. Hendrikx *
* Mekelweg 2            * Tel. 015-2782255                 *                 *
* 2628 CD Delft         * Fax  015-2786730                 *                 *
***************Semi-Quantitative XRF analysis ********************************
C:\UQ5\USER\TUD_TA\Jobs\JOB.151    2011-06-09
molten scrap without salt flux

Spectrometer's configuration:  PW2400 Rh 60kV        Method   : UniQuant
C:\UQ5\USER\TUD_TA\Appl\AnySample.kap 2011-03-28
Calculated as :  Elements     Matrix (Shape & ImpFc) :  9|Al-base
X-ray path    =  Vacuum       Film type     = No supporting film
Case number   =  0  All known
Eff.Diam.     = 23.0 mm       Eff.Area      = 415.3 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass   = 2000.000 mg
Dil/Sample    =  0                          Sample Height = 1.00 mm
           <    means that the concentration is <  50 mg/kg
           <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z         m/m%   StdErr    Z         m/m%   StdErr    Z         m/m%   StdErr
=========================  =========================  =========================
SumBe..F   0       0.016   29+Cu      2.99    0.18     52 Te      <
11+Na      0.055   0.023   30+Zn      2.48    0.08     53 I       <
12+Mg      1.31    0.13    31+Ga      0.0114  0.0007   55+Cs      0.0091  0.0027
13+Al     92.20    0.17    32+Ge      <                56+Ba      0.0097  0.0038
14 Si      <               33 As      <                SumLa..Lu  0.016   0.044
15+Px      0.0060  0.0007  34 Se      <                72 Hf      <
15 P                       35 Br      <                73+Ta      <
16 Sx                      37 Rb      <                74 W       <
16+S       0.0351  0.0018  38+Sr      0.0061  0.0007   75+Re      <
17+Cl      0.137   0.015   39 Y       <                76 Os      <
18+Ar      <               40+Zr      0.0330  0.0016   77+Ir      0.0058  0.0012
19+K       0.0243  0.0027  41 Nb      <                78+Pt      0.0055  0.0019
20+Ca      0.0374  0.0042  42+Mo      0.0073  0.0011   79+Au      <
21 Sc      <               44 Ru      <                80+Hg      <
22+Ti      0.0433  0.0048  45 Rh      <                81 Tl      <
23+V       0.0054  0.0007  46 Pd      <                82 Pb      <
24+Cr      0.0529  0.0059  47 Ag      <                83 Bi      <
25+Mn      0.339   0.017   48 Cd      <                90 Th      <
26+Fe      0.184   0.020   49 In      <                92 U       <
27 Co      <               50 Sn      <                94 Pu
28 Ni      <               51 Sb      <                95 Am

==== Light Elements =====  ==== Noble Elements =====  ===== Lanthanides =======
SumBe..F   0       0.016   44 Ru      <                57+La      <
 4 Be                      45 Rh      <                58+Ce      0.0090  0.0024
 5 B                       46 Pd      <                59 Pr      <
 6 C                       47 Ag      <                60+Nd      <
 7 N                       75+Re      <                62 Sm      <
 8 O                       76 Os      <                63 Eu      <
 9 F       <               77+Ir      0.0058  0.0012   64 Gd      <
                           78+Pt      0.0055  0.0019   65 Tb      <
                           79+Au      <                66 Dy      <
                                                       67 Ho      <
                                                       68 Er      <
                                                       69 Tm      <
                                                       70 Yb      <
                                                       71 Lu      <

KnownConc= 0                   REST= 0                  D/S= 0
Sum Conc's before normalisation to 100% :   83.1 %
```