REMELTING BEHAVIOUR OF PURE AND AZ63 MAGNESIUM CHIPS

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ABSTRACT

REMELTING BEHAVIOUR OF PURE AND AZ63 MAGNESIUM CHIPS

Magnesium is a widely used light metal in many areas such as the automotive, aerospace, and medical industries. Magnesium has become widely used in industrial applications despite its poor corrosion resistance and high cost. It has great machinability, weldability, and remarkable mechanical properties such as lightweight, strength, and creep resistance. Magnesium is considered by the European Union as a critical raw material. The demand for magnesium has been increasing and it is used as a substitute for other heavy materials in many applications. Thus, recycling magnesium scrap is important due to limited raw material accessibility and environmental concerns. Secondary sources of magnesium should contribute to the economy and the procedure should be as efficient as possible to prevent metal loss. Magnesium is typically remelted under a salt flux (chloride and fluoride mix) which removes the surface oxides and other contaminants from the metal or under a cover gas that covers the surface against oxidation. This research studies the effects of salt composition, different fluorides, and the compaction degree of turnings on the recovery efficiency of pure and AZ63 magnesium alloy chips that were remelted under different chemical compositions of NaF, CaF_2, $MgCl_2$, KCl, and NaCl salt fluxes. The purpose is to minimize the metal loss and increase the coalescence ability of the metal. Metal yield and coagulation efficiency were reported XRD, SEM-EDX, XRF, and TGA analysis were performed for the characterization of chips and remelted samples. The melting point and density of the salt fluxes were determined by the FactSage software.

ÖZET

SAF VE AZ63 MAGNEZYUM TALAŞLARININ ERİME DAVRANIŞI

Magnezyum, otomotiv, havacılık ve medikal endüstrileri gibi birçok alanda yaygın olarak kullanılan bir hafif metaldir. Zayıf korozyon direncine ve yüksek maliyetine rağmen, magnezyum endüstriyel uygulamalarda yaygın olarak kullanılmaktadır. Mükemmel işlenebilirliğe, kaynaklanabilirliğe ve hafiflik, dayanıklılık ve sürünme direnci gibi dikkate değer mekanik özelliklere sahiptir. Magnezyum, Avrupa Birliği tarafından kritik bir hammadde olarak kabul edilmektedir. Magnezyum talebi artmakta ve birçok uygulamada diğer ağır malzemelerin yerine kullanılmaktadır. Bu nedenle, sınırlı ham madde erişilebilirliği ve çevresel kaygılar nedeniyle magnezyum hurdanın geri dönüştürülmesi önemlidir. İkincil magnezyum kaynakları ekonomiye katkıda bulunmalı ve metal kaybını önlemek için prosedür mümkün olduğunca verimli olmalıdır. Magnezyum tipik olarak yüzey oksitlerini ve diğer kirletici maddeleri metalden uzaklaştıran bir tuz akışı (klorür ve florür karışımı) veya oksidasyona karşı yüzeyi kaplayan bir örtü gazı altında yeniden eritilir. Bu araştırma, NaF, CaF_2, $MgCl_2$, KCl ve NaCl tuz akışlarının farklı kimyasal bileşimleri altında yeniden eritilmiş saf ve AZ63 magnezyum alaşımlı talaşların geri kazanım verimliliği üzerindeki tuz bileşiminin, farklı florürlerin ve tornalamaların sıkıştırma derecesinin etkilerini incelemektedir. Amaç, metal kaybını en aza indirmek ve metalin kaynaşma kabiliyetini arttırmaktır. Metal verimi ve pıhtılaşma oranı raporlandı XRD, SEM-EDX, XRF ve TGA analizleri, cipslerin karakterizasyonu için yapıldı ve yeniden eritildi örnekler. Tuz akışlarının erime noktası ve yoğunluğu, FactSage yazılımı ile belirlendi.

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CHAPTER 1

INTRODUCTION

Magnesium is the 8th most abundant element in the earth crust, and it is a light metal utilized in various applications, including the automotive, aerospace, and medical fields [1]. Magnesium has a long history of use in industrial applications despite having a low level of corrosion resistance and being expensive. It possesses exceptional mechanical qualities like lightweight strength, creep resistance, and excellent machinability and weldability [2]. Magnesium is becoming increasingly in demand, and it is utilized in place of other heavier minerals in many applications.

Primary magnesium metal production falls under two categories due to differences in magnesium ore sources. The first is the electrolysis of molten magnesium chloride, where $MgCl_2$ is used as a molten electrolyte to obtain metallic magnesium by electrolysis using direct current. This process is called the electrolysis process. The second is the Pidgeon process or silicothermic reduction process; the raw material dolomite is fed into a reduction tank heated externally by a reduction furnace during the Pidgeon method to produce magnesium. The calcined dolomite is then thermally reduced to metallic magnesium using 75% ferrosilicon as a reducing agent in a vacuum. Due to its expanding application areas and the European Union's views magnesium as a critical raw material, recycling magnesium metal has become important in recent years. Primary magnesium production demands a high energy consumption. However, considering that the production of secondary magnesium requires only 5% of the energy required to produce the primary metal, recycled magnesium provides significant benefits both economically and in terms of its environmental impact [2]. Recycling of magnesium alloys, even used for structural applications, can be recycled into products with the same mechanical, physical, and chemical properties as the primary magnesium metal [3]. There are several ways to recycle magnesium metal such as remelting, fluxing, vacuum distillation, and electrolysis.

Magnesium oxide is one of the most stable oxides at all temperatures, and it becomes increasingly stable when the temperature decrease. Magnesium is covered with magnesium oxide and magnesium hydroxide. Therefore, the metal losses can be high both before and during the recycling process.

This research studies the effects of salt composition, different fluorides, and the compaction degree of turnings on the recovery efficiency of pure and AZ63 magnesium alloy chips.

CHAPTER 2

STATE OF THE ART

2.1. Primary Production of Magnesium

The raw materials required to produce magnesium are available from several sources. Magnesium is produced from six different raw materials: magnesite, dolomite, carnallite, serpentine, bischofite, and seawater [4]. The chemical formulas and contents of the pure raw materials are given in Table 2. 1.

Table 2. 1. Sources of magnesium [4].

Raw Material	Chemical Formula	Mg Content (calculated value, %)
Magnesite	$MgCO_3$	28.8
Dolomite	$(Ca,Mg)CO_3$	13.2
Carnallite	$KCl \cdot MgC1_2 \cdot 6H_2O$	8.7
Serpentine	$2MgO \cdot 2SiO_2 \cdot H_2O$	22.2
Bischofite	$MgC1_2 \cdot 6H_2O$	12.0
Sea Water	Mg^{++}	0.12

Primary magnesium production refers to the process of extracting magnesium metal from ores or other sources. There are two main methods used for primary magnesium production: the Pidgeon process or silicothermic reduction process and the electrolytic process. There are some differences between these two processes in terms of raw materials used, energy consumption, purity of magnesium metal, production capacity, and environmental effects [5, 6].

2.1.1. Pidgeon Process

The Pidgeon Process, a vacuum silicothermic reduction method commonly used for producing primary magnesium metal, was created by Canadian inventor Lloyd Montgomery Pidgeon at the start of the 1940s [7-9]. Pidgeon process takes place in 5 steps which are calcination, reduction, separation, purification, and casting. The procedure for the Pidgeon process is given in detail in Figure 2. 1. Dolomite is used as the main raw material for the Pidgeon process, ferrosilicon is used as the reducing agent and fluorite is used as a catalyst [10]. Dolomite is calcined in a rotating kiln that runs at temperatures between 1000 and 1300 °C [11]. The reaction is shown in Equation 2.1[12].

$$(CaCO_3 \cdot MgCO_3)_{(s)} + \text{heat} \rightarrow (CaO \cdot MgO)_{(s)} + 2CO_{2(g)} \quad (2.1)$$

The calcination product is then placed in reduction vessels after being compressed into pellets and heated to 1200 °C[13]. During the reduction process, the air was extracted from the reduction vessels, and magnesium vapor emerged [12]. The following Equation 2.2 is how the reduction process is described.

$$2(CaO \cdot MgO)_{(s)} + Si(Fe)_{(s)} \rightarrow 2Mg_{(g)} + (2CaO \cdot SiO_2)_{(s)} + Fe_{(s)} \quad (2.2)$$

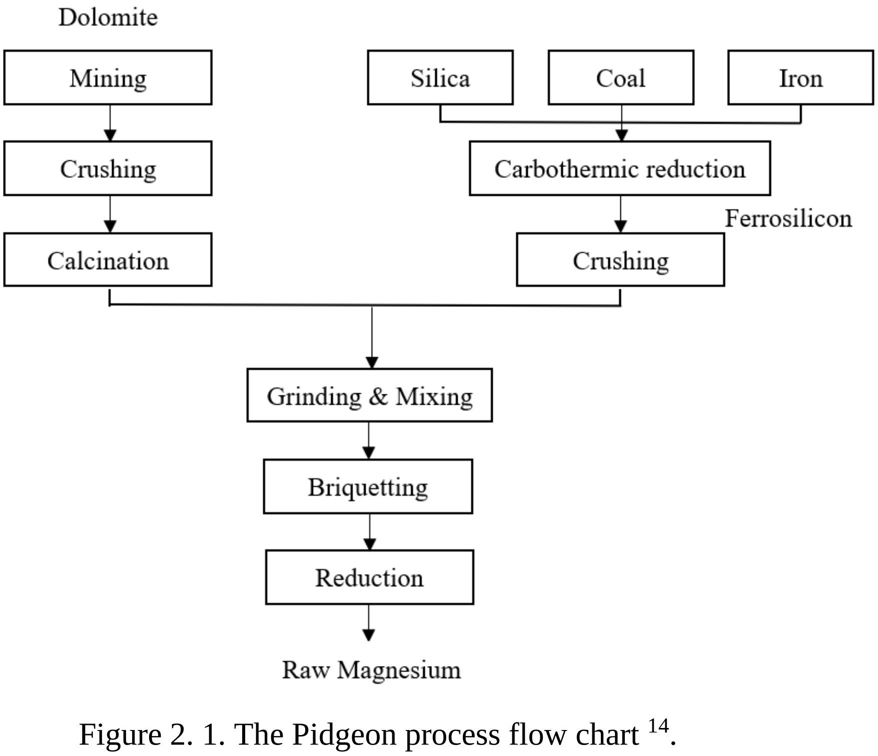

Figure 2. 1. The Pidgeon process flow chart [14].

Magnesium is separated from the silica after reduction in the separation process using distillation or vacuum separation. The magnesium obtained from the separation step must then be further refined because it is not sufficiently pure. Because molten magnesium is extremely combustible and poses major safety risks, its surface must be coated with a sufficient flow or coating gas that prevents oxidation. To create magnesium ingots, molten magnesium is subsequently moved from the melting furnace and poured into ingots[10]. In a casthouse, primary magnesium that is produced as crown (Mg > 99.5% by wt.) is cast into ingots with or without alloying additives [15]. The Pidgeon method is currently among the most popular because it can produce magnesium that is extremely pure and because its raw material, dolomite, is readily available[1].

2.1.2. The Electrolytic Process

Magnesium is produced electrochemically using salts containing chloride, which are either naturally occurring or can be produced from other raw materials including serpentine, magnesite, bischofite, or carnallite [16]. The preparation of magnesium chloride, known as the first step, magnesium chloride is first prepared by reacting dolomite ($MgCO_3 \cdot CaCO_3$) with hydrochloric acid (HCl) to obtain a magnesium chloride solution. Subsequently, to purify the magnesium chloride, contaminants including calcium, iron, and aluminium are taken out of the magnesium chloride solution. A graphite anode and a molten salt electrolyte are used to electrolyze the purified magnesium chloride melt at a temperature of around 700–750 °C. The electric current causes the reduction of magnesium ions at the cathode while the oxidation of chlorine ions at the anode. For further processing, the molten magnesium is poured into ingots or other forms [14]. The flow chart of the electrolysis process is shown in Figure 2. 2.

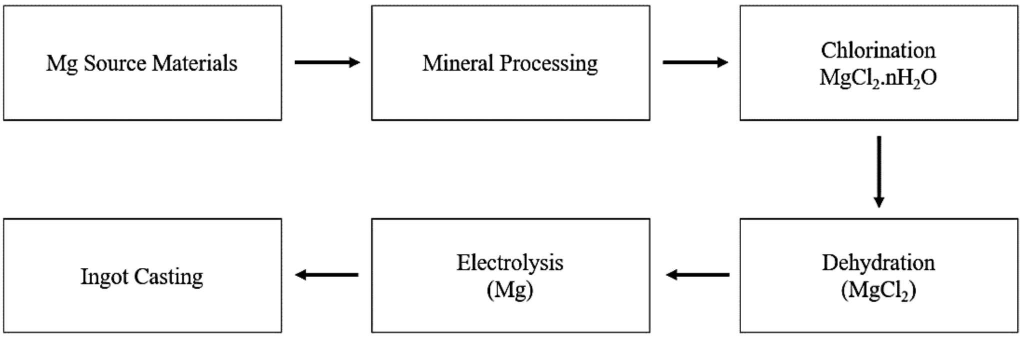

Figure 2. 2. Flow chart of the electrolysis process [4].

There are both advantages and disadvantages when comparing these two processes. First, they differ in terms of raw materials. While dolomite is used in the Pidgeon process, raw materials such as carnallite and magnesite are used in the electrolysis process. Primary magnesium processes vary according to the sources of the countries. The advantages of the electrolysis process are homogeneous product production, continuity, and energy savings. It is the production of high purity and abundant magnesium in the Pidgeon process and the low equipment cost. On the downside, the electrolysis process causes significant corrosion of the equipment and the cost of treatment for wastewater, waste gas, and waste residue, and requires an acidic atmosphere. The disadvantage of the Pidgeon process is that the reduction furnace has a short lifetime and a discontinuous production process. Approximately 20% of the primary magnesium production capacity is produced by electrolysis and 80% by the Pidgeon process[10]. The choice between the two approaches is influenced by a number of factors such as raw material availability, energy prices, required purity levels, and production capacity[17]. Most CO_2 emissions are reduced when magnesium is produced using electrolysis [18].

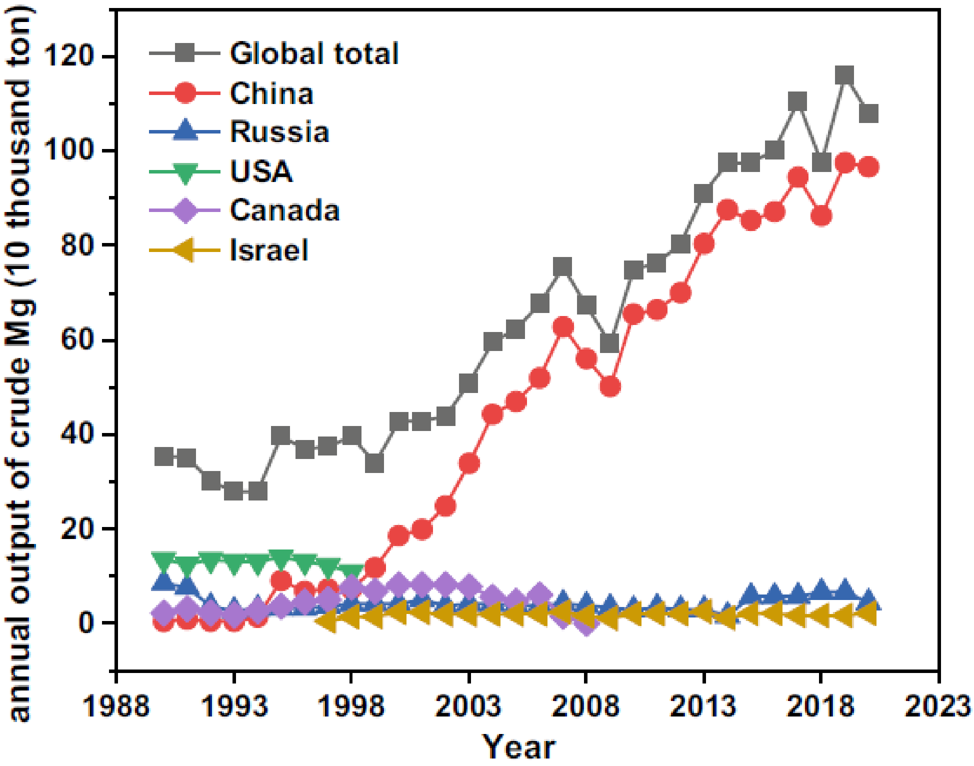

Figure 2. 3. Primary production amount of magnesium between 1988-2020 [19].

Less than 100,000 tons are produced each year globally using the electrolytic method (see in Figure 2. 3.), and the majority of these operations have been terminated or only partially suspended. Compared to the Pidgeon process, the electrolytic method uses substantially more energy and costs more money to produce magnesium[19].

The Pidgeon process, one of the primary processes, and the electrolysis process occur before the melting and refining stage in the manufacturing chain for magnesium. This process is crucial for magnesium to have the required purity and quality. It is common to employ primary magnesium ingots heated in a furnace until molten[20]. Magnesium is typically melted using an electric induction furnace. The molten magnesium is often subjected to a degassing procedure to release trapped gases, including hydrogen. To do this, vacuum and inert gas purging are frequently combined. Gas removal ensures that the final magnesium product has the required mechanical properties[21]. The molten magnesium is further refined throughout the refining process to reach the required purity level. Among the several refining techniques available are fractional crystallization, distillation, and solid-state purification. By eliminating any remaining impurities, these methods help to purify the molten magnesium to the requisite purity[22].

Melt processing is widely utilized in the primary production of magnesium as part of the refining process. By eliminating impurities, melt processing helps to further purify and improve the quality of molten magnesium[23].

2.2. Usage Areas of Magnesium and Magnesium Alloys

Germany was the only country producing electrolytic magnesium economically until 1916. Magnesium is used in military flares and tracer bullets in the US, Britain, France, Canada, and Russia. Global magnesium production fell between World War 1 and 2. Presently, China exports more magnesium than any other country [24]. The worldwide production and availability of magnesium are illustrated in Figure 2. 4.

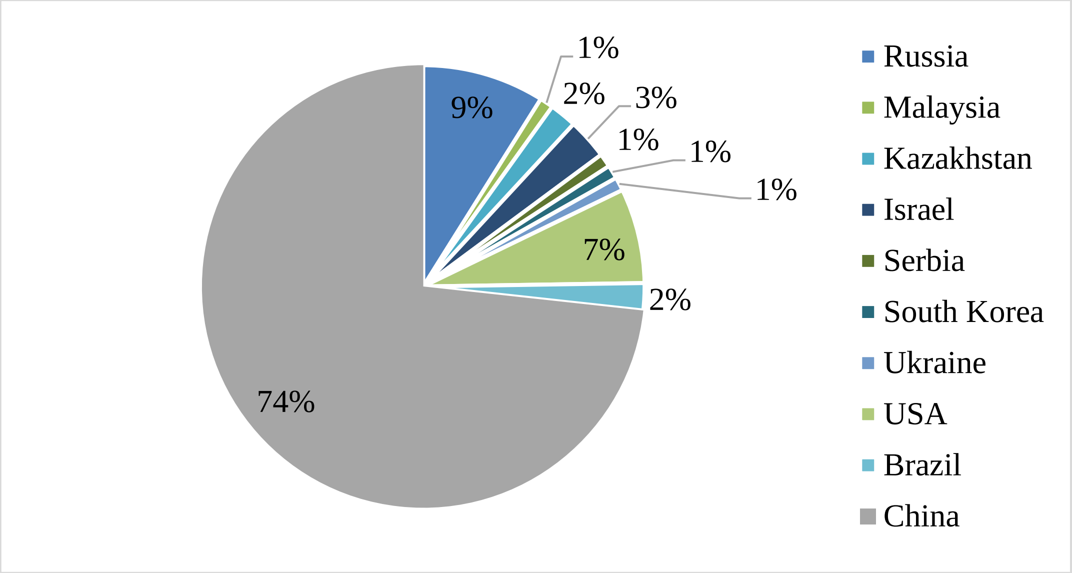

Figure 2. 4. Countries producing magnesium globally [24].

Magnesium alloys can be produced in various techniques, including casting, extrusion, and rolling. The particular alloy and the required characteristics of the completed product determine the production procedure. This process is known as alloying when magnesium is mixed with other elements to create a new substance with a specific set of desired properties[24, 25]. Magnesium metal has a significant economic role by enhancing materials' strength, hardness, and corrosion resistance, particularly when combined with aluminium [17]. As alloying components, aluminium, zinc, manganese, and rare earth metals are widely employed.

Magnesium alloys have a wide range of uses and are commonly used in a variety of industries due to their unique properties[26]. Magnesium is a silvery-white, a lightly machinable metal widely used in various applications due to its excellent properties, such as a high strength-to-weight ratio and good corrosion resistance. Table 2. 2. lists its chemical and physical characteristics [27].

Table 2. 2. Chemical and Physical Properties of Magnesium [28].

Atomic Mass	24.305 g/mol
Density	1.74 g/cm^3 at 20 °C
Melting Point	650 °C
Boiling Point	1105 °C
Elastic Modulus	45 GPa at 20 °C
Tensile Strength	60-220 MPa at 20 °C
Thermal Conductivity	156 W/mK

Magnesium and its alloys have a wide range of uses in many industries, including aerospace, automotive, electronics, construction, and medical equipment shown in Figure 2. 5.

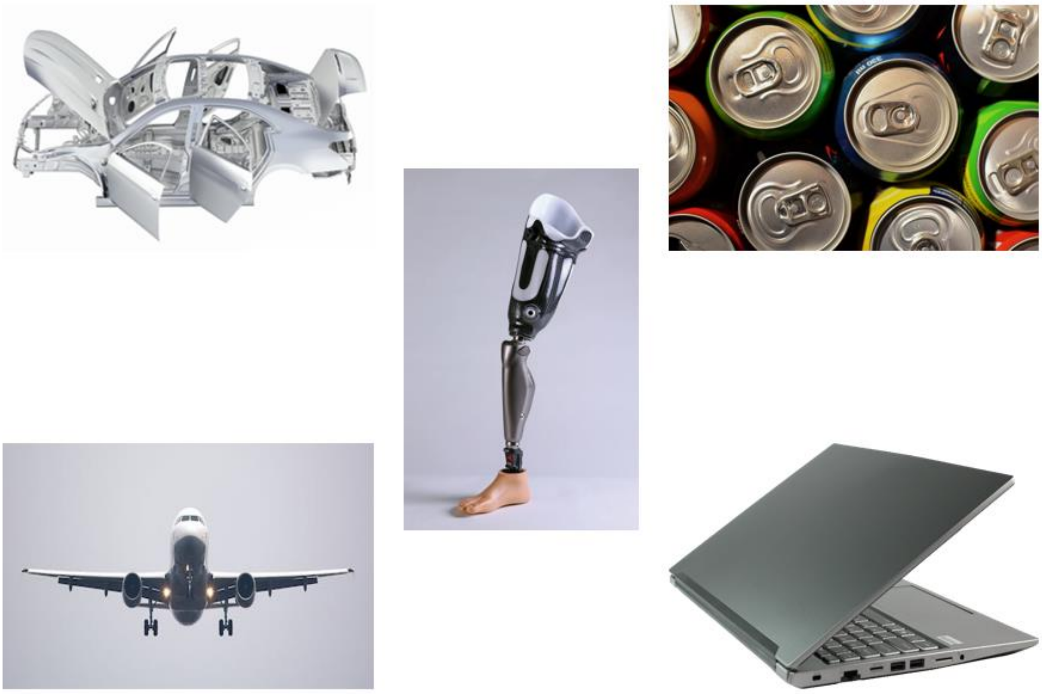

Figure 2. 5. Applications of magnesium alloys [19].

Figure 2. 6. illustrates the usage area of magnesium alloy. They are used in various parts, such as engine blocks, transmission cases, steering wheels, and brake pedals. Additionally, magnesium is an excellent conductor of electricity and is used in the manufacture of electronic devices such as laptop computers, cell phones, and digital cameras. It is used in medical equipment because of its biocompatibility and corrosion resistance and in the construction of implants such as bone screws, plates, and pins [19].

Magnesium is mainly used in the alloying of aluminium. The AZ series of alloys are most frequently used, according to statistics [24]. Aluminium and its capacity to withstand corrosion may be strengthened by adding magnesium in relatively small amounts. Many aluminium alloys contain magnesium [26].

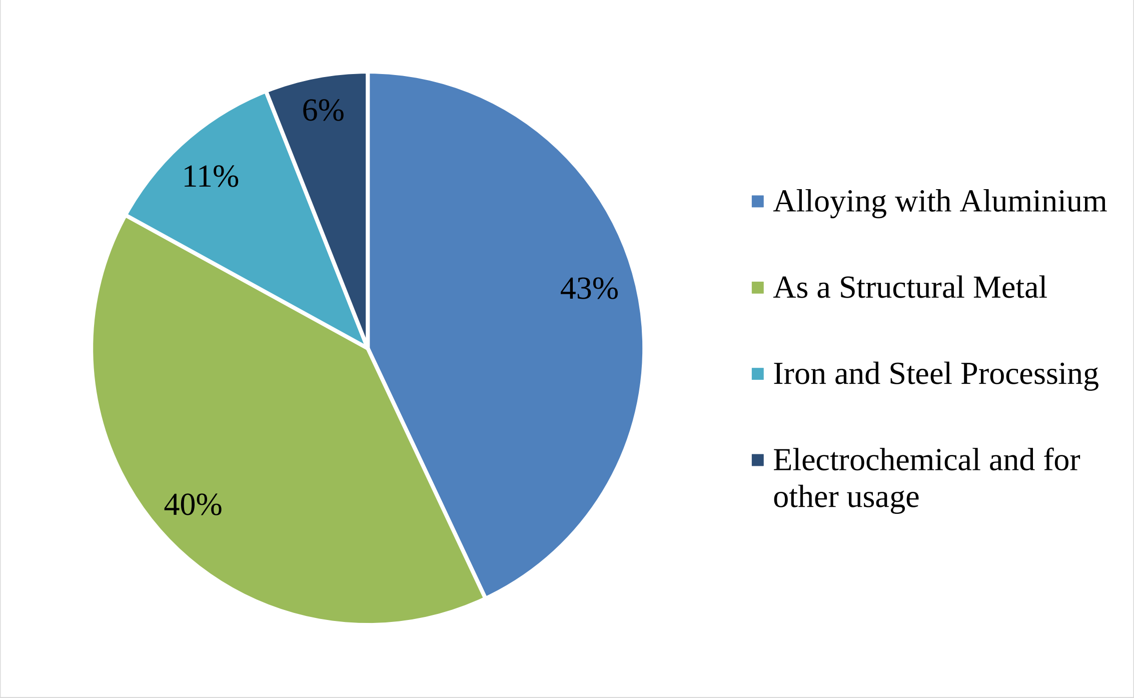

Figure 2. 6. Usage areas of magnesium metal [24].

2.3. Importance of Magnesium

The evaluation and the list of essential raw materials are meant to highlight the supply concerns of key components of the European Union economy [29]. The European Union study evaluated the risks and importance of sourcing 41 raw materials not produced in Europe but critical to their economic viability from 2010 to 2020 [30]. It is calculated by classifying each material according to supply risk, environmental risk, and economic importance shown in Figure 2. 7. For a material to be considered important, it must be subject to high supply risk or high national ecological risk and must be of high economic importance [31]. The OECD (Organisation for Economic Co-operation and Development) projects that by the end of 2060, demand for these important raw materials would increase by twofold, from 79 billion tons in 2020 to 167 billion tons. This prediction is made in a study in the EU list of vital raw materials (2020) [32]. One of these materials is magnesium metal [33]. The demand for magnesium has increased and it's used as a substitute for other heavy materials in many applications. Thus, recycling magnesium became important due to limited raw material accessibility and environmental concerns [34].

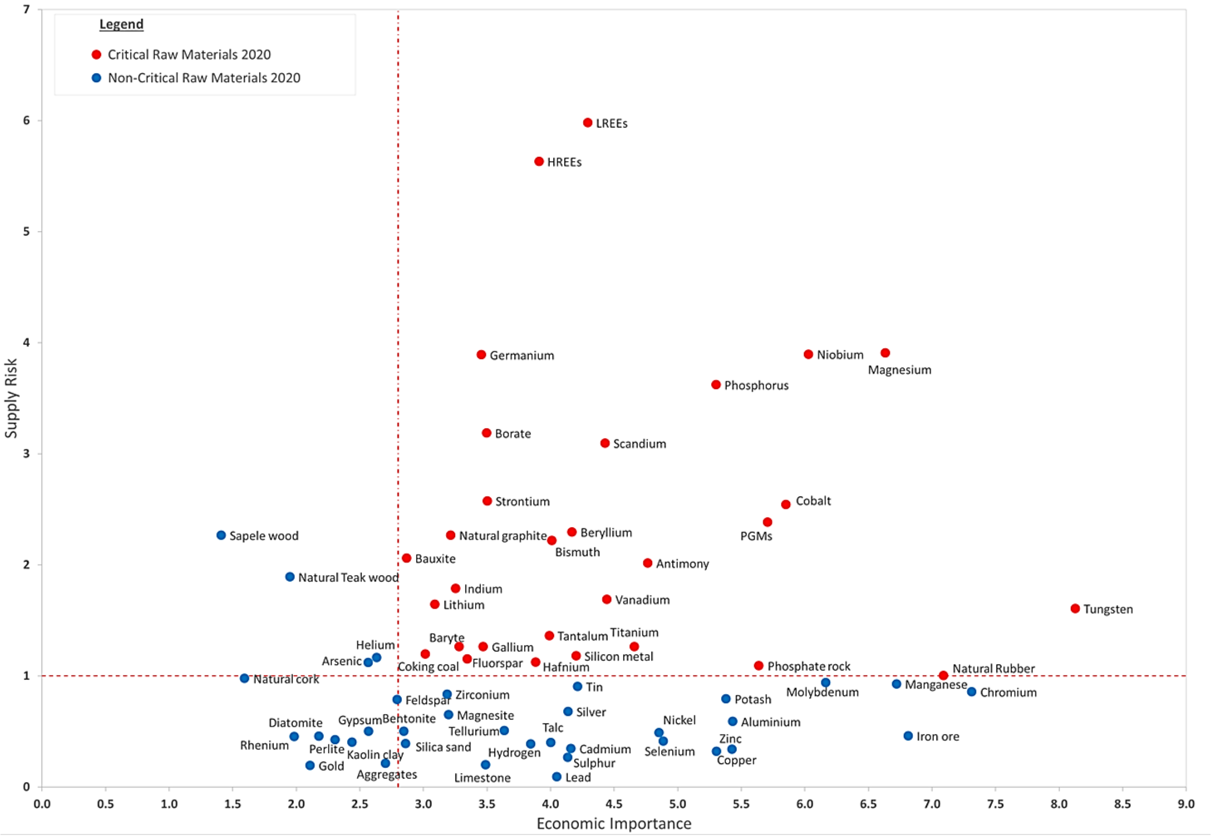

Figure 2. 7. Critical raw material list from the European Union [29].

Government and trade policies affect resource supply risks. There are several supply risks associated with magnesium metal. These are, respectively, limited natural resources, production restrictions, environmental regulations, increased demand, and competition for substitute materials. Due to its small geographic spread, magnesium's supply is susceptible to supply chain interruptions, trade restrictions, and geopolitical unrest [31]. The production of primary magnesium metal requires much energy as it must be extracted from its ores at high temperatures and using electricity. As energy costs may affect the availability and price of magnesium, this makes the cost of manufacturing vulnerable to changes in those prices. In many countries, strong environmental regulations must be followed when dealing with hazardous waste and pollutants that might be created during the production of magnesium. As a result of compliance, the supply of magnesium may be constrained, and production costs might increase. As it is known, since the demand for magnesium metal is increasing gradually in terms of industrial applications, it is a factor affecting its availability and price range. As the use of magnesium alloys increases, recycling becomes increasingly important from an economic and environmental aspect since they are difficult to recycle and include impurity elements or oxide particles [35].

Magnesium metal is not environmentally hazardous, but the mining and production procedures can have a negative impact on the environment. These are energy use, land use, water use, air pollution, and waste disposal, respectively [36]. Magnesium production requires a significant amount of energy in its processes. Using fossil fuels to generate this electricity can contribute to climate change while increasing greenhouse gas emissions. Removing magnesium requires cleaning and removing large areas. This can result in habitat destruction and loss of biodiversity. Magnesium production is a process that requires a significant amount of water and puts pressure on water resources, especially in areas where water is scarce [37]. Magnesium production can release various air pollutants, including particulate matter, nitrogen oxides, and sulfur dioxide, contributing to air pollution and adversely affecting human health and the environment. Magnesium production produces waste products such as sludge and brine that can be difficult to dispose of and potentially contaminate soil and water safely [38].

Recent years have seen a large increase in the usage of sleeve-type shaft kilns in Europe and Japan due to their ability to combine energy savings, environmental protection, and improved performance [10].

2.4. Oxidation Behaviour of Magnesium

Magnesium, a highly reactive metal, quickly reacts with oxygen to produce magnesium oxide. The oxidation of magnesium occurs at the metal's surface and is characterized by forming a thin oxide layer that acts as a defense against additional oxidation [39, 40]. Magnesium may oxidize in various corrosive environments, such as air, water, and others [41]. In the presence of air, magnesium oxidizes fast, forming a thin oxide coating on the surface as shown in Figure 2. 8. [42]. The oxide layer builds, and the weight increases as oxidation proceeds [43].

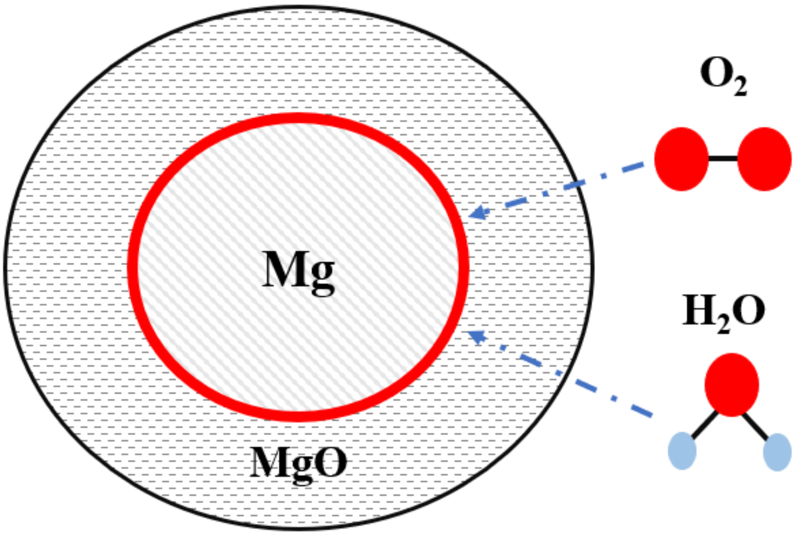

Figure 2. 8. Representation of the oxide layer formed on magnesium [42].

High temperatures can make the oxide layer porous, which speeds up oxidation rates. Temperature-dependent oxidation rates increase with temperature. Magnesium oxidizes more gradually in water than in air, and the pH and other ions present in the water also affect the speed of oxidation [44]. In neutral or acidic water, magnesium oxidizes gradually, forming a thin layer of magnesium hydroxide on the surface. The chemical stability of MgO in aqueous solutions is unstable. In aqueous solutions with pH values lower than pH is equal to twelve, magnesium oxide interacts with water to create magnesium hydroxide, which offers only minimal corrosion resistance. Magnesium oxidizes more quickly in alkaline water, forming a thick layer of magnesium hydroxide that may eventually flake off and expose the underlying metal to more oxidation [45].

Figure 2. 9. shows the oxidation of molten magnesium, the resulting oxide layer, and how oxygen diffuses to the metal surface through the oxide layer's pores (or more likely, how metal ions diffuse to the air-oxide interface).

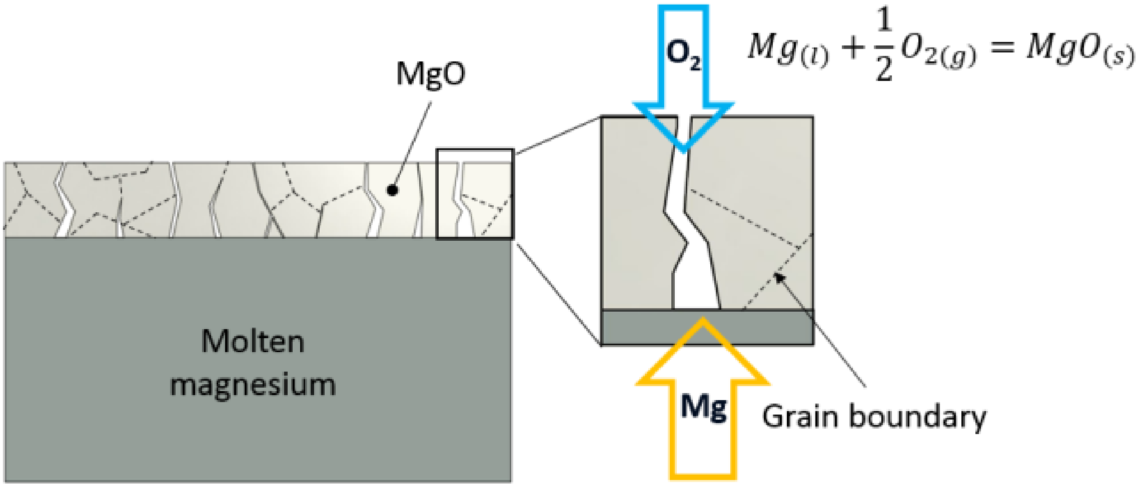

Figure 2. 9. Illustration of the formation of a damaged protective oxide layer on magnesium [46].

Magnesium interacts with air like a liquid, producing a considerable quantity of heat, or an exothermic reaction, as opposed to aluminium and steel [46]. The main benefit of magnesium alloys is their low density and the lightest metal for structural engineering is magnesium [45]. Alloying, surface treatments, and coatings are a few methods for preventing magnesium from oxidizing. The corrosion resistance of magnesium can also be improved by applying surface treatments like polishing or shot peening, which reduce surface roughness and increase the surface area of the protective oxide layer. Magnesium may form intermetallic compounds, which are more stable and less reactive than pure magnesium, and increase its oxidation resistance, by alloying it with other metals like aluminium or zinc. The quick production of a thin layer of oxide on the surface, which serves as a barrier against further oxidation, distinguishes the oxidation behavior of magnesium. The environment influences the rate of oxidation, and magnesium's oxidation resistance may be improved or controlled by a variety of techniques.

Pure magnesium metal reacts quickly to generate a coating of magnesium oxide on its surface when it is exposed to oxygen or air [43]. Molten magnesium generally has a tendency to ignite and burn because it oxidizes more quickly than magnesium does at low temperatures. Pure magnesium melts at 650 °C, whereas its ignition temperature ranges from 620 °C to 650 °C [45]. The chemical process for magnesium oxide and magnesium hydroxide is given in Equation 2.3 and Equation 2.4 [47].

$$Mg_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow MgO_{(s)} \tag{2.3}$$

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \tag{2.4}$$

One of the characteristics of the AZ63 magnesium alloy is its high specific strength and stiffness, which makes it a suitable material for lightweight structural applications. Nevertheless, AZ63 is prone to corrosion, especially in damp environments. It is typically coated with a protective layer or alloyed with rare earth elements to boost its resistance to corrosion. A coating of magnesium oxide forms on the surface of AZ63 when it is exposed to air or oxygen, going through a similar oxidation process to that of pure magnesium [47]. The chemical process is given in Equation 2.5.

$$2Mg_{(s)} + O_{2(g)} + x\ Al_{(s)} + y\ Zn_{(s)} \rightarrow 2MgO_{(s)} + x\ Al_2O_{3(s)} + y\ ZnO_{(s)} \tag{2.5}$$

Figure 2. 10. illustrates another characteristic of magnesium combustion: high ultraviolet and visible light emissions, which can account for up to 10% of the total energy emitted [48].

Figure 2. 10. Combustion of magnesium metal.

A controlled environment, such as a vacuum or an inert gas, or the application of coatings, films, or other protective layers to the metal's surface are a few techniques to slow the pace of oxidation. The resultant oxide layers protect the underlying metal against corrosion, although their precise composition and thickness will vary depending on the alloy's unique composition and the environment in which it is used. In addition to having great castability, weldability, strong damping capacity, and fairly high thermal and electrical conductivity, magnesium alloys are recyclable [45].

The Ellingham diagram (see in Figure 2. 11.) is a visual illustration of the Gibbs free energy shift in oxide formation as a function of temperature [49]. According to their standard free formation energies, the graphic illustrates the stability of various metal oxides at various temperatures [50, 51].

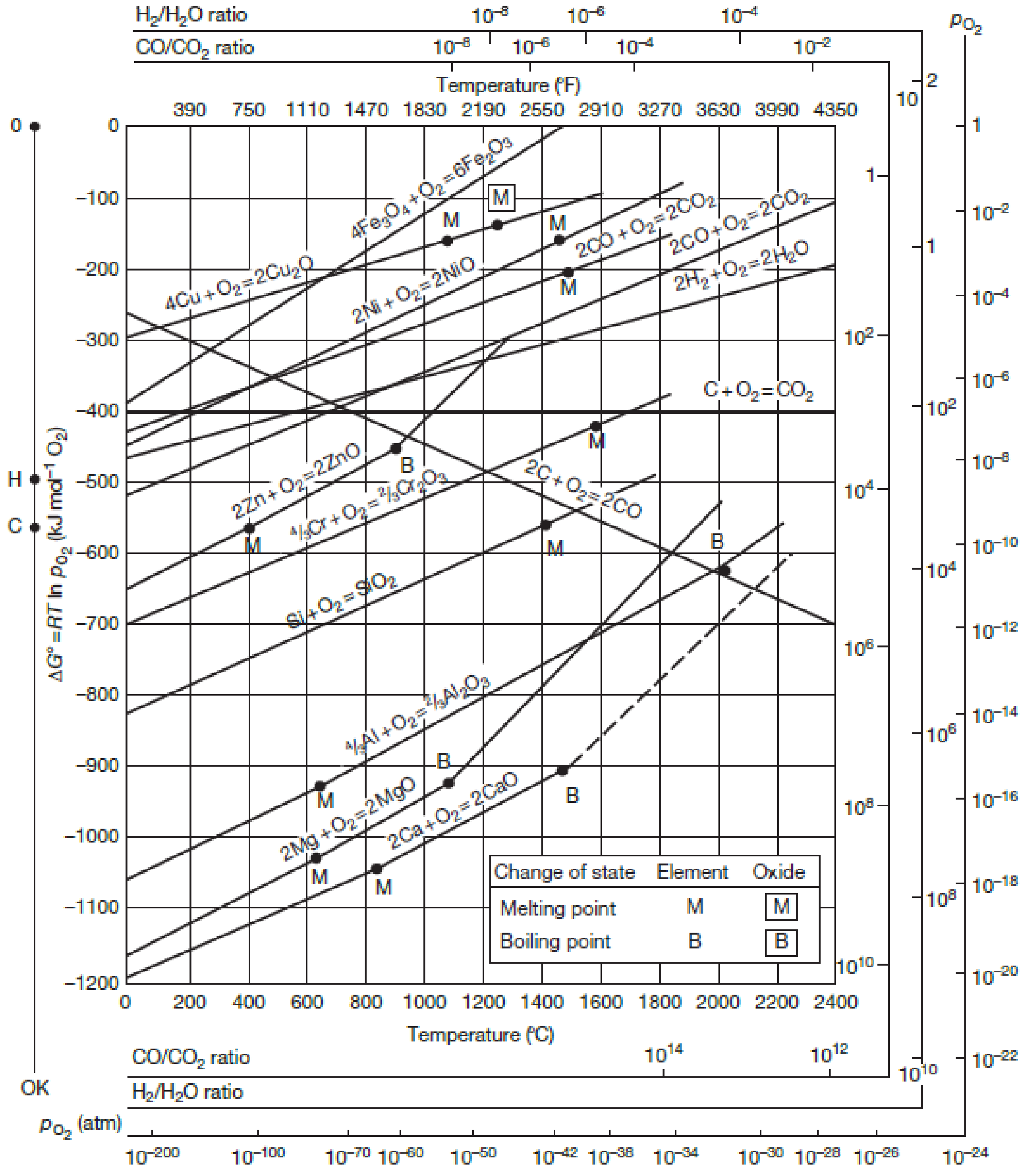

Figure 2. 11. Ellingham Diagram [52].

The Gibbs free energy shift in the production of magnesium oxide (MgO) is represented as a function of temperature in the Ellingham diagram. The following equation may be used to model how magnesium oxide is created from magnesium metal and oxygen gas (Equation 2.6):

$$2Mg + O_2 \rightarrow 2MgO \tag{2.6}$$

The graphic illustrates how the production of magnesium oxide from Mg and O_2 is thermodynamically advantageous since the free energy change is negative. MgO is stable 650 °C and does not combine with carbon to generate magnesium metal. The Ellingham diagram may be used to forecast the circumstances under which this reaction will take place, including the temperature and oxygen partial pressure [53].

2.5. Secondary Production of Magnesium

Secondary magnesium production refers to production of magnesium from different magnesium wastes and residues, such as production interruptions, machining chips, slag, and end-of-life magnesium products. The use of magnesium is increasing worldwide and there is a high amount of magnesium waste. Therefore, magnesium is highly recyclable [1]. Recycled magnesium can serve as an extra source of supply for primary manufacturing. The process of obtaining magnesium from secondary sources, such as recycled magnesium waste, magnesium alloys, and other magnesium-containing materials. Pre- and post-consumer waste are good sources of secondary magnesium [54]. In order to fulfill the rising demand for this useful metal and lessen the environmental effect of primary magnesium production, secondary magnesium manufacturing is an important and sustainable strategy. Compared to primary and secondary manufacturing, secondary production has significantly lower environmental impact and utilize fewer primary resources. Recycled magnesium uses only 5% of the energy needed to generate it and retains all of its chemical, physical, and mechanical qualities [2]. Additionally, using secondary magnesium maintains the material in a circular economy and lowers its carbon footprint [35]. Because magnesium oxidizes so readily, novel recycling techniques that can lessen the oxidation of in-house scrap are necessary to minimize metal losses and contamination. The more materials are recycled, the less waste will end up in landfills, rivers, and the atmosphere, which also uses less energy [2].

Only a few of the procedures involved in the secondary manufacture of magnesium include the collection, sorting, and processing of magnesium waste and other commodities containing magnesium. Different types of scrap may be processed together, so it is crucial to sort the scrap effectively [1]. There are eight categories for the classification of magnesium scrap, as shown in Table 2. 3.

Table 2. 3. System for classifying magnesium scrap [55].

Mg Scrap Classes	Characterization
Class 1A	High-grade clean scrap without impurities (e.g., scrap castings, biscuits, etc.)
Class 1B	Clean scrap with a high surface area in proportion to the weight
Class 2	Clean scrap with aluminum or steel inserts. No copper or brass impurities
Class 3	Clean, dry, and uncontaminated turnings and swarfs
Class 4	Flux-free residues (e.g., dross, sludge)
Class 5	Painted or coated scrap with/without Al or steel inlays. No Cu or brass
Class 6	Oily and/or wet turnings and swarfs
Class 7	Unclean and contaminated metal scrap (e.g., post consumer scrap) may contain: Si (Al alloys, shot blasting), Cu contaminated alloys, Ni coatings, Non-magnesium sweepings
Class 8	Flux-containing residues from magnesium recycling

Class 1A, 1B: Denser and high surface area scrap are the two subtypes of class 1 scrap. Depending on the targeted metal quality, class 1A scrap can be processed using powder or dust-free methods. However, due to its high oxide level, Class 1B can only be recycled by flux processing[56]. Scraps of grades 1A and 1B can be recycled to create high-purity alloys[2].

Class 2: The casting machine cannot directly recycle Class 2 scrap since it has extra components. Any casting with nickel or copper inclusions can be recycled into products other than pressure-casting grade materials through an external procedure. It needs to be carefully cleaned before being remelted to decrease different pollutants [55].

Class 3: Class 3 scrap is typically greasy, wet, and spilled or leaked from die-casting equipment. The oil from the scrap must be removed, and it must also be dried before remelting, which adds to the cost of processing. This is more than the value of the recovered metal; hence, recycling this material results in a net loss. However, given today's circumstances, there is no other choice from an environmental standpoint [57].

Class 4: All kinds of chips, swarfs, and small machinings are considered class 4 scrap. It can range significantly in size from chips to tiny flakes. Smaller pieces are more challenging to process, which raises recycling costs and lowers recycling effectiveness [56].

Class 5, 6, 7 and 8: Class 5, 6, and 7 scraps, slag, and sludge are all considered flux-free residues and are not considered hazardous waste. The majority of methods for recovering magnesium from these residues rely on flux-based recovery procedures. Most of the magnesium may be recovered, and any unprocessed residues can be further treated using filtration methods before being backfilled at locations that have received official approval. If the leftovers include at least 50% magnesium, the cost of recycling these scrap classes will be equivalent to the value of the metal recovered. Less than 50% of the metal content in the residue makes it unprofitable [38].

High-quality magnesium products are produced via a variety of procedures, including melting, refining, and alloying, using these wastes. The steps involved in secondary magnesium production are shown in Figure 2. 12., respectively.

The first step in producing secondary magnesium is gathering and classifying items that contain magnesium, by-products. The sources of these materials are frequently industrial sites, recycling operations, and manufacturing facilities. After the resources are gathered, they are sifted to eliminate any impurities that can damage the final product quality, such as iron, aluminium, and copper. Magnetic separation, eddy current separation, and air classification are examples of mechanical and manual procedures used in the separation process. After the separation process is applied, it is melted in a furnace to produce liquid magnesium. Magnesium can be refined to raise its quality after it has been melted and poured. Refining entails eliminating any leftover impurities and modifying the chemical makeup of magnesium to satisfy specifications. Alloying is the last stage in the secondary manufacturing of magnesium. Production can follow with several techniques, including rolling, extrusion, alloying, and casting. Due to their excellent strength-to-weight ratio, high thermal conductivity, and exceptional corrosion resistance, magnesium alloys are extensively utilized in various sectors, including automotive, aerospace, and electronics. Secondary magnesium production is a practical and cost-effective way to both meet the increasing demand for magnesium and reduce the environmental impact of primary magnesium production [1, 54].

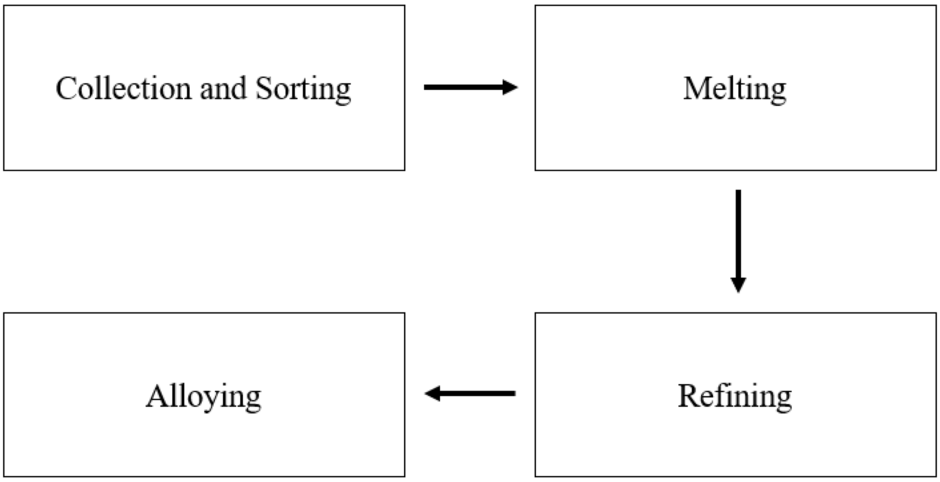

Figure 2. 12. Steps of secondary production of magnesium.

The production of secondary magnesium has several positive and negative environmental effects. Secondary production can minimize the adverse environmental consequences of primary magnesium production by removing the need for further mining and refining processes. This might lead to less trash creation, greenhouse gas emissions, and energy usage. During the smelting and purification of magnesium waste, sulfur dioxide, and nitrogen oxides can all be discharged into the atmosphere and the poor air quality that might result from these contaminants could damage the local population's health. Non-renewable resources like coal, oil, and natural gas may power energy-intensive processes like melting and refining magnesium scrap. Using non-renewable energy sources, which can produce greenhouse gas emissions, may accelerate climate change. Water pollution and the refining of magnesium scrap can result in waste streams that contain contaminants such as heavy metals. If not properly managed, these waste streams have the potential to contaminate water sources and damage aquatic ecosystems.

Facilities can use renewable energy sources such as solar and wind power to reduce their reliance on non-renewable energy sources and reduce greenhouse gas emissions. To limit these consequences, facilities can take many steps to reduce energy usage, lower waste generation, and prevent contamination.

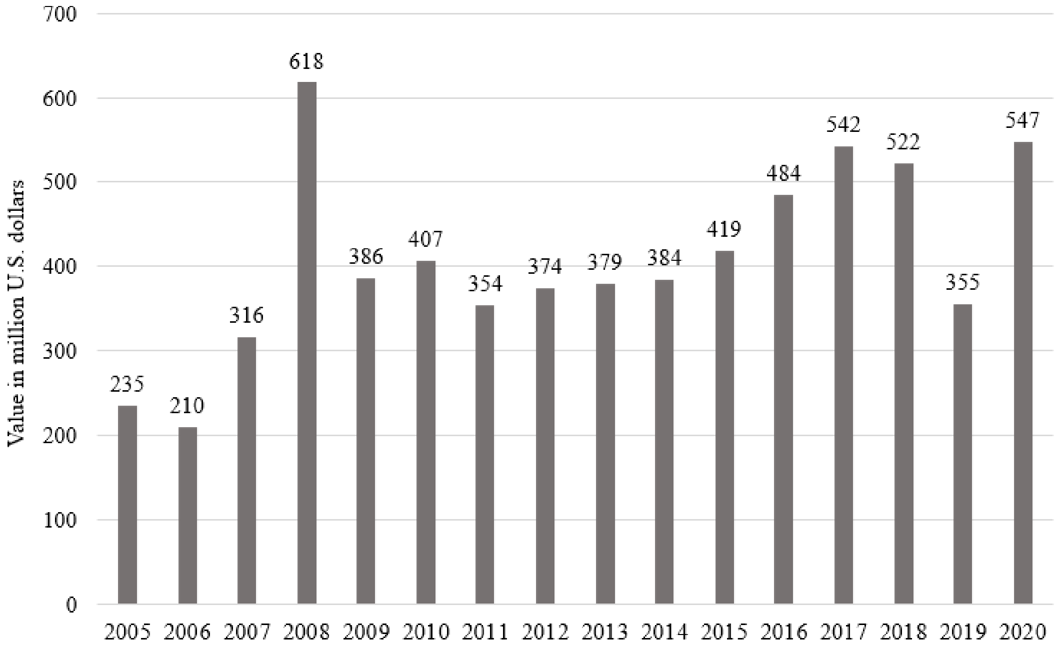

Figure 2. 13. From 2005 to 2020, the amount of magnesium that was reused from scrap on a yearly basis in the United States [58].

The specific amount of magnesium recycled annually is an indicator of overall industrial activity and magnesium demand in the US over a given time period [18]. In Figure 2. 13**.,** the recycled magnesium scraps are shown in millions of dollars by year [58]. Secondary magnesium was recovered in 2022 using 83,000 tons of new scrap and 37,000 tons of used scrap. 42% of the secondary magnesium recovered was utilized in castings, ingots, and other products, while around 58% was used in aluminum-base alloys [59].

2.6. Remelting Techniques of Magnesium Scrap

Magnesium usage has been increasing, thus there is a rising demand for more efficient methods for sorting and refining magnesium to recycle all forms of scrap types [55]. It is classified into two categories: fluxless refining techniques and other flux refining methods. There are several techniques that are used in magnesium remelting shown in

Figure 2. 14. such as cover gas, vacuum distillation, and remelting under salt flux. Due to magnesium's susceptibility to oxidation, recycling is theoretically possible without sacrificing quality but is extremely time-consuming. Because of this, contaminated magnesium is seldom used to make new, pure magnesium alloys. Because they are easy to recycle, alloys are constantly available [17].

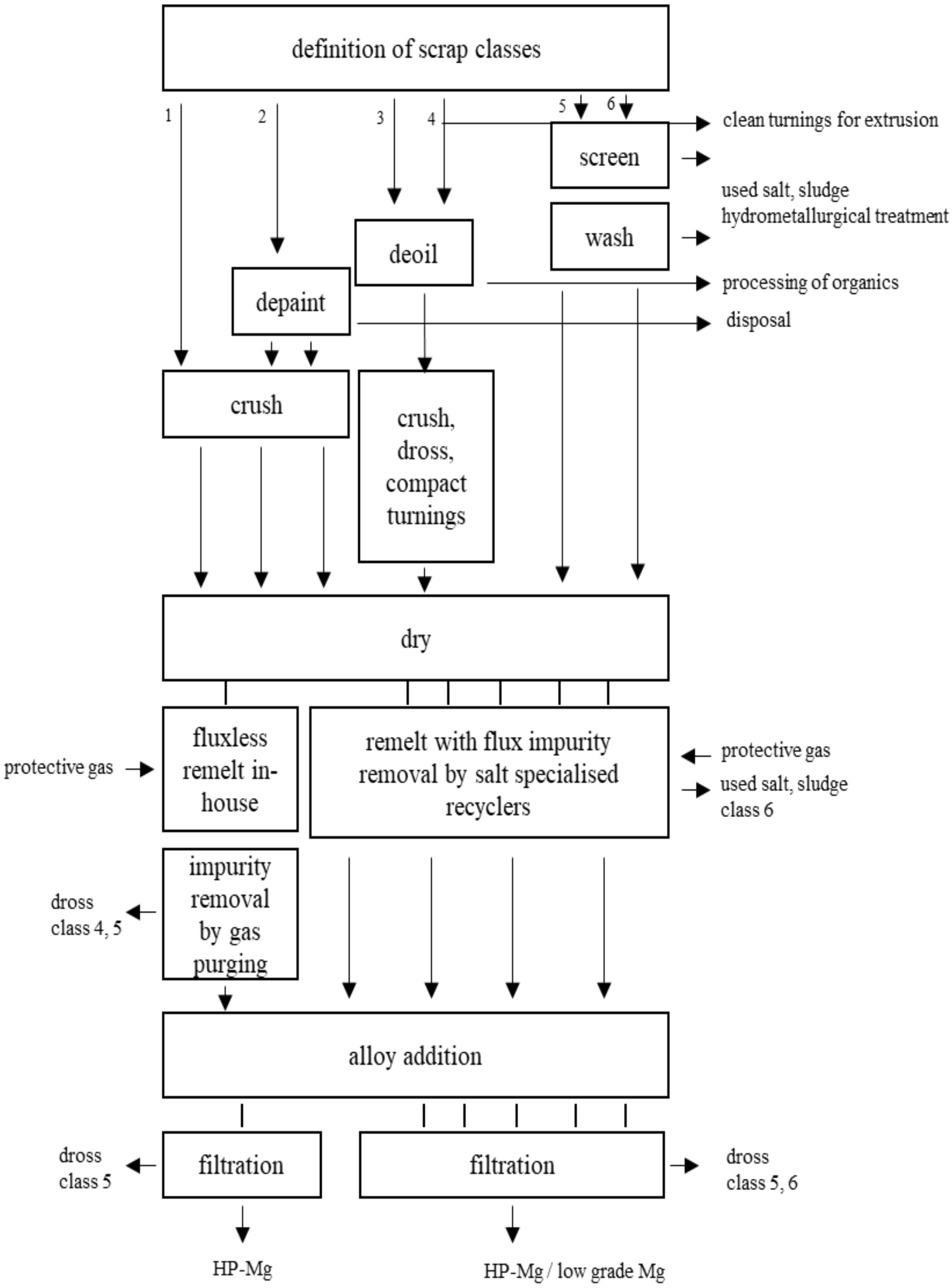

Figure 2. 14. Process for recycling magnesium based on the type of scrap [2].

2.6.1. Vacuum Distillation Refining:

Vacuum distillation is one of the solutions for recycling any scrap magnesium. For usage in the semiconductor sector, this process seeks to transform magnesium scrap into very high-purity (99.999%) magnesium [56]. However, vacuum distillation techniques have poor and inconsistent efficiency and the processes for vacuum distillation are intermittent and produce a little amount of recycled magnesium [60]. Magnesium in condensed, fine form is likewise quite pyrophoric. Magnesium must be vaporized at a higher temperature as shown in Table 2. 4.

Table 2. 4. Vapor pressure of magnesium at different temperatures [56].

Temperature (°C)	Pressure (atm)
600	0.0013
650	0.0039
700	0.0094
750	0.021
800	0.043
900	0.152
1000	0.432
1050	0.684
1095	1.00

The vacuum distillation column is shown in Figure 2. 15. The column, crucible, and vertical condenser, which has many levels of horizontally running high-grade graphite baffles, are all constructed of high-grade graphite. The column can be made from high-purity steel instead of high-purity graphite, although the magnesium that results could be a bit less pure. The column is housed in three zones of a resistance furnace. While the second zone heats the condenser over the boiling point of magnesium, the third zone controls the temperature of the column below that threshold [2].

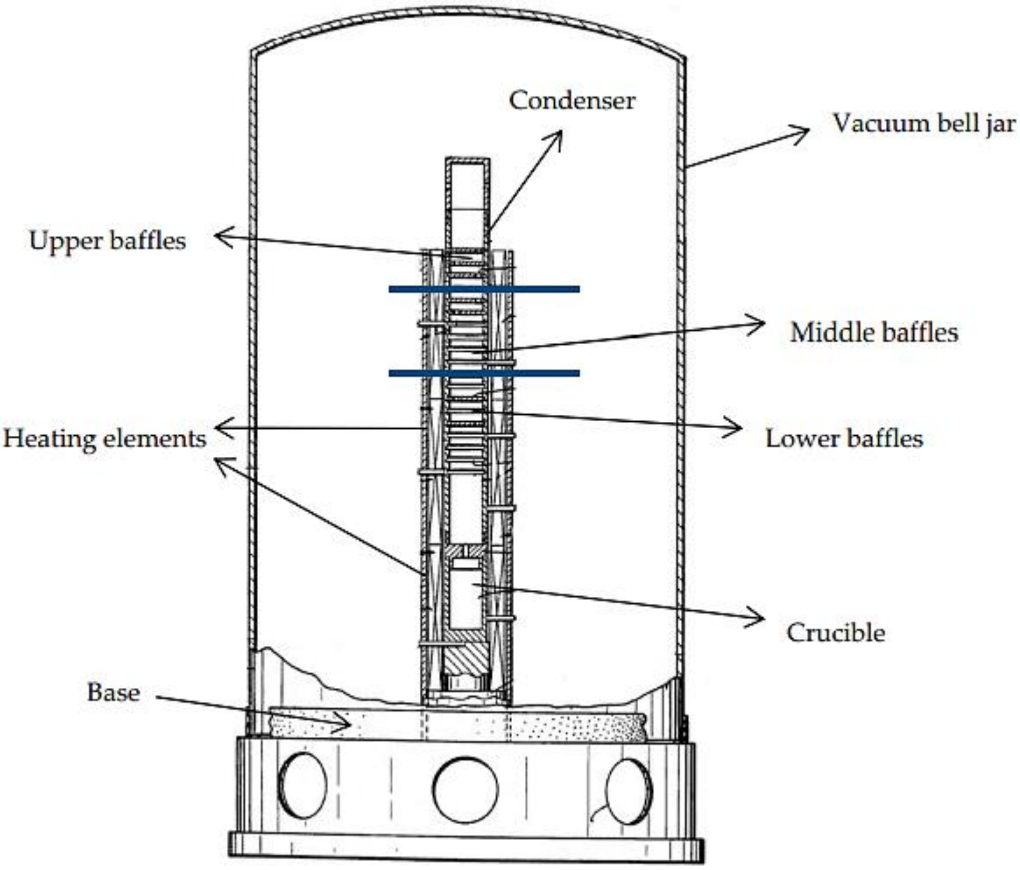

Figure 2. 15. Components of a vacuum distillation setup [61].

The magnesium inside the crucible is supposed to evaporate in the first zone. It is desirable for the temperature to decrease as the height of the column rises. The vapours must be slowed down by the baffles in order for each baffle's unique condensation conditions to be satisfied. Under each condition, either pure magnesium or certain impurities can condense. The magnesium will then condense onto the baffles, producing a pure product. The magnesium can be reached in the condenser's two vertical portions, and the positioning of baffles may be adjusted as well. The column is then subjected to a vacuum. Magnesium is heated in the crucible until it either reaches its boiling point or until the vacuum pressure within the chamber is exceeded by the vapor pressure. The two baffles at the condenser's extreme ends restrict the flow of the magnesium vapours, while the baffles in the middle gather the majority of the condensed material. When the vapor pressure drops below the magnesium vapor pressure, the metal condenses out of the gas.

As a result, it has relatively little potential for use in the recycling sector [55]. During the vacuum remelting process, the magnesium scrap is melted in a vacuum atmosphere to avoid oxidation and contamination of the metal. Additionally, the vacuum aids in eliminating contaminants like hydrogen, which can lead to flaws in the finished product.

High-purity magnesium alloys are frequently created using this technique for aerospace and other high-performance applications [62].

2.6.2. Cover Gas Remelting:

As cover gases, mixtures of SO_2 or SF_6 with CO_2, N_2, Ar or dry air are frequently employed to prevent excessive oxidation and burning of molten magnesium [19]. The cover gas remelting scheme is in Figure 2. 16**.** Magnesium has been processed to the required standards, it is either pumped or tilt-poured into a holding/casting furnace. A gas combination containing SF_6 is the most typical cover gas employed. After that, the magnesium solidifies into substantial ingots. Flux refining's key benefit is its capacity to clean up filthy magnesium scrap. The technique is a reasonably cost-effective method for refining magnesium because of the cheap initial capital cost of the equipment as well [55].

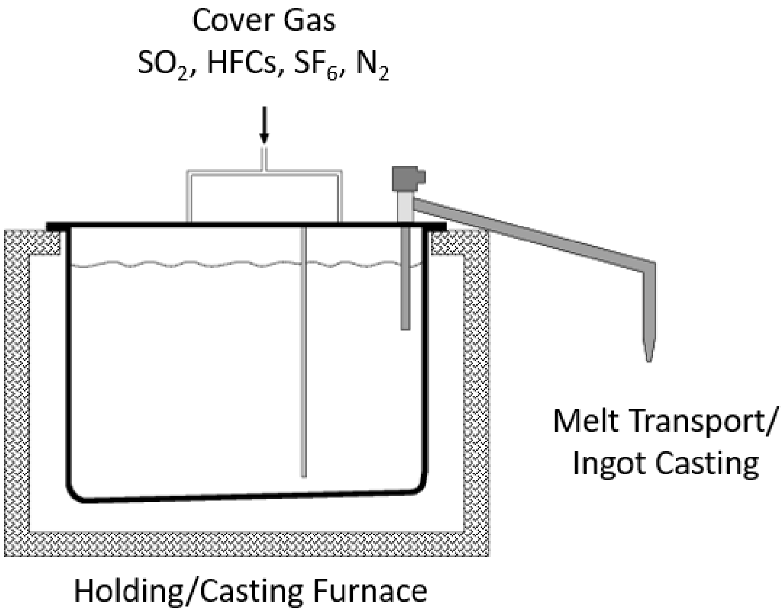

Figure 2. 16. Scheme of cover gas remelting [56].

The protective environment of air, CO_2, and 0.3-0.5% SF_6 is used in a technique that includes a filtration mechanism that is claimed to effectively reduce non-metallic impurities. Molten metal is moved into ingot molds, transfer pots, holding pots, or die-cast shot sleeves using a pump with an appropriate suction filter[63]. Research on the protective layers that develop on molten magnesium and its alloys under gas protection has been ongoing ever since SF_6 was shown to be a greenhouse gas, with the goal of discovering viable industrial substitutes for SF_6 gas for melt protection. In 2018, the European Union banned the use of SF_6 gas [53].

2.6.3. Remelting Under a Salt Flux:

Utilizing salt flux during recycling aids in removing and suspending the oxide coating, as well as enhancing droplet coagulation and minimizing dross production. By wetting the oxide coating and starting its deterioration, the salt flux removes it off the surface of the molten magnesium droplets. In the flux are pieces of the oxide sheet that had their magnesium removed. Additionally, flux shields the metal from the furnace's environment, halting the growth of additional oxides. The diameter of the metal droplets grows as a result of the coalescence of the droplets, increasing the likelihood that they will escape the salt flow. Therefore, the efficiency of the recycling process will be higher the better a salt's capacity to coalesce [64].

Salt flux uses both fluorides (CaF_2 and NaF) and chlorides (NaCl, KCl, and $MgCl_2$). Chlorides are frequently employed to increase the flux's fluidity and are combined to reduce the melting point of recycled magnesium. The addition of fluorides separates the oxide coating that covers the metal surface and encourages coagulation [65]. In order to improve coalescence, salt flux boosts the interfacial tension between the metal and the oxide. Fluxes made of salt purify the metal of impurities, keep the melt from oxidizing, and enhance the amount of metal produced. Cleaning metal, reducing excessive oxide formation, removing non-metallic impurities in the melt, and cleaning furnace walls may be accomplished using this technique. A salt fluxes capacity to coagulate will increase the yield of the recycling process [66]. The effectiveness of recycling magnesium is significantly influenced by coalescence. The addition of flux to molten metal causes impurities to react and form skimmable dross or slag, which may then be removed. This technique is useful for cleaning metal, reducing excessive oxide growth, removing non-metallic contaminants from the melt, and cleaning furnace walls [67, 68].

By modelling with the commercial program FactsageTM and DSC data, Figure 2. 17. demonstrates that a eutectic ternary combination of $MgCl_2$/KCl/NaCl has a melting temperature of 383 °C and a eutectic composition of 55-20.5-24.5 wt% [69]. Leading research teams have chosen the chloride combination $MgCl_2$/KCl/NaCl as the most potential high-temperature material for the next generation of molten salt technology [70-73].

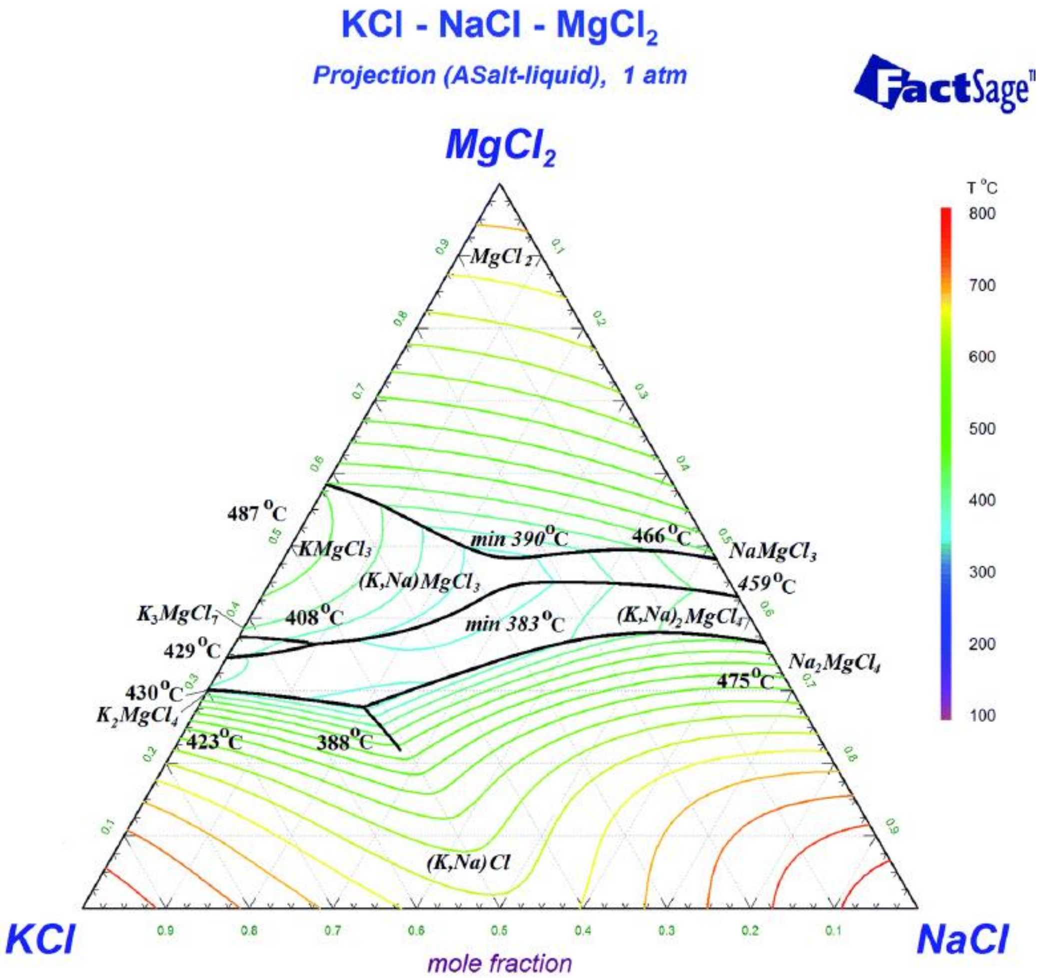

Figure 2. 17. Ternary phase diagram of NaCl MgCl$_2$ KCl by using FactSage Software [74].

The duties of the salt fluxes are as follows:

- Covering the molten metal to prevent oxidation.
- Increasing the net metal yield.
- Refining the metal from non-metallic inclusions and dissolved metallic impurities.
- Enhance thermal efficiency in the furnace.
- Promoting the coalescence of metal droplets to form the molten bath.
- Lowering the freezing point of the salt flux.

Using salt flux to recycle magnesium has both advantages and disadvantages. Positive aspects include the capacity to purify contaminated magnesium scrap, suitability for all classes of scrap, and reduced oxidation during melting[2]. The oxide layer might undergo spherical transformation when it is cracked without being removed [66]. To achieve the lowest free energy and promote coalescence, the oxide layer is too thick to be broken either by thermal expansion or the spherical transformation of droplets. The activity of the surfactants is a more important factor to consider while integrating. Figure 2. 18. shows the effect of fluoride to coalescence efficiency between various fluoride additions.

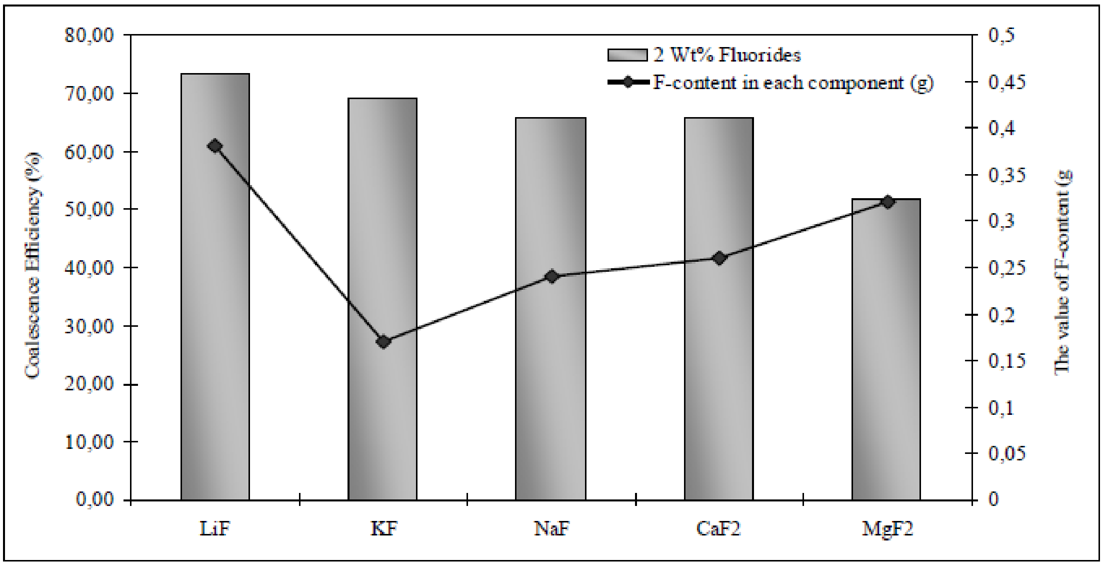

Figure 2. 18. Effect of various fluoride-containing salts on coagulation of magnesium chips [75].

The percentages of fluorine ions contained in the salts are respectively LiF 73%, MgF_2 61.3%, CaF_2 48.7%, NaF 45.2%, KF 32.7%. The presence of additional elements such as lithium, sodium, calcium, or potassium is thought to have a significant impact on coalescence efficiency in the magnesium system, making it impossible to draw the conclusion from these experiments that the presence of more fluorine ions leads to greater coagulation [75]. Salt fluxes with fluoride salt additions produce more metal because there is less metal suspended in the salt phase [64]. LiF and MgF_2 are still uneconomical options to be employed in magnesium salt fluxes due to their excessively high pricing. However, KF, NaF, or CaF_2, whose costs are substantially lower, would be smart choices to use in magnesium salt fluxes [75].

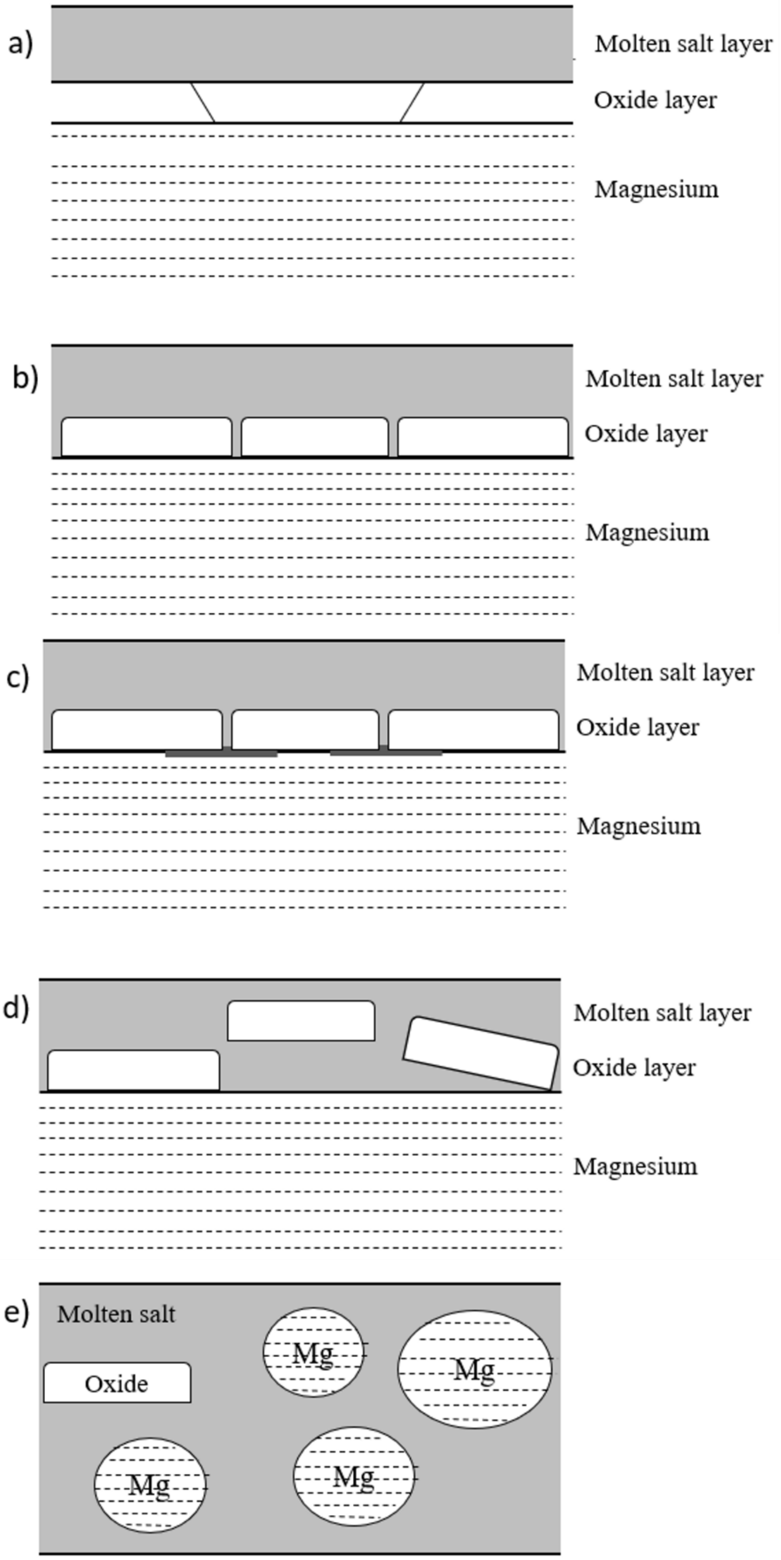

Figure 2. 19. An illustration of the oxide separation caused by the molten salt. (a) interaction between the oxide layer and molten salt, (b) corrosion of the oxide surface from the boundaries, (c) the diffusion of chloride to the oxide/Mg interface, (d) the oxide layer detaches from the salt and (e) the magnesium droplets [41].

Figure 2. 19. schematically shows the recommended process for removing the oxide from the surface of molten magnesium. The salt initially corrodes the borders of the oxide grain (Figure 2. 19.b). Molten salt builds up and finally pours at the oxide-magnesium interface (Figure 2. 19.d). Finally, the inside of the salt layer begins to develop and distribute magnesium droplets (Figure 2. 19.e). This process is related to hot corrosion, which takes place when a metal is exposed to a chloride-rich environment and develops a protective oxide layer [41].

Foundries reduce the formation of oxides, non-metallic inclusions, and dross when melting and processing molten magnesium alloys. The biggest problem with remelted magnesium alloy chips and light scrap is that they have a large surface area of oxidized and hydroxide active surface area, and fluxes are used to solve these problems. When flux is introduced to molten metal, impurities react to create scrapable dross or slag. Salt fluxes should be less dense than the melt in order to cover the melt surface and stop oxidation. The oxide films detach off the metal and float in the flux together with other contaminants. Therefore the viscosity of salt rises [66]. Even oxide concentrations as low as 10% can thicken the flux to the point where it precludes coalescence, according to studies on the effects of oxide concentrations and particle sizes on flux viscosity[76]. When the remelting process is finished, the fluidity of the salt layer rapidly decreases, and as a result, so does effectiveness. To encourage metal/dross separation, it should have a low viscosity [77].

Recycling is crucial to lowering the cost of magnesium-cast components. This method is widely used to recycle waste magnesium that has been polluted or to produce magnesium alloys with specific properties [78]. Chips made of magnesium alloy provide a significant recycling challenge since they have a sizable surface area that is MgO-coated. The reactions of the chips with moisture cause significant oxidation, which results in metal losses[79].

CHAPTER 3

MATERIALS AND METHODS

The experimental setup and procedure for recycling the pure magnesium and AZ63 magnesium alloy chips are explained in the following sub-chapters.

3.1. Materials

Pure and AZ63 magnesium chips (shown in Figure 3. 1.) were machined from ingots to increase the surface area, and the composition of the ingots are shown in Table 3. 1. Salt composition, temperature, salt factor, and the compaction degree of turnings on the recovery efficiency were selected as the parameters. A mixture of NaCl (ISOLAB, 99.5%), KCl (SIGMA-ALDRICH, 99.0%), $MgCl_2$ (TEKKIM, 98.0%), CaF_2 (SIGMA-ALDRICH, 97.10%), and NaF (TEKKIM, 98.0%) was used as the salt flux for the remelting experiments.

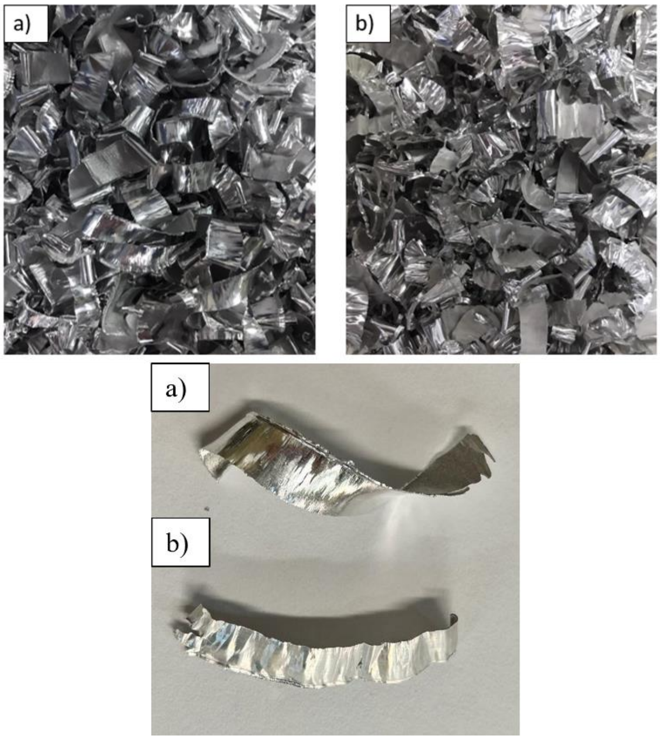

Figure 3. 1. a) AZ63 magnesium alloy chips b) pure magnesium chips

Table 3. 1. Chemical compositions of pure magnesium and AZ63 magnesium alloy (wt.%).

Pure Mg	Mg	Be	Fe	Mn	Al	Si	Ni	Cu	Zn
	99.960	0.0001	0.0038	0,0181	0.0045	0,0048	0.0005	0.0019	0.0033
AZ63	Mg	Be	Fe	Mn	Al	Si	Ni	Cu	Zn
	90.283	0.0012	0.0032	0.6628	5.6007	0.0033	0.0008	0.0003	3.4386

3.2. Experimental Setup

A laboratory-scale resistance chamber furnace shown in Figure 3. 2.a (Protherm Furnaces PLF series 140-160 max temp: 1600 °C) that can heat up to 1600 °C was used for remelting experiments. The casting furnace (Protherm, shown in Figure 3. 2.b), was used in the premelting of the salt flux. A graphite rod was used to stir the molten salt to help the homogenization and gas release, and an iron mold was used to cast the pre-melted salt. A clay-bonded graphite crucible in A2 (95x109x61 in mm) was used for the remelting experiments, and A5 (124x152x86 in mm) size crucible was used for the premelting salts experiments. The tools that were used for the remelting experiments are shown in Figure 3. 3

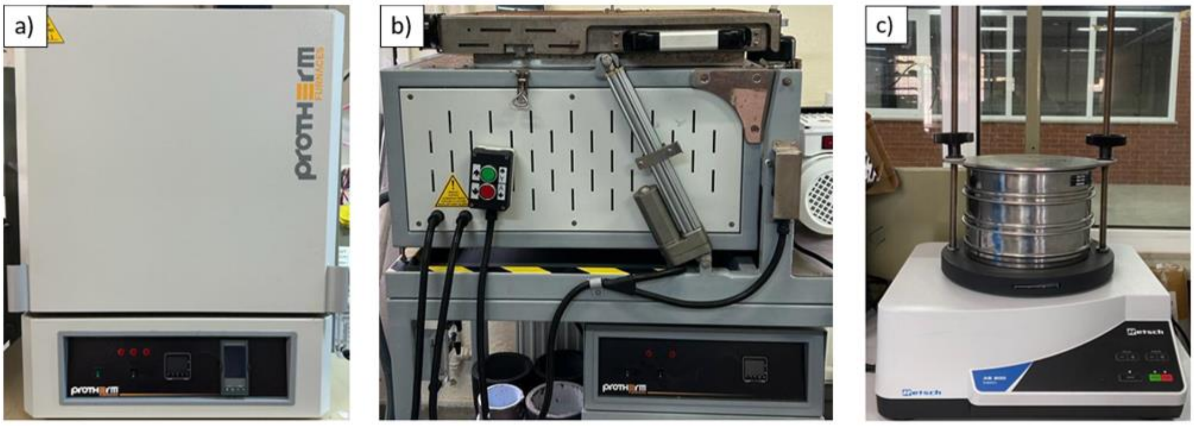

Figure 3. 2. (a) Protherm laboratory-scale electrical resistance chamber furnace (b) Protherm tiltable casting furnace (c) Retsch AS 200 BASIC vibratory sieve shaker.

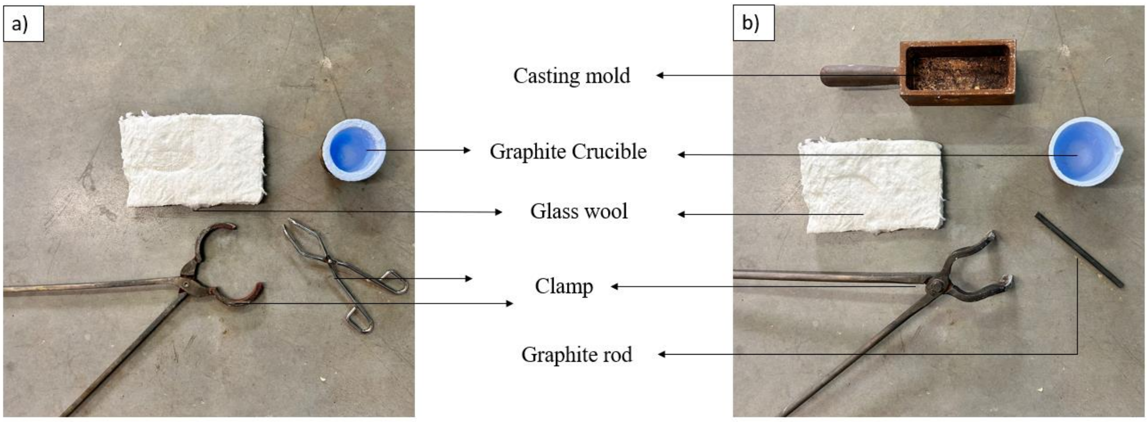

Figure 3. 3. Setup for the a) remelting process and b) premelting of salt process

3.3. Experimental Procedure

This chapter covers the procedure of the remelting experiments both for the chips and salt as well as the characterisation of the samples.

3.3.1. Pre-melting of the Salt Flux

To examine the impact of premelting, salt was premelted to achieve a homogeneous flux before being used in the remelting trials of the chips. A salt mixture was prepared using different compositions of NaCl, KCl, $MgCl_2$, and CaF_2 or NaF salts for pre-melting. The salt compositions and parameters are shown in Table 3. 2.

Table 3. 2. Salt compositions (wt%).

$MgCl_2$	NaCl	KCl	CaF_2 / NaF	Salt Condition
57.00	25.00	16.00	2	Manually Mixed Salt
56.33	24.33	15.33	4	Premelted Salt
56.17	24.17	15.17	4.5	
56.00	24.00	15.00	5	
55.83	23.83	15.83	5.5	
55.67	23.67	14.67	6	
55.00	23.00	14.00	8	Manually Mixed Salt

The mixed fluxes were pre-melted in the graphite crucible at 750 °C in the casting furnace and casted into an iron mold coated with BN. Reaching the target temperature molten salt was poured into the mold. After cooling down, the flux was crushed into fine powder and used for the chips remelting experiments. The procedure for pre-melted salt preparation is shown in Figure 3. 4.

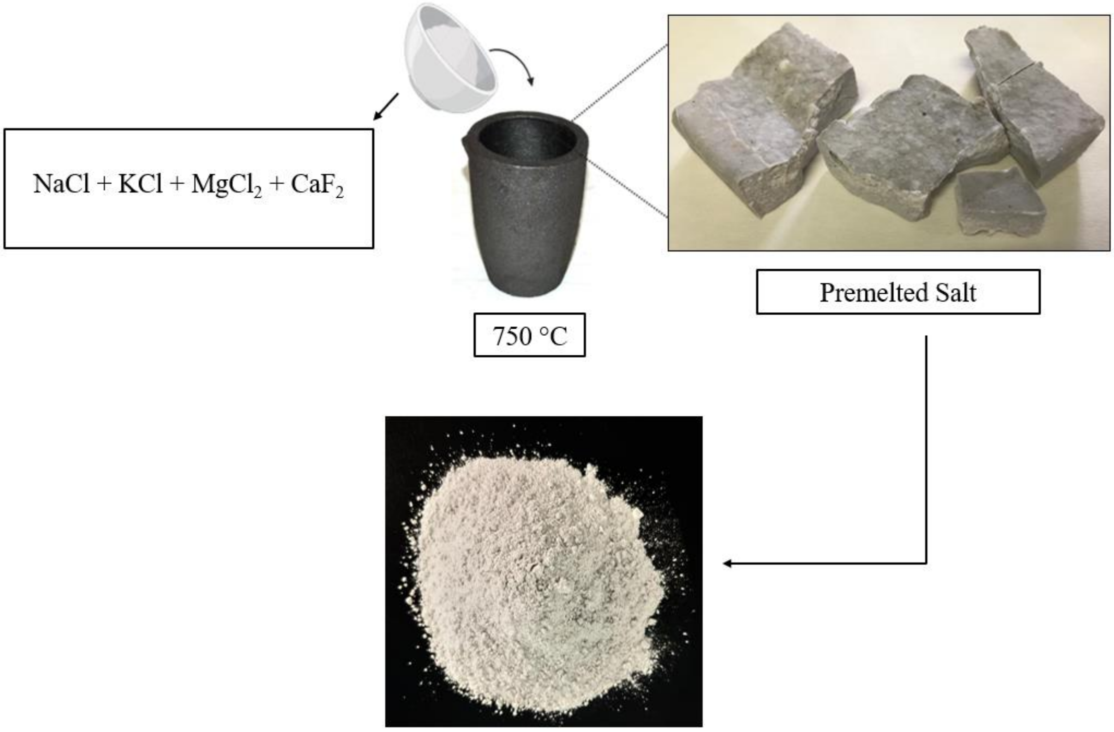

Figure 3. 4. Schematic representation of preparing the pre-melted salt flux.

3.3.2. Pressing of Magnesium Chips

Pressing was carried out to observe the effects of compaction and surface area on the recycling yield. Since the AZ63 magnesium alloy is brittle and the chips are more difficult to shape than pure magnesium chips, this process was applied only to pure magnesium in the laboratory. Figure 3. 5. shows the shape of the loose and pressed chips.

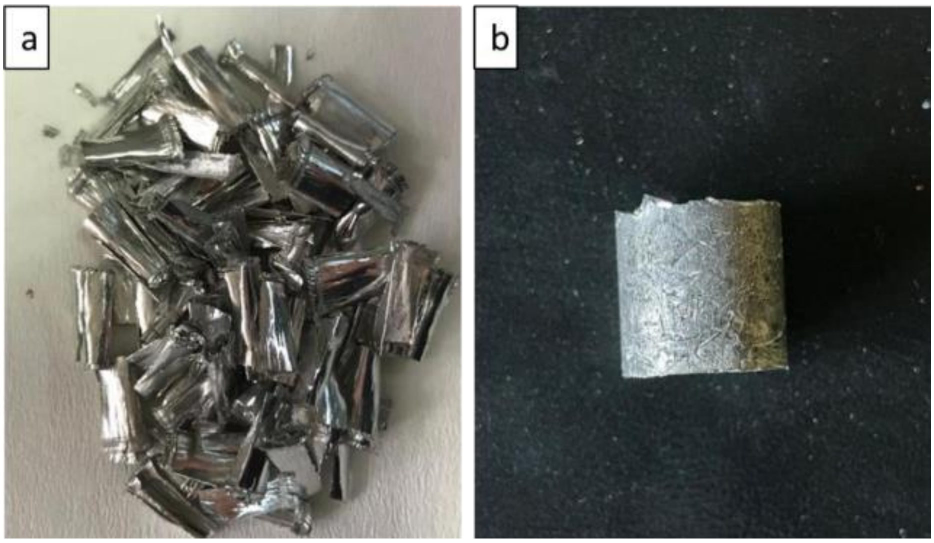

Figure 3. 5 a) Loose chips b) Pressed chips (d=20 mm).

3.3.3. Remelting Experiments

Chips made from pure, and AZ63 magnesium alloy ingots were used for remelting experiments. A salt mixture was prepared using different combinations of NaCl, KCl, $MgCl_2$ and CaF_2 or NaF salts. The samples were remelted in a clay-bonded graphite crucible by a laboratory-scale electrical resistance chamber furnace at 850 °C with a 6 K/min heating rate under an open atmosphere, with a holding time of 15 minutes. The schematic representation of remelting experiments for both AZ63 and Pure magnesium chips is given in Figure 3. 6.

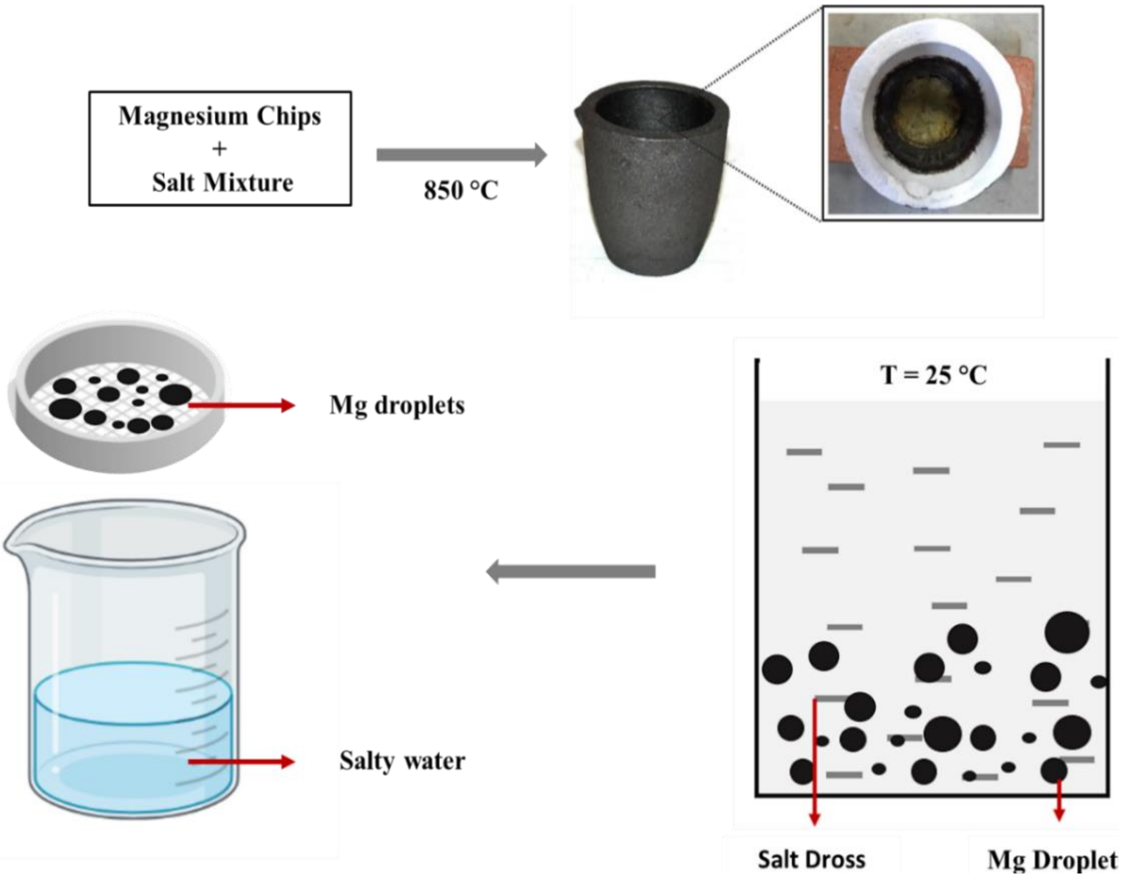

Figure 3. 6 . Schematic representation of remelting experiments for both AZ63 and Pure magnesium chips.

Experiments were repeated 3 times to get an accurate result. Each remelting experiment employed 4 grams of chips, and each experiment's salt-to-scrap ratio was set at 10 to thoroughly cover the scraps during remelting. Experimental parameters are shown in detail in Table 3. *3*.

Remelting experiments of pure magnesium chips are in the experiment 1-19 given in Table 3. *3*. Pure magnesium chips were remelted to evaluate the impact of the F-amount in the salt, seven various CaF_2 (1-7) and NaF (13-17) addition amounts (2%, 4%, 4.5%, 5%, 5.5%, 6%, and 8 wt.%) were studied.

Pre-melted salt was used to compare the effect of salt on pure magnesium chip at different CaF_2 (4%, 4.5%, 5%, 5.5%, 6 wt.%) were investigated (8-12).

Experiments for pressed chips to examine how compression affects remelting 5% wt.% of CaF_2 salt flux both salt and pre-melted salt were used (18 and 19).

Five different amounts of CaF_2 addition (4%, 4.5%, 5%, 5.5%, 6 wt.%) AZ63 magnesium chips were investigated. Both salt and pre-melted salt were used to compare the effect of salt in different CaF_2 compositions (shown in Table 3. 3. 20-29). After all samples had cooled, the salt slag was washed, and the metal droplets were collected on a Retsch AS 200 BASIC vibratory sieve shaker (Figure 3. 2.c).

Table 3. 3. Experimental parameters for all remelting experiments.

Sample	**Exp. #**	**Salt Composition (wt.%)**					**Salt Type**	**Sample Condition**
		$MgCl_2$	**NaCl**	**KCl**	**CaF_2**	**NaF**		
Pure Mg Chips	1	57.00	25.00	16.00	2	-	Manually Mixed Salt	Loose Chips
	2	56.33	24.33	15,33	4	-		
	3	56.17	24.17	15.17	4.5	-		
	4	56.00	24.00	15.00	5	-		
	5	55.83	23.83	15.83	5.5	-		
	6	55.67	23.67	14.67	6	-		
	7	55.00	23.00	14.00	8	-		
	8	56.33	24.33	15,33	4	-	Premelted Salt	
	9	56.17	24.17	15.17	4.5	-		
	10	56.00	24.00	15.00	5	-		
	11	55.83	23.83	15.83	5.5	-		
	12	55.67	23.67	14.67	6	-		
	13	56.33	24.33	15,33	-	4	Manually Mixed Salt	
	14	56.17	24.17	15.17	-	4.5		
	15	56.00	24.00	15.00	-	5		
	16	55.83	23.83	15.83	-	5.5		
	17	55.67	23.67	14.67	-	6		

(cont. on next page)

Table 3.3 (cont.).

	18	56.00	24.00	15.00	5	-		Pressed Chips
	19	56.00	24.00	15.00	5	-	Premelted Salt	
AZ63 Mg Alloy Chips	20	56.33	24.33	15,33	4	-	Manually Mixed Salt	Loose Chips
	21	56.17	24.17	15.17	4.5	-		
	22	56.00	24.00	15.00	5	-		
	23	55.83	23.83	15.83	5.5	-		
	24	55.67	23.67	14.67	6	-		
	25	56.33	24.33	15,33	4	-	Premelted Salt	
	26	56.17	24.17	15.17	4.5	-		
	27	56.00	24.00	15.00	5	-		
	28	55.83	23.83	15.83	5.5	-		
	29	55.67	23.67	14.67	6	-		

After drying and weighing the metal droplets, the metal yield and the coagulation efficiency were calculated according to Equation 3.1 and Equation 3.2:

$$\text{Metal Yield}(\%) = \frac{m_{\text{recovered metal}}}{m_{\text{scrap}}} \times 100 \tag{3.1}$$

$$\text{Coagulation Efficiency}(\%) = \frac{m_{\text{coagulated droplets}}}{m_{\text{recovered metal}}} \times 100 \tag{3.2}$$

Where $m_{\text{recovered metal}}$ is the total quantity of metal recovered after remelting, m_{scrap} is the total amount of the charged scrap in the experiment, and $m_{\text{coagulated droplets}}$ is the number of droplets bigger than 0.3 g which is the double amount of magnesium chip weight. At least two chips must be combined to be counted as coagulated droplet and one chip weighs around 0.162 g (shown in Table 4. 1.)

TGA (Thermogravimetric Analysis - Perkin Elmer Diamond) heat from 25.00 °C to 815.00 °C at 10.00 °C/min heating rate under N_2 atmosphere for $MgCl_2 \cdot 6H_2O$ salt and heat from 25.00°C to 810.00 °C at 5.00 °C/min heating rate under O_2 atmosphere for pure and AZ63 magnesium chips, SEM (Scanning Electron Microscope - FEI QUANTA 250 FEG) - EDS (Energy Dispersive X-ray Spectroscopy - Oxford Aztec), and XRD (X-ray diffraction analysis – Philips X'Pert Pro), XRF (X-ray fluorescence spectroscopy – Spectro IQ II) analyses were performed on salt mixtures before and after the experiments.

3.4. Thermochemical Calculations of the Salt Flux

TGA analysis was performed to use the magnesium chloride salt ($MgCl_2 \cdot 6H_2O$) in its anhydrous form in the experiments. According to the results of the TGA analysis (given in Figure 3. 7.), when it is held at 275 °C for 1 hour, the water is removed completely and as a result, anhydrous $MgCl_2$ was obtained for use in the experiments. A laboratory scale resistance chamber furnace was used see in Figure 3. 2. a.

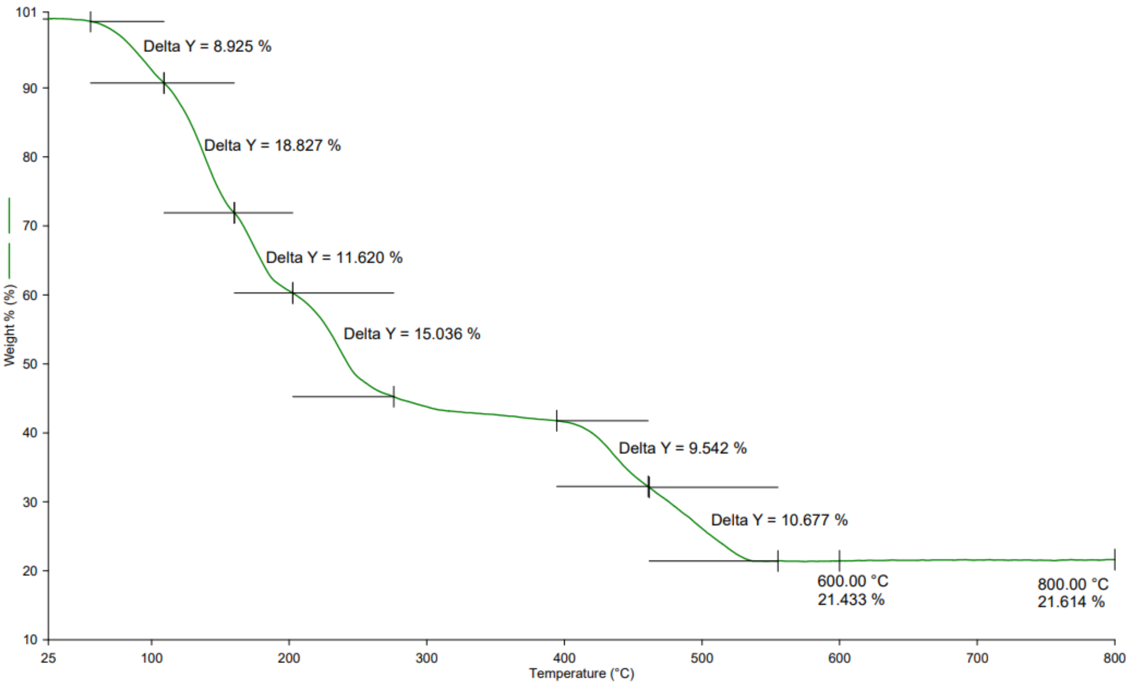

Figure 3. 7. TGA Analysis for $MgCl_2 \cdot 6H_2O$

Liquid salt formation and temperature vs. density studies of salt mixtures were performed with FactSage software for use in experiments. Subheading 4.1.2 shows the graphs and results in detail. Three different salt mixtures were considered for the FactSage study, and the following chemical compositions were investigated:

1. NaCl 24.33%, KCl 15.33%, $MgCl_2$ 56.33%, and CaF_2 4 wt.%
2. NaCl 24.00%, KCl 15.00%, $MgCl_2$ 56.00%, and CaF_2 5 wt.%
3. NaCl 23.67%, KCl 14.67%, $MgCl_2$ 55.67%, and CaF_2 6 wt.%

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the results of characterization and re-melting experiments were given for both Pure and AZ63 magnesium chips. Results were compared and utilized with results in the literature. The parameters of salt composition, temperature, salt factor, and the compaction degree of turnings on the recovery efficiency were discussed. The purpose is to minimize the metal loss and increase the coalescence ability of the metal.

4.1. Characterization Results

4.1.1. Pure and AZ63 Magnesium Chips

SEM/EDX and TGA analyses were utilized to characterize the samples of pure and AZ63 magnesium chips in this part of the research. The physical properties such as weight, thickness, and surface area of randomly selected 50 chips were characterized and results are shown in Table 4. 1.

Table 4. 1. Physical properties of the pure and AZ63 magnesium chips.

		Width (mm)	Length (mm)	Weight (g)	Thickness (mm)	Surface Area (mm^2)
Pure Mg	Avg.	17.58	33.24	0.162	0.1401	1168.72
	Dev. ±	0.78	1.64	0.02	0.036	78.19
AZ63	Avg.	17.5	33.18	0.1045	0.1795	1161.52
	Dev. ±	0.91	1.62	0.01	0.025	86.31

SEM analysis and EDX mapping for pure magnesium chips are shown in Figure 4. 1. An oxide layer covers the surface of chips, some carbon was detected which may be contamination.

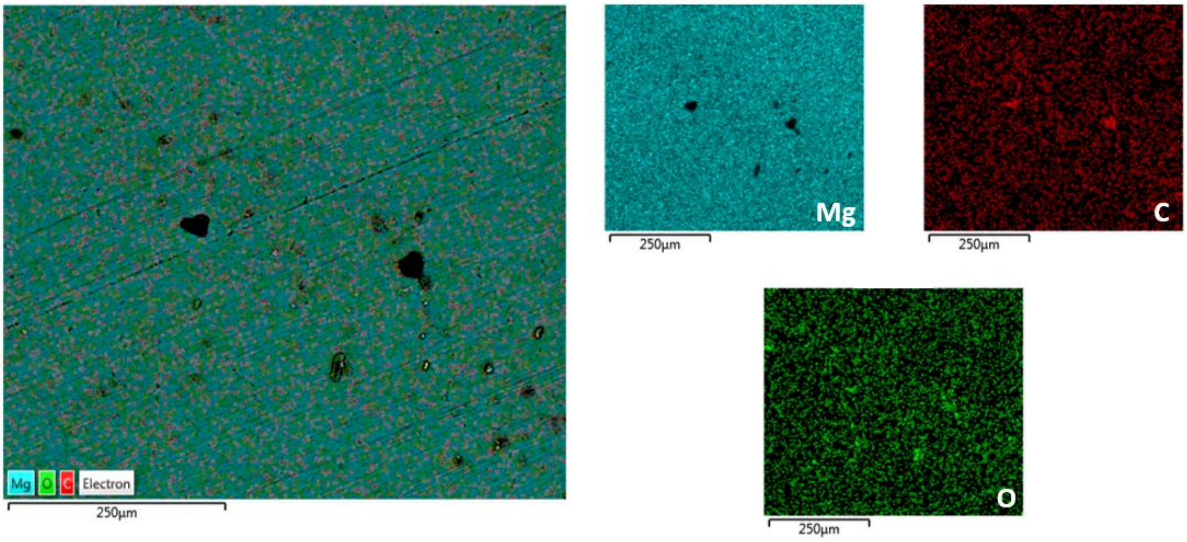

Figure 4. 1. SEM Analysis and EDX mapping for pure magnesium chips.

Figure 4. 2. illustrates the SEM analysis and EDX mapping for the AZ63 magnesium chips. The bright areas in certain locations on the surface of the AZ63 chips were detected as aluminium and zinc intermetallic as shown in the EDX mapping analysis.

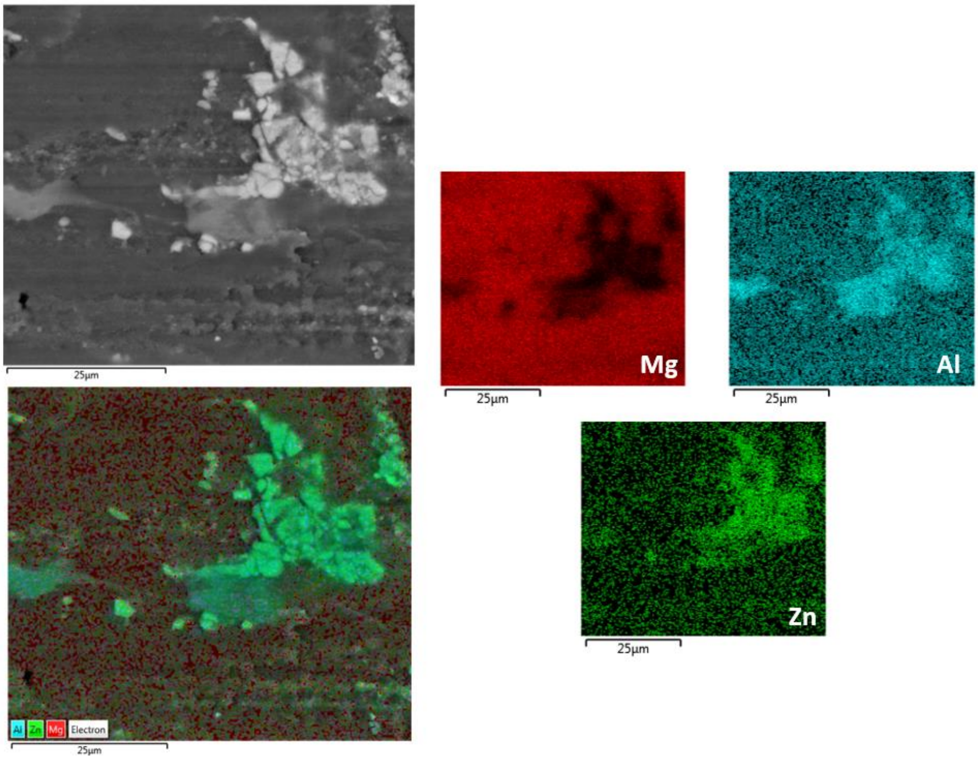

Figure 4. 2. SEM Analysis and EDX mapping for AZ63 magnesium chips.

The cross-section of the pure and AZ63 magnesium chips was given in Figure 4. 3. and Figure 4. 4. respectively. Analysis was carried out in order to see the oxide layer in the chips from the cross-sectional area. However, the desired image could not be obtained because the oxide in the chips is not only covered as a layer on the surface but also on the entire surface.

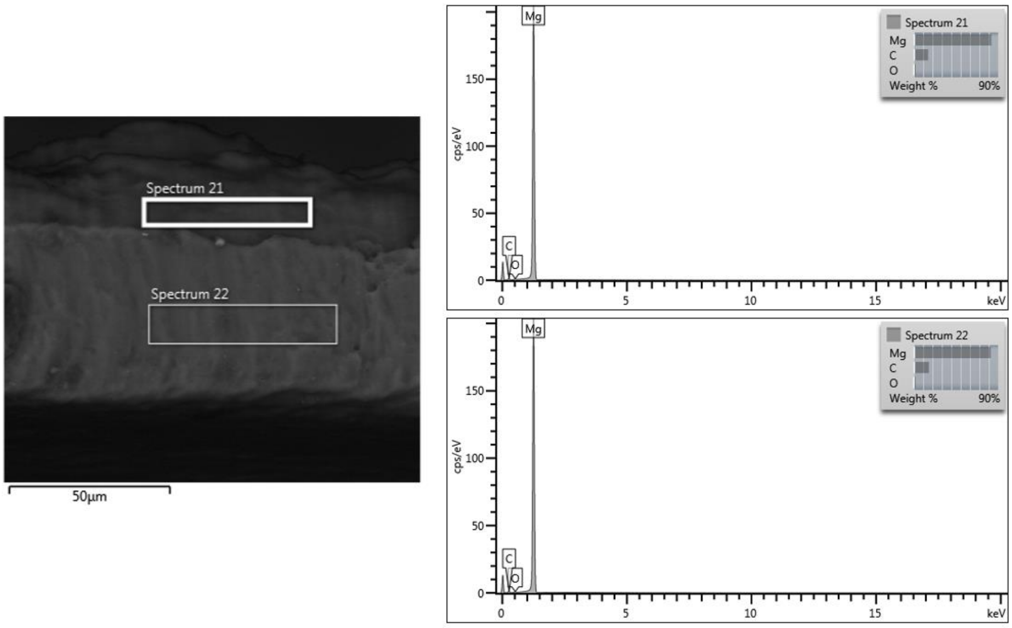

Figure 4. 3. SEM image of the cross-section of a pure magnesium chip.

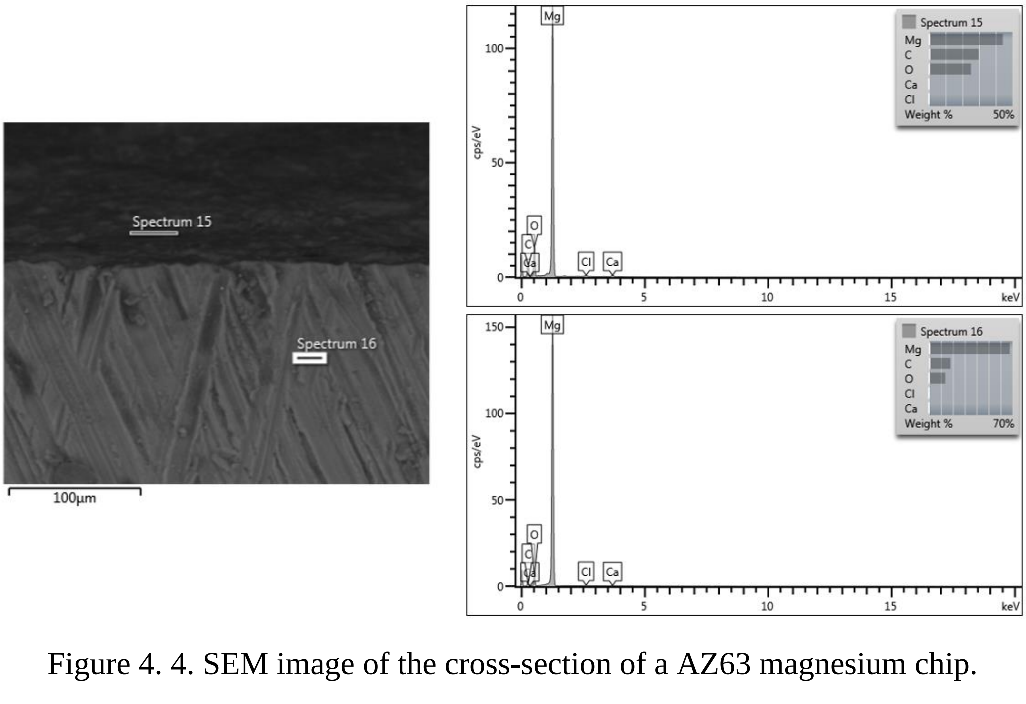

Figure 4. 4. SEM image of the cross-section of a AZ63 magnesium chip.

Figure 4. 5. And Figure 4. 6. illustrates the TGA analysis of pure and AZ63 magnesium chips under oxygen atmosphere. Mass increase was observed with the oxidation of pure and AZ63 magnesium chips. Mass increase in pure magnesium was observed at ≈530 °C, and for AZ63 at ≈470 °C. The reason for the higher metal yield in the experiments performed with the realization of mass gain at higher temperature of pure magnesium chips was supported.

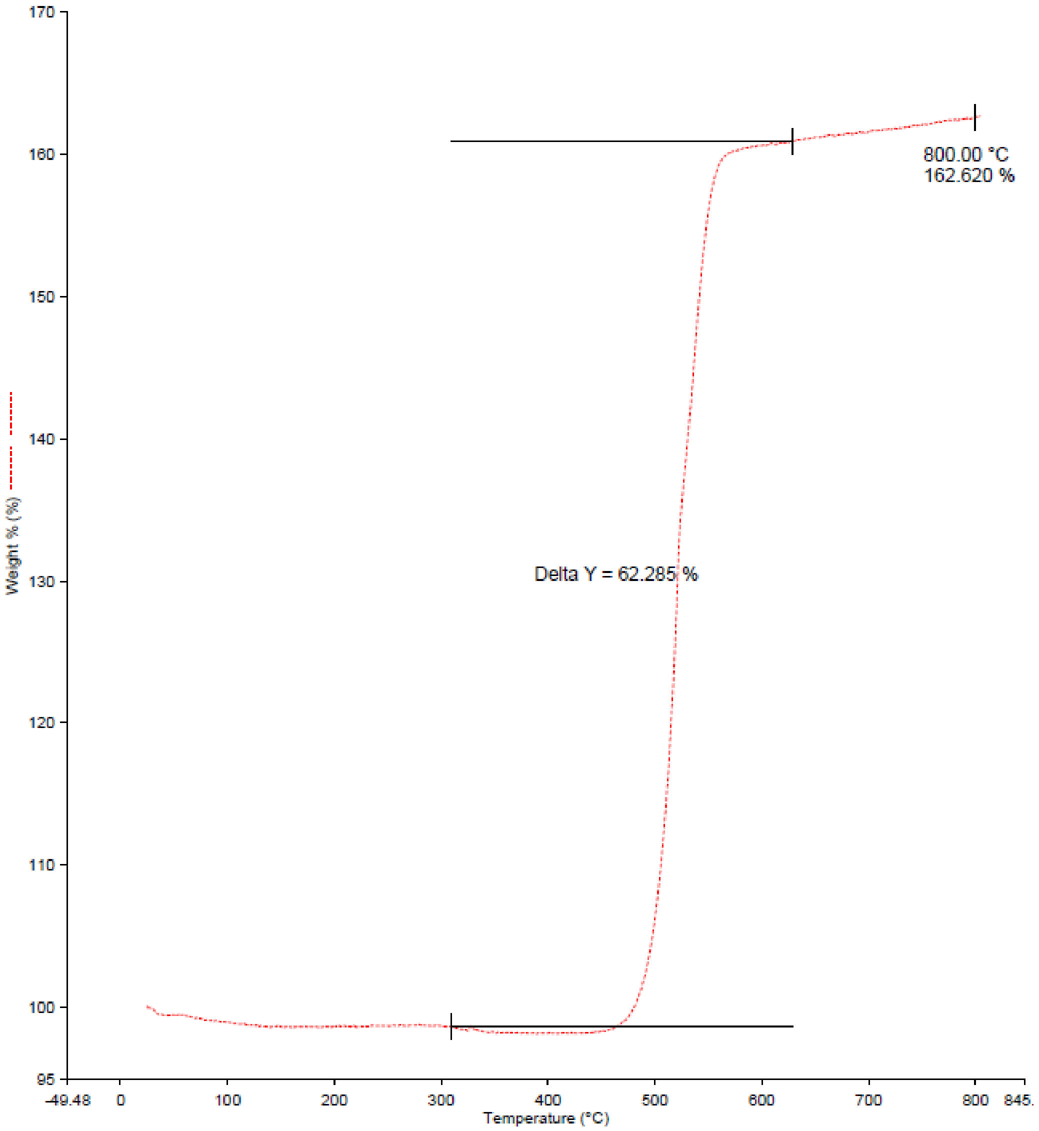

Figure 4. 5. TGA analysis of AZ63 magnesium chips.

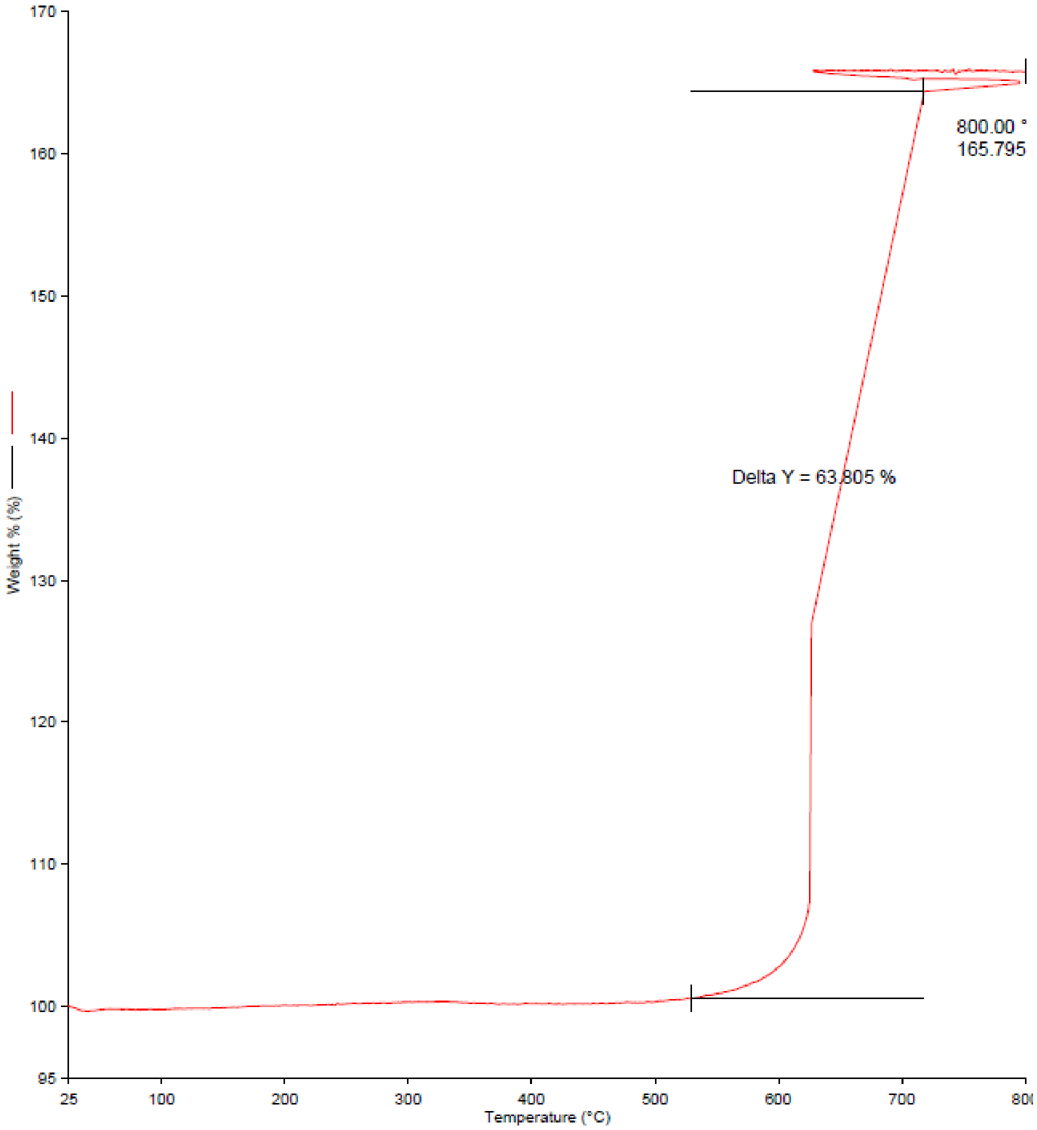

Figure 4. 6. TGA analysis of pure magnesium chips.

The height and diameter measurements of the pressed sample were collected from 3 distinct sites with a force of 6 N each, and the average dimensions were calculated and shown in Table 4. 2. The measurements were used to calculate density which was calculated as 1.649±0.02 g/cm^3, which corresponds the 95% of the density of magnesium metal (1.738 g/cm^3). The chips' mass, thickness, and surface area were all measured, and the samples underwent SEM-EDX analysis for examination.

Table 4. 2. Characterization of the pressed chips.

Sample	m (g)	h (cm)	r (cm)	V (cm^3)	d (g/cm^3)
1	3.895	1.2985	0.7578	2.343	1.6626
2	4.056	1.3917	0.7572	2.507	1.6181
3	4.025	1.3341	0.7580	2.408	1.6715
4	4.093	1.3804	0.7571	2.486	1.6465

The SEM/EDX examination of pressed pure magnesium chips is seen Figure 4. 7 An average of 25 chips, or ≈292 cm^2 in area, are used in each experiment. After pressing, 25 chips have a surface area of ≈9.90 cm^2. 96% of the surface area was decreased while pressing with a density that was near to the bulk magnesium density, which lowers oxidation and lowers metal losses. It is believed that the pressure exerted during pressing might partially break the oxide layer.

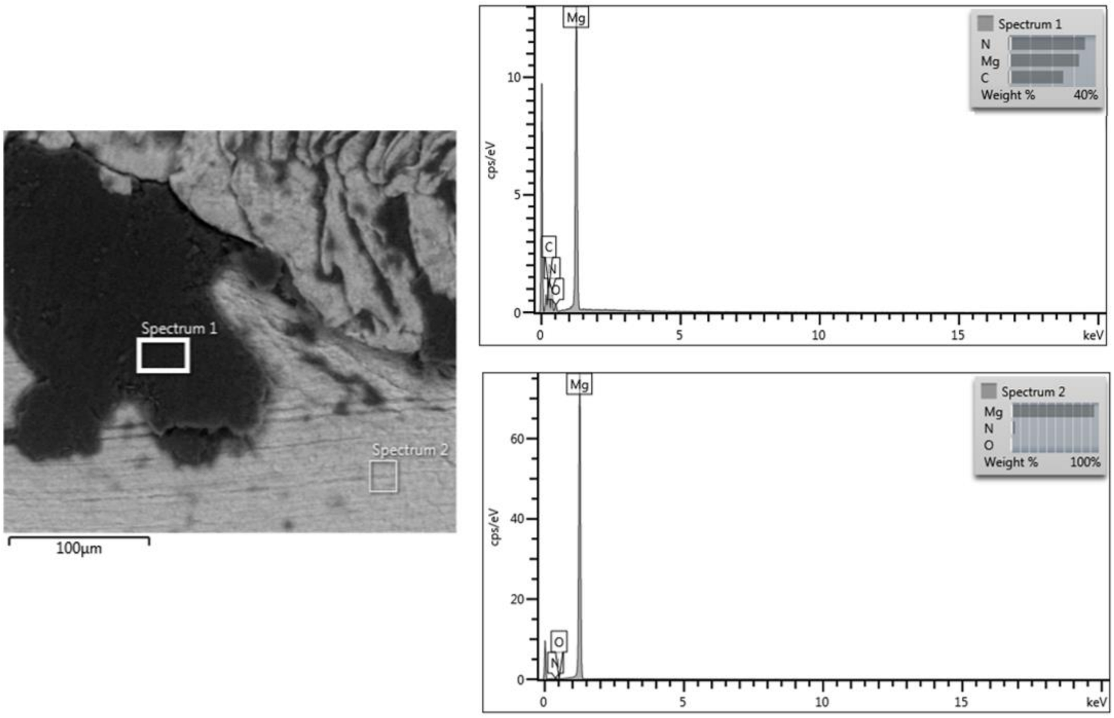

Figure 4. 7. SEM Analysis for pressed chips surface area.

4.1.2. Thermochemical Calculations of the Salt Flux

The salt mixes used in the experiments had their characteristics observed using FactSage software. The degree of liquid salt formation as a function of temperature is shown in Figure 4. 8.

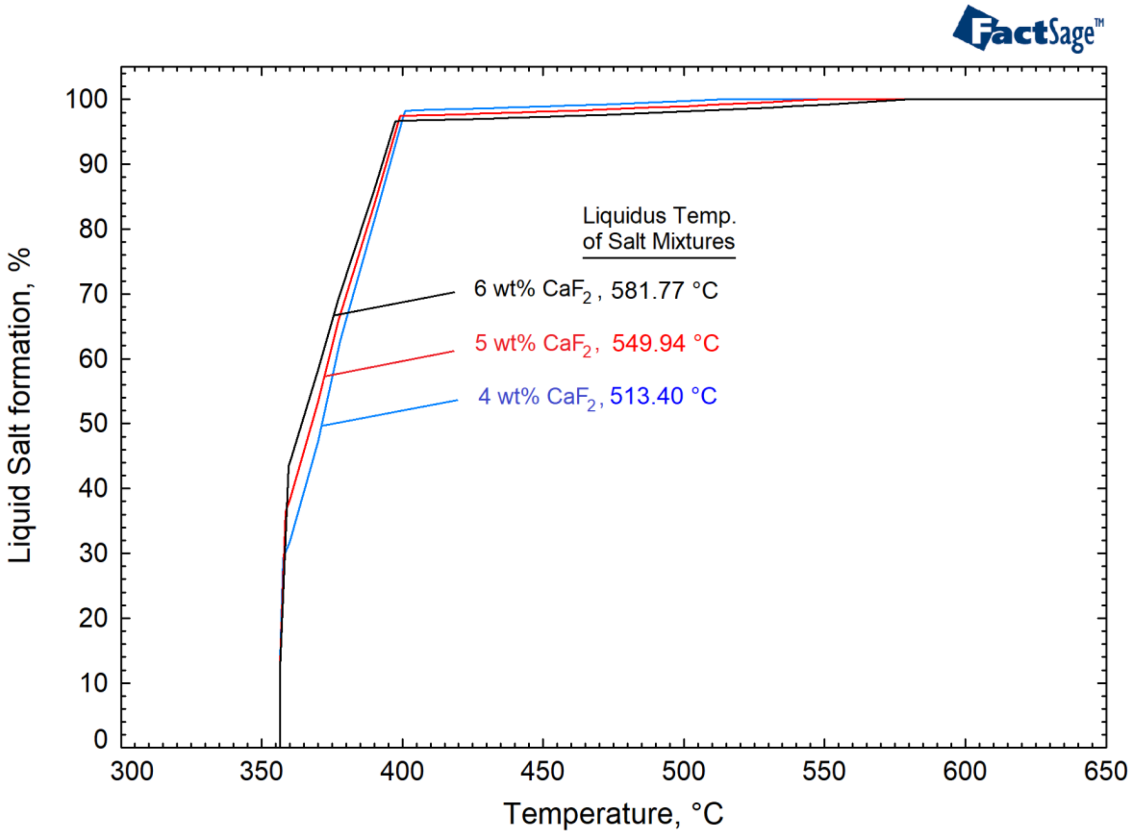

Figure 4. 8. Temperature vs. Liquid Salt Formation graph for 4%, 5%, and 6 wt.% CaF_2 calculated using FactSage.

Calculations show that CaF_2 has a clear impact on the melting point of salt mixtures. The melting point of the salt mixes increased with increasing CaF_2 concentration. The melting temperature increased by around 30 to 35 degrees for every 1 wt.% of CaF_2. As a result of the mixture's extreme heterogeneity in practice, the melting process begins with the salt that has the lowest $T_{melting}$. As a result, only premelting at a temperature higher than the melting points of at least one salt component may result in the calculated melting temperatures being reached. For 4 wt.%, 5 wt.%, and 6 wt.% of CaF_2, the homogeneous salt mixtures melting points were determined to be 513.4, 549.9, and 581.7 °C, respectively. Although CaF_2 increases the melting temperature of the salt mixture, the melting is still lower than all pure substances present in the flux such as:

NaCl (801 °C), KCl (770 °C), $MgCl_2$ (714 °C), and CaF_2 (1418 °C).

Figure 4. 9. illustrates the FactSage calculations of the densities of different compositions of CaF_2 at 850 °C. The density changed from 4 wt.% to 6 wt.% CaF_2 is between 1.638 and 1.665 g/cm^3. The effect of CaF_2 on the density is not as obvious as its effect on temperature.

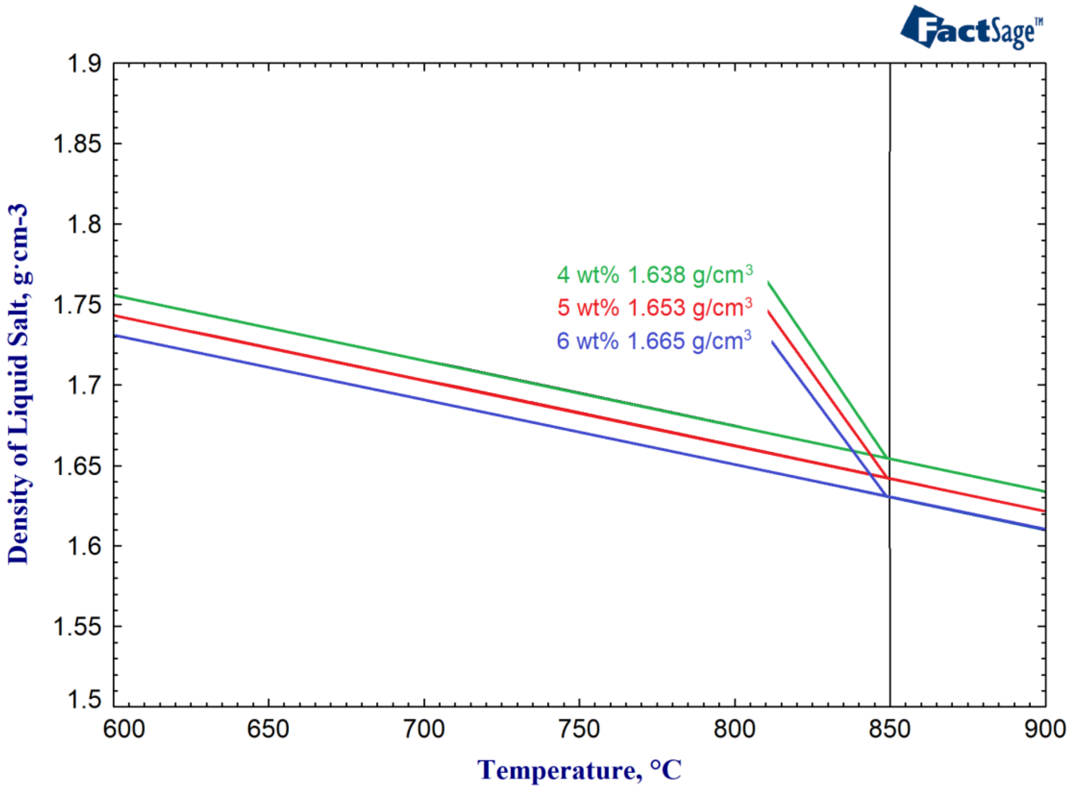

Figure 4. 9. Temperature vs. Density graph for 4%, 5%, and 6 wt.% CaF_2 calculated using FactSage.

The density of the salt flux in a magnesium recycling process will typically be higher than the density of the recycled magnesium metal. Salt fluxes are often composed of a mixture of salts with a density greater than pure magnesium metal [64]. At 20 °C, pure solid magnesium metal has a density of 1.74 g/cm^3, while at melting point, it has a density of 1.59 g/cm^3 [80]. Calculations were made on the melting temperatures and densities of salt fluxes made from various compositions, as well as information regarding how these salt fluxes behaved when used in remelting experiments.

Figure 4. 10. presents the after-remelting experiment XRD results of NaCl, $MgCl_2$, KCl and CaF_2 salt flux and Figure 4. 11. illustrates the XRD analysis of NaCl, $MgCl_2$, KCl and NaF salt flux after remelting experiment. After the experiment cool down

to room temperature, it was washed with distilled water and dried in the oven. The reason for that, is to dissolve the chlorines in the water and to obtain clearer results in the XRD analysis. The composition of the salt flux is 56% $MgCl_2$, 24% NaCl, 15% KCl and 5% CaF_2 and 56% $MgCl_2$, 24% NaCl, 15% KCl and 5% NaF.

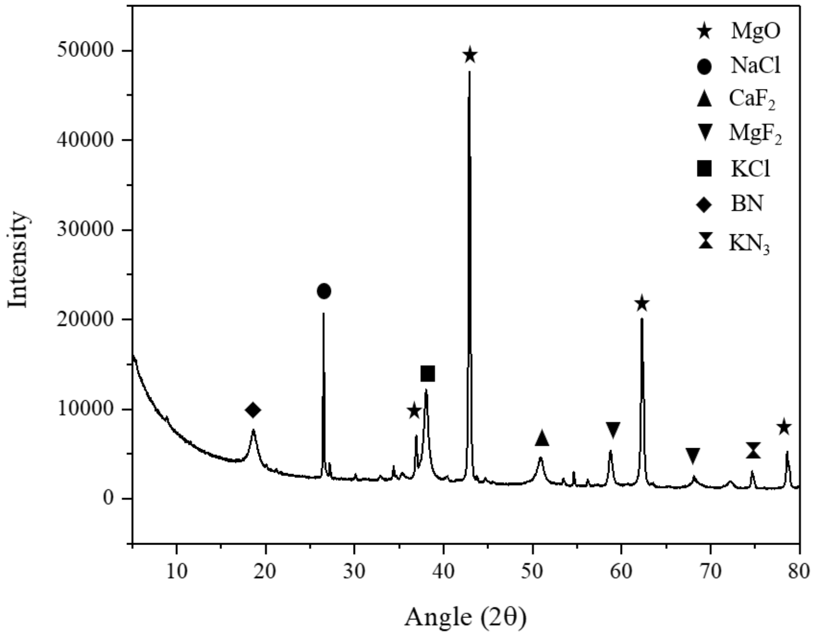

Figure 4. 10. XRD analysis of NaCl, $MgCl_2$, KCl and CaF_2 salt flux after remelting experiment.

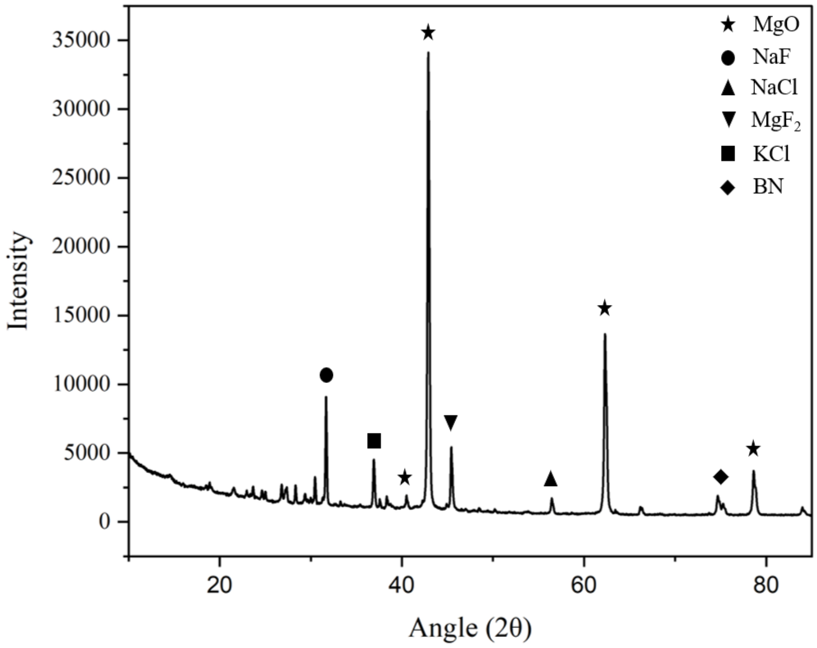

Figure 4. 11. XRD analysis of NaCl, $MgCl_2$, KCl and NaF salt flux after remelting.

The MgO phase was observed as the main phase since inert gas was not used or re-melting was not performed under vacuum during both experiments. The graphite crucible used for remelting is coated with boron nitride for easier separation of samples, which explains the BN phase result in XRD analysis. It was observed from fluoride compounds from MgF_2 as a result of XRD after re-melting any sample under salt flow. These compounds were not present in the salt stream before remelting; this indicates that some chemical reaction occurs due to scrap-salt interactions. Although the reason for the formation of the KN_3 phase seen in the XRD analysis in the salt flux containing 5% CaF_2 is not known, it can be interpreted in two ways, it may have reacted with nitrogen in the air, or it is thought that it may have formed as a result of the reaction of the sample with boron nitride, which makes it easier to separate from the graphite crucible. The possible reactions are shown below:

$$CaF_2 \rightarrow Ca^{2+} + 2F^{-} \quad (4.1)$$

$$NaF \rightarrow Na^{+} + F^{-} \quad (4.2)$$

$$KCl \rightarrow K^{+} + Cl^{-} \quad (4.3)$$

$$NaCl \rightarrow Na^{+} + Cl^{-} \quad (4.4)$$

$$Mg^{2+} + O^{2-} \rightarrow MgO \quad (4.5)$$

$$MgO(s) + 2F^{-} \rightarrow MgF_2(l) + ½\ O_{2(g)} \quad (4.6)$$

$$KN_3 \rightarrow K^{+} + 3N^{3-} \quad (4.7)$$

The results of XRF analysis of the premelted and manually mixed salts after remelting are shown in Table 4. 3. As expected, Na (sodium), Mg (magnesium), Cl (chloride), K (potassium), and Ca (calcium), were observed in all salt fluxes.

Table 4. 3. The elemental concentration of the premelted and manually mixed salt after remelting was measured by XRF analysis.

	Premelted Salt	**Manually Mixed Salt**
Na	23.39	22.27
Mg	51.14	52.87
Cl	19.11	16.07
K	10.63	11.67
Ca	1.05	1.07

Figure 4. 12. shows the SEM/EDX results of the salt flux after the experiment. The pre-experimental content of the salt flux is NaCl, $MgCl_2$, KCl and CaF_2.

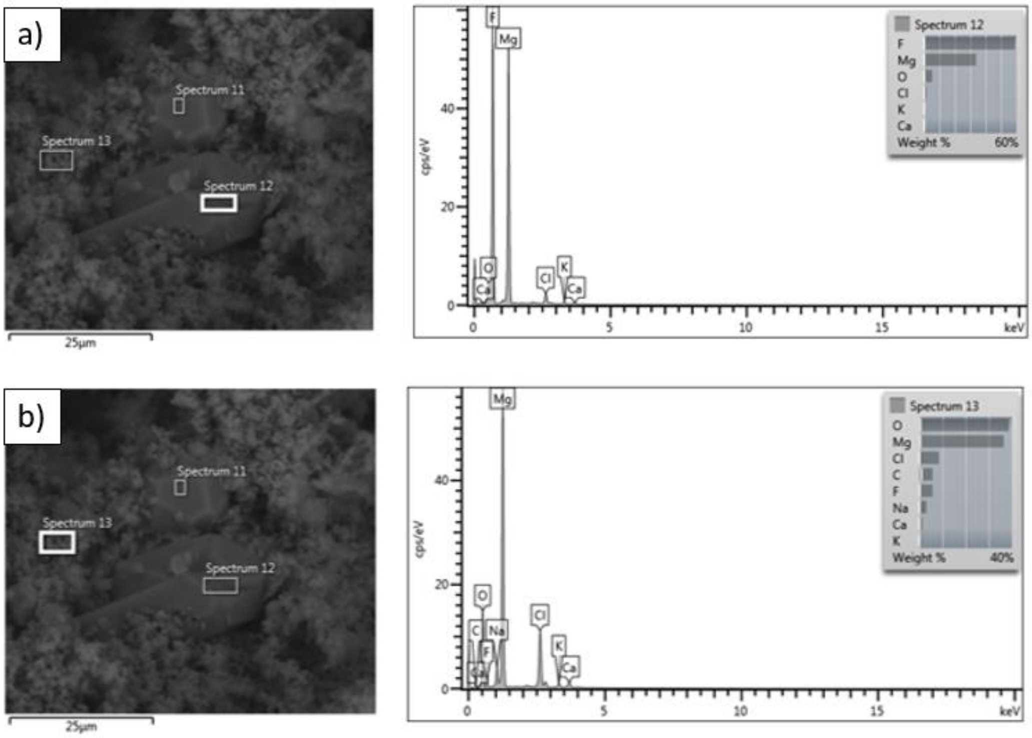

Figure 4. 12. SEM/EDX Analysis of the salt flux after experiment.

The reason for that, it shows a high amount of magnesium peak is because it has a 56% $MgCl_2$ content. Magnesium and fluoride reacted and formed MgF_2 crystal. The CaF_2 salt is insoluble in water, so it appears in all samples after re-dissolved. MgO particles were observed in the salt mixture due to its contact with air. Figure 2. 19b shows contributions with major peaks of Mg and O. Surface oxides removed and absorbed by the salt flow are normally inclusions.

4.2. Remelting Results

In this chapter, the effect of CaF_2 and NaF salt mixtures of different compositions, the effect of pre-melted salt and the degree of compaction of the turnings on metal yield and coagulation efficiency for pure and AZ63 magnesium chips were investigated.

4.2.1. AZ63 Magnesium Alloy Chips

AZ63 magnesium chips were obtained for recycling in two forms: salt mixture with different CaF_2 ratios and the effects of pre-melted salt to metal yield were studied. Loose chips were formed by folding the samples by hand, and the salt/scrap ratio was chosen as 10 in order to place them under the crucible and completely cover the salt in order to prevent oxidation. Figure 4. 13. shows the coalescence efficiency and metal yield results under different amounts of CaF_2.

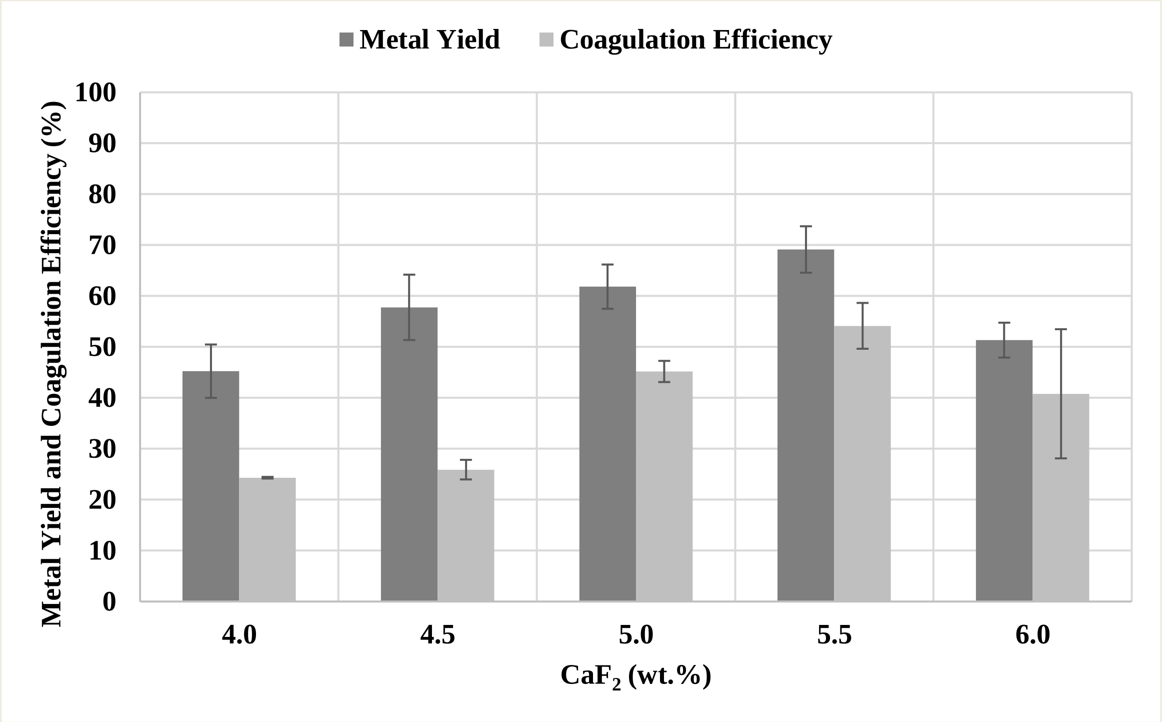

Figure 4. 13. Effect of different CaF_2 concentrations percentages on metal yield and coagulation efficiency of AZ63 magnesium alloy.

Coagulation efficiency and metal yield both increased of up to 5.5 wt.% of CaF_2. With the addition of 5.5 wt.% CaF_2, metal yield and coagulation efficiency reached 69.13% and 54.14%, respectively. At 4 wt.% CaF_2, 45.24% and 24.31% for metal yield and coagulation efficiency, and at 4.5 wt.% CaF_2 for metal yield 57.77% and coagulation efficiency 25.9%, respectively was calculated. In 5 wt.% CaF_2, metal yield 61.84% and 45.18% coagulation efficiency were calculated. On the other hand, with a high CaF_2 content of 6 wt.%, coagulation was still observed in metal yield and coagulation efficiency 51.34% and 40.80%. The decrease in coagulation efficiency with increasing CaF_2 may be due to the increased melting point of the flux due to the increased amount of CaF_2. The increase in melting point causes further oxidation of the scraps before they are covered by the liquid flux. The alloy in the study of Akbari et al. was AZ31 magnesium alloy. The increase in melting point results in more oxidation of scraps before it is covered by the liquid flux. Akbari et al. reported a metal yield and coagulation efficiency of 82.02% and 86% after 5 wt.% of CaF_2 addition. Akbari et al. reported that after 5 wt.% CaF_2, some undissolved particles appeared on the surface of the magnesium droplets, preventing the droplets from coagulating, and exhibiting a "supersaturation" effect caused by fluoride at a concentration of more than 5% by weight [75].

The metal yield results from AZ63 magnesium chips remelted in the pre-melted salt flux are shown in Figure 4. 14. Various CaF_2 additions were used to examine the impact of pre-melting on metal yield.

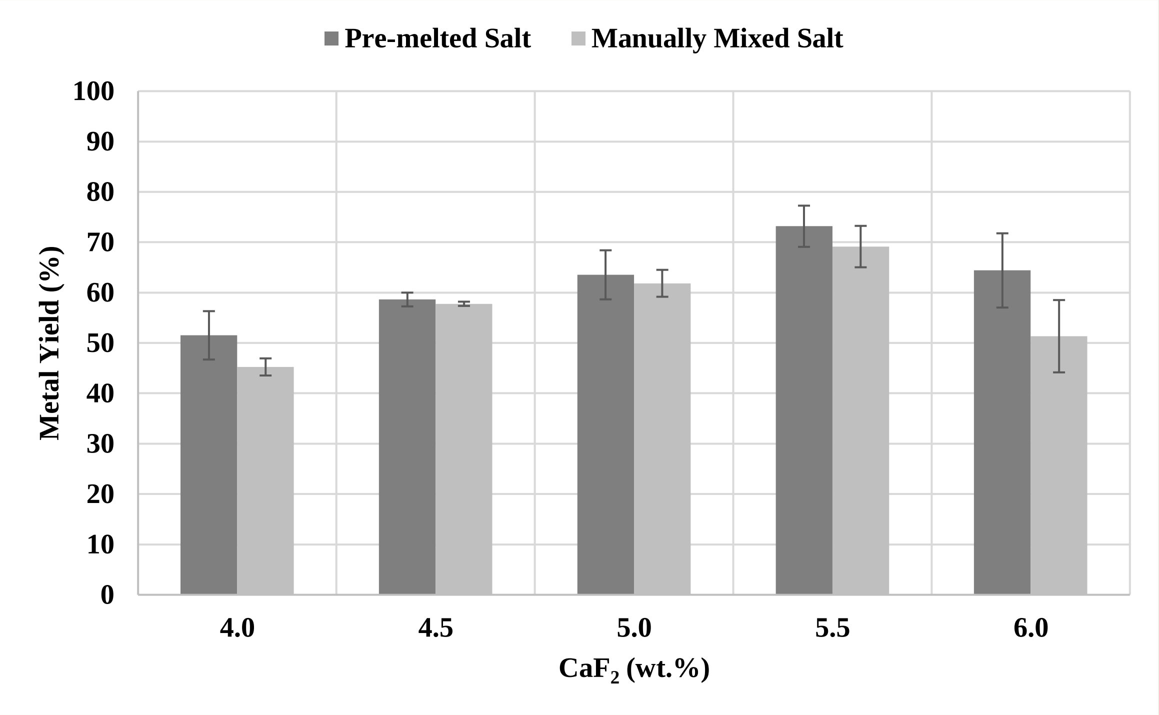

Figure 4. 14. The effect of premelting the salt with different CaF_2 addition on metal yield on AZ63 magnesium alloy.

The effect of pre-melted salt on metal yield was investigated for AZ63 magnesium chips. For 4 wt.% CaF_2 the metal yield 51.51%, 58.63% for 4.5 wt.% CaF_2, 63.52% for 5 wt.% CaF_2 and 64.40% for 6 wt.% CaF_2. The highest value for the AZ63 alloy was found to be 73.17%, with CaF_2 of 5.5 wt.% for the pre-melted salt. However, when these two different salts were compared, it was observed that the effect of the pre-melted salt on metal yield was not increased as needed.

4.2.2. Pure Magnesium Chips

Magnesium chips were charged for recycling in two forms: manually folded and pressed in steel molds. The samples were remelted at 850 °C with a holding time of 15 minutes in a graphite crucible. The impact of various CaF_2 concentrations on the metal yield and coagulation efficiency of loose magnesium chips after remelting is shown in Figure 4. 15.

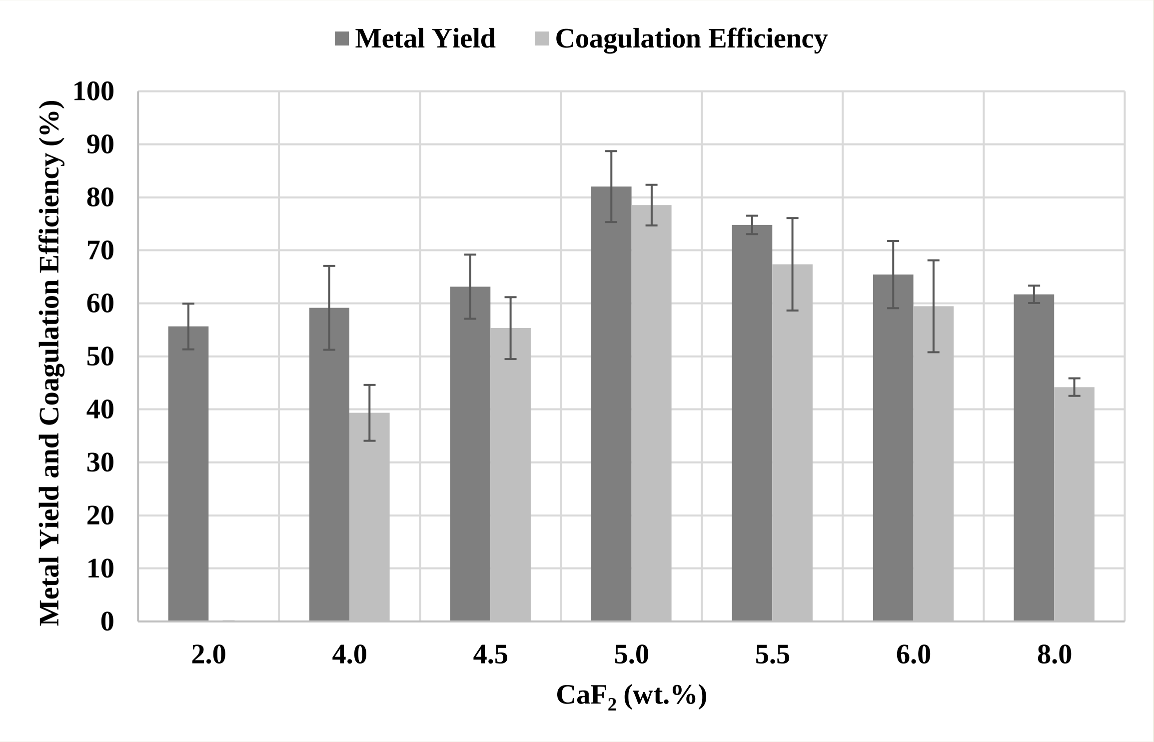

Figure 4. 15. Effect of different CaF_2 percentages on metal yield and coagulation efficiency of pure magnesium.

Metal yield was almost 55%, whereas no coagulation was observed for 2 wt.% CaF_2. Compared to metal yield, coagulation efficiency was more significantly impacted by fluoride. Inadequate F- content to remove the oxide layer might be the cause of the lack of coagulation with a 2 wt.% CaF_2 addition. Following the addition of 2 wt.% of CaF_2, an increase was seen in both coagulation efficiency and metal yield that continued up to 5 wt.% of CaF_2 and reached 82% and 78.5% for metal yield and coagulation efficiency, respectively. After 5 wt.% of CaF_2 was added to the AZ31 alloy, Akbari et al. found metal yield and coagulation efficiency of 82.02% and 86%, respectively. Despite the fact that the two alloys are different, the metal yield value is consistent with the literature, suggesting that the oxidation losses are not considerably different between the two alloys. coagulation efficiency, on the other hand, is a more procedure-dependent outcome. Following the peak, both values dropped until the CaF_2 content dropped to 8 wt.%, or 61.70% and 44.21% for metal yield and coagulation efficiency, respectively. After 5 wt.%, the rising melting point of the flux might be to blame for the drop in coagulation efficiency that accompanied an increase in CaF_2. The increased melting point causes scraps to oxidize more before being covered by the liquid flux, which prevents coagulation and raises metal losses. A different theory suggests that after 5 wt.% CaF_2, some undissolved particles appeared on the surface of the magnesium droplets, preventing the droplets from coagulating and exhibiting a "supersaturation" effect brought on by fluoride at a concentration of more than 5 wt.% [75].

Pure magnesium scraps were remelted in the manually mixed and premelted salt flux, and Figure 4. 16. illustrates the metal yield results. Premelting was compared to manually mixed salt with CaF_2 additions ranging from 4 wt.% to 6 wt.% for the metal yield.

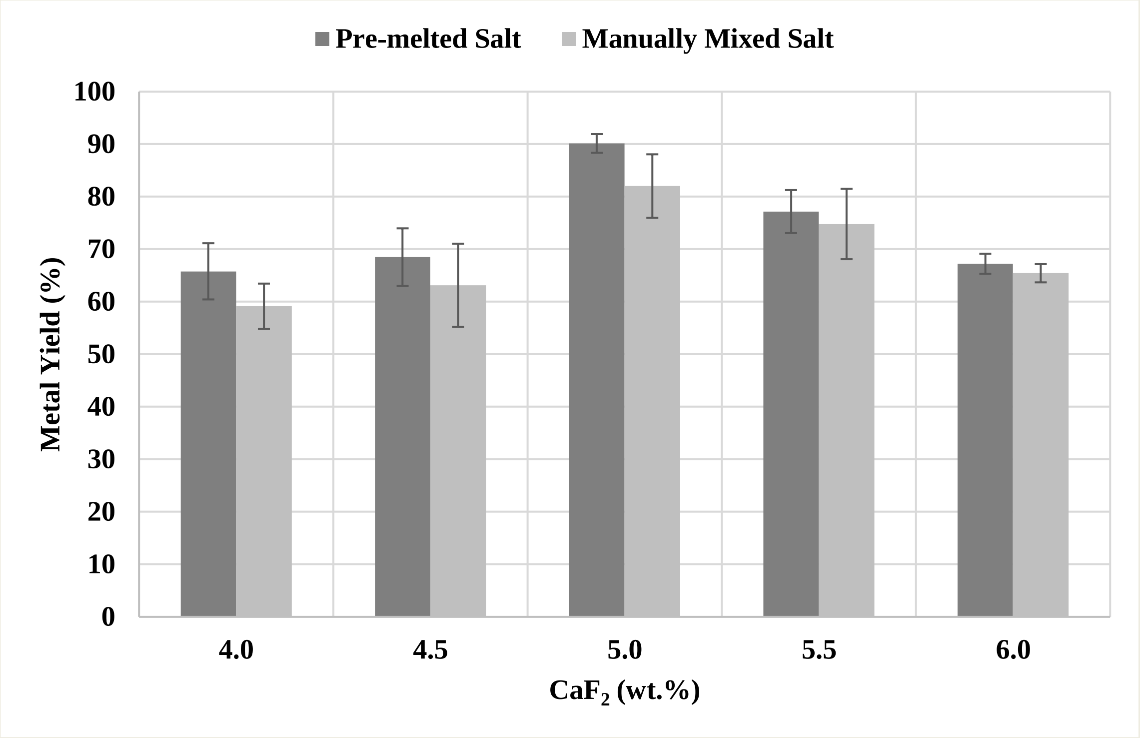

Figure 4. 16. The effect of premelting the salt with different CaF_2 addition on metal yield on pure magnesium.

Both manually mixed salt flux and premelted salt flux, the influence of CaF_2 on metal yield was shown in a comparable way. However, remelting scraps in a premelted salt greatly increased the metal yield and the calculations for the following salt concentrations: 65.79 at 4 wt.% CaF_2, 68.49 at 4.5 wt.%, 90.13 at 5 wt.%, 77.17 at 5.5 wt.%, and 67.23 at 6 wt.%. The premelted salt had a metal yield that was, on average, 7.10% greater. The homogenous premelted salt mixture's lower melting temperature might be the cause of the premelted salt's higher yield. It stops oxidation and metal losses because the salt melts before the metal does since it reaches the molten state first. Although magnesium has a significant tendency to oxidize, the greatest yield of metal recovery was 90.13%, which is encouraging.

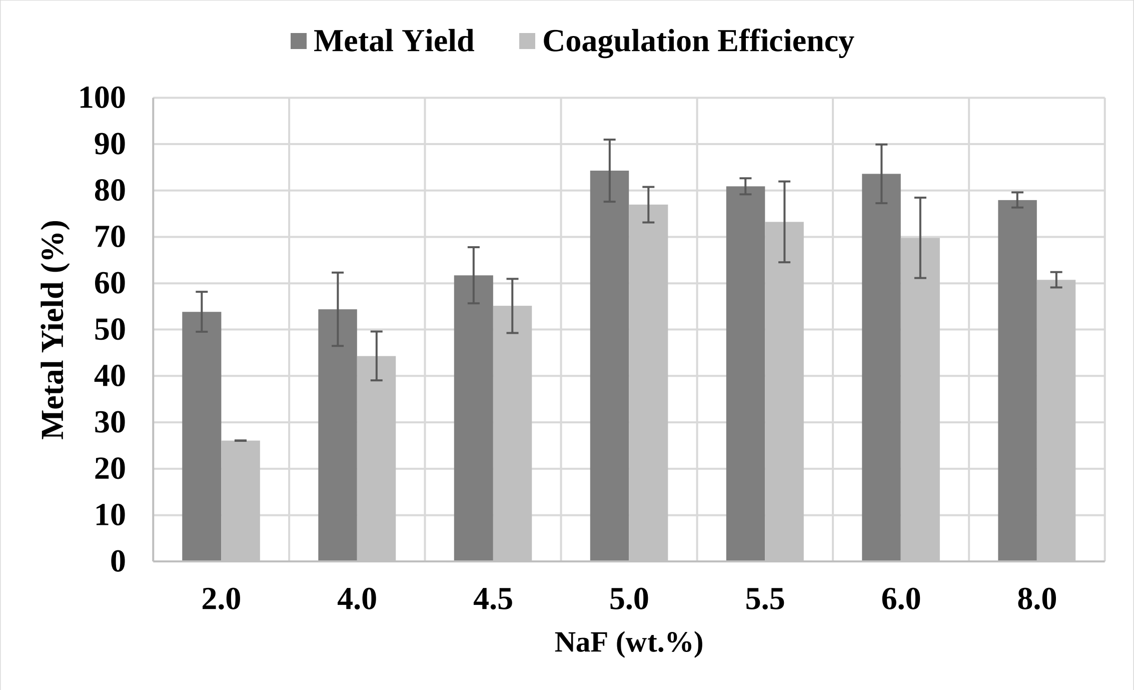

Figure 4. 17. The effect of premelting the salt with different NaF addition on metal yield on pure magnesium.

NaF salt flux was used instead of CaF_2 salt to see the difference in metal yield and coagulation efficiency behaviour of a different fluoride to pure magnesium chips. The reason for this is that the NaF salt is lower in price than the CaF_2 salt and it aims to reduce the magnesium recycling cost. With the addition of a 5 wt.% NaF salt, the highest metal yield and coagulation efficiency among the results were observed and were found to be 84.29% and 76.94%, respectively. Compared with Figure 4. 15., the metal yield of 5% NaF salt and 5% CaF_2 salt is different 2%. With the addition of 2 wt.% NaF, metal yield 53.85% coagulation efficiency 26.05% was obtained. Although the magnesium chip did not show recovery behaviour with the addition of 2 wt.% CaF_2, 26.05% more recovery was observed in the NaF salt. metal yield 54.39% and coagulation efficiency 44.32% for 4 wt.% NaF, metal yield 61.72% and coagulation efficiency 55.11% for 4.5% NaF, metal yield 80.91% and coagulation efficiency 73.24% for 5.5 wt. % NaF and 6 wt.% NaF, metal yield was calculated as 83.60% and coagulation efficiency as 69.8%. The results obtained by adding 8 wt.% NaF are metal yield 77.97% and coagulation efficiency 60.75%, respectively. It was thought that with the increase of the fluoride ratio, both the ability to dissolve the oxide layer would increase and therefore the coalescence of the metal droplet would increase [41]. However, it was clearly observed that the salt flux has a fluoride capacity and the effect of adding excess fluoride reduces the metal yield and recovery efficiency.

When CaF_2 and NaF salts are compared, the fluoride content in CaF_2 is 48.67%, and the fluoride content in NaF is 45.25%. NaF salt can be preferred because of its low cost and low melting point. However, a high difference could not be obtained between the two salts in terms of metal recovery and recovery.

Van Linden et al. investigated different fluoride salts and their effect at different temperatures for aluminium recycling by melting it under salt. Van Linden et al. claims that 10% NaF gives maximum efficiency to the coalescing and recovery of aluminium while melting scrap. It also states that the required temperature for the salt flux to melt should be 760-800 °C. However, according to the experiments, 10% fluoride addition will create saturation. Since they wanted to recycle the aluminium scrap, it was considered that there was not enough temperature for magnesium in terms of temperature and the experiments were optimized at 850 °C [76].

Figure 4. 18. illustrates the effect of pressing chips before remelting on the metal yield.

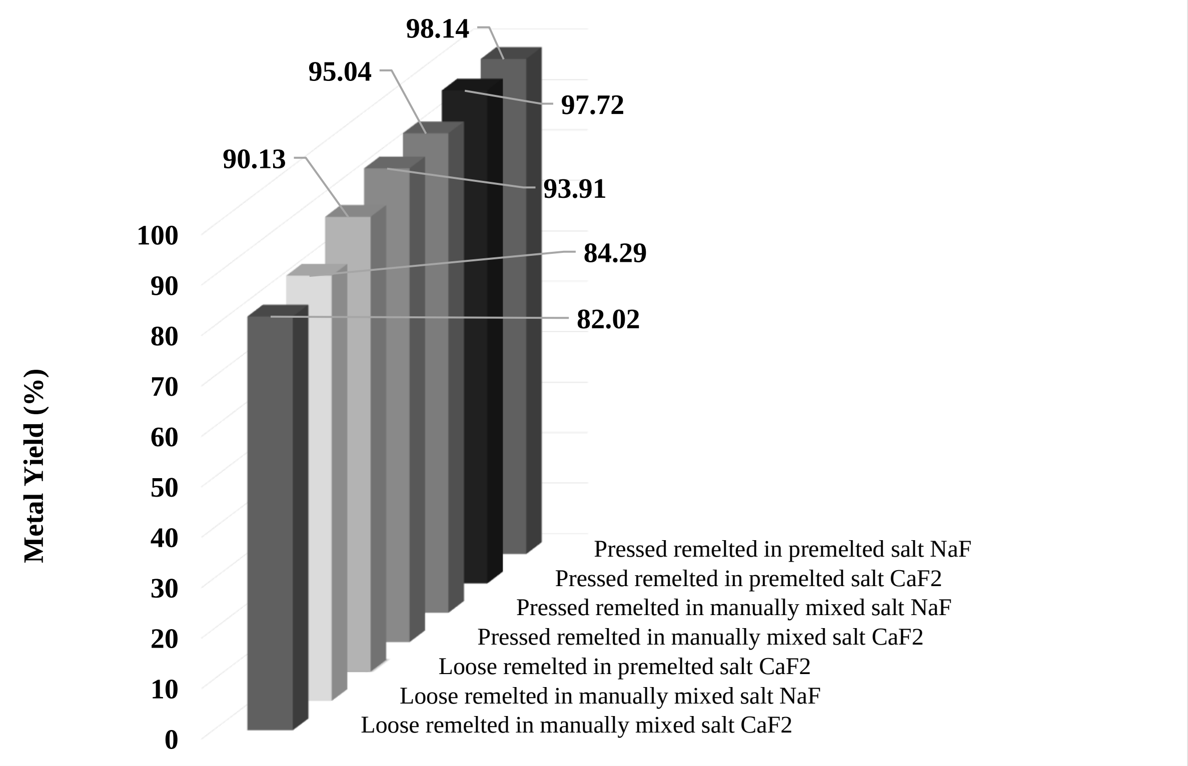

Figure 4. 18. Salt/Scrap ratio vs metal yield% of chips and pressed pure magnesium.

The impact of remelting the chips under a premelted and manually mixed salt flux while in a loose and pressed state is seen in Figure 4. 18. The maximum metal yield, which was 97.7% as compared to 90.1% before press, was obtained by remelting the pressed chips under a premelted salt with 5 wt.% CaF_2. When pressing the chips, metal yield increased in the case of salt flux that had been manually mixed from 82 wt.% to 93.9 wt.%. Due to the reduction in surface area, which directly affects the level of oxidation during remelting, pressing greatly boosted the yield. Additionally, pressing may result in cracks in the oxide layer of the chips, which eases the removal of oxides.

CHAPTER 5

CONCLUSIONS

The effects of CaF_2 and NaF addition, compaction degree of chips, and premelting of the salt mixture on metal yield and coagulation efficiency were investigated for pure and AZ63 magnesium chips. The following conclusions can be drawn:

- NaF and CaF_2 showed an increasing trend of metal yield and coagulation efficiency towards 5 wt.% addition and started to decrease after the peak.
- NaF with 5 wt.% addition showed 84.29% metal yield where 5 wt.% CaF_2 showed 82.02% for pure magnesium chips. In addition to the higher yield of NaF, it is also cheaper than CaF_2.
- NaF with 5 wt.% addition showed 76.94% coagulation efficiency where 5 wt.% CaF_2 showed 78.53% for pure magnesium chips.
- Premelting of the salt showed a better yield for all samples and salt mixtures due to the homogenization of the salt composition as well as decreasing the liquification temperature.
- Pressing the chips increased the metal yield due to the reduction of the surface area in contact with the atmosphere which reduced the oxidation.
- The highest metal yield (over 97%) was achieved by remelting pressed chips under a premelted salt flux with 5 wt.% fluorides addition.

CHAPTER 6

FUTURE WORK

- Alternative fluoride salts can be investigated instead of CaF_2 and NaF salts.
- The oxidation tendency of AZ63 magnesium alloy can be investigated.
- The environmental impact of the salts used in recycling process can be investigated.
- Metal quality can be tested using the RPT (Low Pressure Test), after the magnesium is recycled.
- Alloy chip quality differences and their effects on metal yield can be studied in more depth.
- The gases released during the production of the pre-melted salt can be analyzed using Gas Chromatography (GC) and its effects on the environment can be investigated.

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