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EFFECT OF CAF_2 ADDITIONS ON THE YIELD OF AZ63 MAGNESIUM CHIPS DURING REMELTING

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Abstract: Magnesium is one of the metals listed in European Union's critical raw materials list. Primary production of magnesium is a high energy demanding process which raised the necessity of recycling the magnesium alloys in an efficient way. Remelting those scraps under a salt flux consist of chlorides (NaCl, KCl, and $MgCl_2$) and fluorides (CaF_2) are a common process however, different alloys might behave differently when it comes to salt-metal-metal oxide interactions. Furthermore, the condition of the salt flux such as dry-mixed or pre-melted (fused) affects the coagulation and metal yield. This work presents results on the effect of CaF_2 concentration and pre-melting the salt flux on metal yield during remelting of chips. A yield up to 75% was observed in the case of remelting of chips under a fused salt flux with 5.5% CaF_2 concentration.

Keywords: Recycling, Machining waste, Salt flux, Fluoride

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1. Introduction

Magnesium alloys are used in aerospace, automotive, electronics, construction, and medical industries due to their unique properties (Demirci, 2006). The demand for magnesium and its alloys has been increasing in the last decades due to the need of substitution of heavier materials in many applications. The European Union reported the risks and importance of sourcing 41 raw materials which are not produced sufficiently in Europe although they have high importance in European economy (Türe and Türe, 2020). Magnesium as a raw material is also included in the list of critical raw materials (Entr, 2014; Ostrovsky and Henn, 2007).

The primary production of magnesium is an energy intensive process as it must be extracted from ores at high temperatures with high electricity consumption. In many countries, strict environmental rules are set thus, the supply of magnesium may be constrained, and production costs might increase with rising energy prices and environmental concerns. Due to the environmental impact of primary metal production, recycling has been also rising to reduce the environmental effects (Lewicka et al., 2021).

Recycling of magnesium scraps are complex due to a thick layer of oxide (Mendis and Singh, 2013). Magnesium is a highly reactive to oxygen and moisture which results in exothermic reactions and forms magnesium oxide (Tenorio and Espinosa, 2002; Nie et al., 2016; Tan et al., 2019). The oxidation reactions of magnesium are given in equations 1 and 2 (Filotás et al. 2020).

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

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \quad (2)$$

AZ63 magnesium alloy is a suitable alloy for weight reduction in structural application and commonly used in magnesium industry. This alloy has high specific strength and stiffness. However, AZ63 has risk to oxidize especially in environments with high moisture. When exposed to air and moisture it goes through a similar oxidation process to that of pure magnesium (Filotás et al. 2020). It is typically coated or alloyed with rare earth elements to improve the corrosion resistance.

Due to the oxide layer on the scraps and high oxidation tendency at high temperature, remelting magnesium alloys is complex. Especially, chips generated during machining processes have a large surface area which increases the oxide amount per unit mass as well as oxidation speed. Remelting scraps are conducted under a salt flux which helps to remove the thick oxide layer, as well as enhances the coalescence of the metal droplets. Furthermore, the molten salt covers surface of the metallic melt and avoids interactions between the metal and air (Akbari and Friedrich, 2010). Salt fluxes typically consist of fluorides (CaF_2 and NaF) and chlorides (NaCl, KCl, and $MgCl_2$) which are used for promoting coagulation and generate a fluid flux respectively (Çağlar Yüksel et al., 2017). Leading research teams have chosen the chloride combination $MgCl_2$/KCl/NaCl in recycling and remelting applications (Maksoud and Bauer, 2015; Ding et al., 2019; Vidal and Klammer, 2019; Sun et al., 2020).

This study investigates the recyclability of chips generated from AZ63 alloy as well as the effect of fluoride concentrations on the metal yield.

2. Materials and Methods

Chips were machined from AZ63 magnesium ingots to generate a high surface area (approximately 30x10 mm) and study its recyclability accordingly. Chips were analysed under Scanning Electron Microscopy (SEM- FEI QUANTA 250 FEG) and Energy Dispersive X-ray Spectroscopy to observe the alloying elements. Additionally, chips were analysed by Thermogravimetric analysis (TGA-Perkin Elmer Diomand) to observe the oxidation behaviour of chips with increasing temperature. Table 1 presents the elemental composition of the ingot. The chips were remelted under the salt flux consisting of NaCl (24 wt.%), KCl (15 wt.%), $MgCl_2$ (56 wt.%), and CaF_2 (4-6 wt.%). A laboratory-scale resistance chamber furnace was used for the remelting experiments. The salt flux was used as dry-mixed and fused to observe the effect of pre-melted salt on the yield.

Table 1. Chemical composition of AZ63 magnesium alloy in wt.%.

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

Dry-mixed salt was prepared by manually mixing the salt components in a mortar while the fused salt flux was prepared by melting the dry-mixed salt mixture at 750 °C and crushing after cooling down. 4 grams of AZ63 magnesium chips shown in the Figure 1 and was charged with the salt mixture in a clay-bonded crucible and heated up to 850 °C and kept at the temperature for 15 minutes. 40 grams of salt mixture was used for each experiment to ensure a full coverage and interaction of the salt with the scrap. Each experiment was carried out three times to define a standard deviation.

Figure 1. AZ63 chips used for the remelting experiments.

CaF_2 was added into the chloride mix in five different concentrations from 4 to 6 wt.% presented in Table 2. CaF_2 was varied to observe the effect of the fluoride content on the metal yield of AZ63 scraps which is missing in the literature. After remelting, the dross and metal in the crucible were separated manually and metal yield was calculated after drying and weighing the samples. The metal yield was calculated according to equation 3.

$$\text{Metal Yield}(\%) = \frac{m_{\text{recovered metal}}}{m_{\text{scrap}}} \times 100 \quad (3)$$

where $m_{\text{recovered metal}}$ is the total amount of recovered magnesium after remelting, m_{scrap} is the total amount of scrap charged for remelting.

Table 2. Experimental parameters

Exp. Nr.	CaF_2 (wt. %)	Preparation method of the salt flux
1-3	4	
4-6	4.5	
7-9	5	Dry-mixed
10-12	5.5	
13-15	6	
16-18	4	
19-21	4.5	
22-24	5	Fused
25-27	5.5	
28-30	6	

3. Results and Discussion

SEM/EDS results of the AZ63 chips are presented in Figure 2. The results show that the alloy is mainly composed of magnesium, aluminium, and zinc. Aluminium zinc intermetallic precipitation is also seen in the SEM image.

The chip samples were also analysed by TGA under oxygen atmosphere up to 800°C (5°C/min). It was observed that the oxidation rate was approximately 1% weight gain per 50°C until 450 °C, however the oxidation rate increased significantly after 450 °C up to 30% weight gain per 50°C. This transition of oxidation behaviour indicates the first liquid formation of the alloy (solidus) which increases the oxidation and shows the necessity of using salt fluxes during remelting.

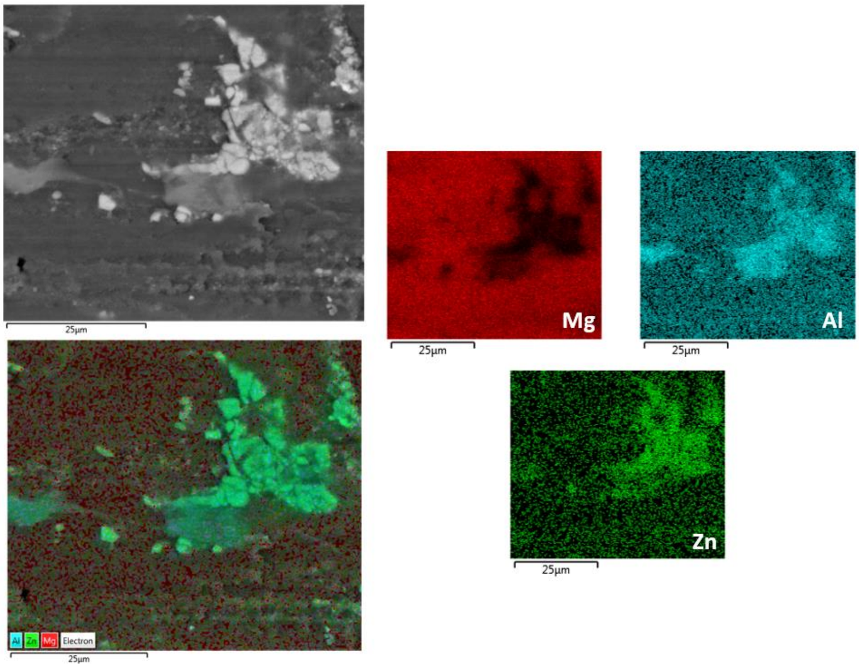

Figure 2. SEM Analysis and EDX mapping for AZ63 magnesium chips.

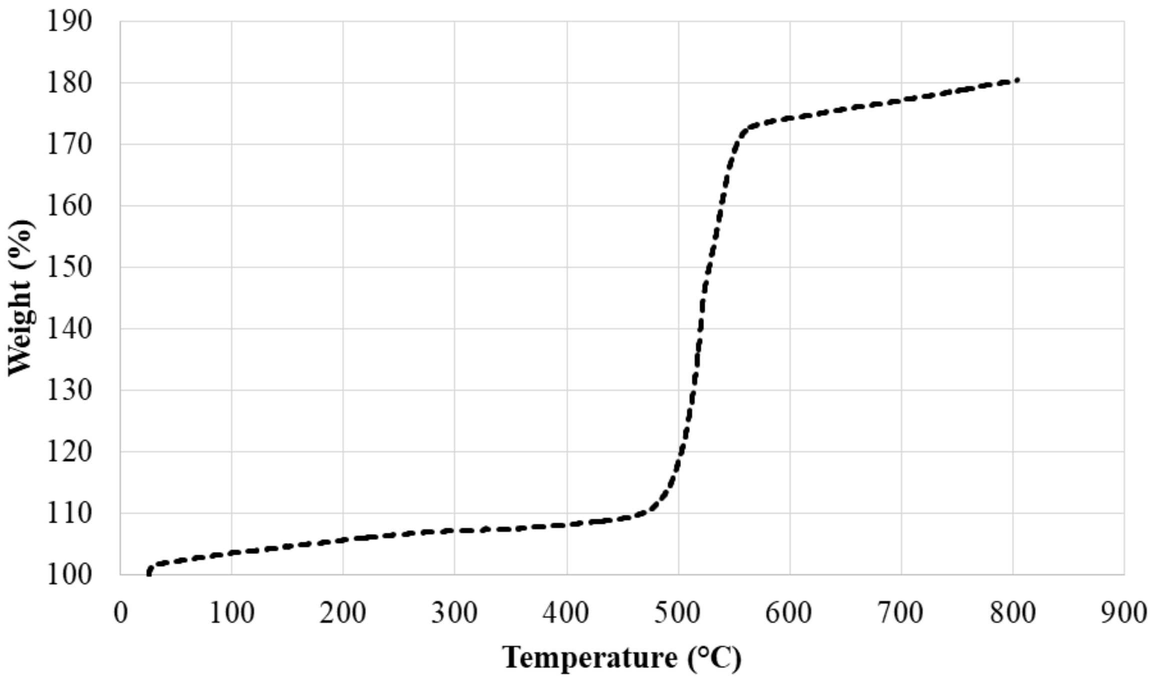

Figure 3. TGA analysis of AZ63 magnesium chips under oxygen flow.

Chips were remelted under dry-mixed and fused salt having CaF_2 concentrations from 4 to 6 wt. %. Figure 4 presents the metal yield of ten different conditions each with three repetitions. In both conditions increasing CaF_2 concentrations increased the magnesium yield until 5.5 wt.% of CaF_2 and decreased after this concentration. 5.5 wt.% showed the highest yield (av. 69% for dry-mixed, av. 73% for fused) which was found in different works as 5 wt.% for pure magnesium (Yörük and Gökelma, 2023) and AZ31 (Akbari et al., 2009) which indicates that different amount of fluoride additions might work different for different alloys. Fused salt showed a higher yield than dry-mixed in all fluoride conditions. The reason for the fused salt worked better is mainly because of its homogeneity which allows it to melt before the chips melt while dry-mixed salt generates a liquid phase at one of the melting points of the components. Early melting protects the metal better from high temperature oxidation.

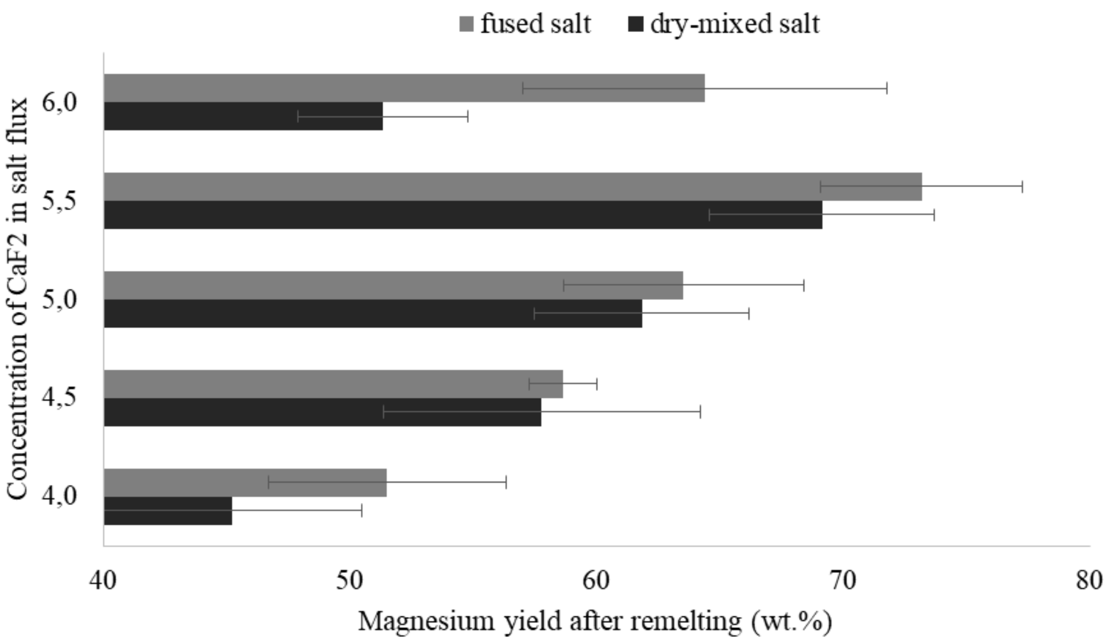

Figure 4. Effects of CaF_2 concentrations and salt pre-melting on metal yield.

Figure 5 presents the recovered magnesium droplets after remelting under dry-mixed and fused salt fluxes. Two size and shape of the droplets are important parameters to understand the coagulation. An efficient coagulation is required to overcome the metal yield issues mainly originating from metal entrapment in the dross. In the lab scale experiments the dross is washed on a sieve so all metals can be included in the yield however, in industrial scale dross is separated to be sold or disposed. Therefore, it is important to achieve an efficient metal-dross separation. The droplets formed in the dry-mixed salt flux are smaller and less spherical in comparison with the droplets formed in the fused salt flux. The main reason for low sphericity is the insufficient removal of the oxide layer due to homogeneity issues. The sphericity of droplets indicates that the salt-oxide interactions were sufficient. Fused salt worked more efficiently since the flux was homogeneous in terms of the melting and F^- concentration in the flux.

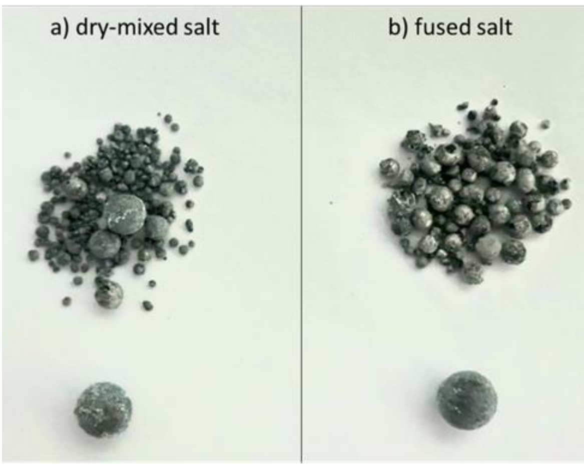

Figure 5. Metal droplets obtained after remelting under (a) dry-mixed and (b) fused salt

4. Conclusions

The effects of premelting the salt flux and CaF_2 content in the salt were studied in this work and the following conclusions could be drawn:

- 5.5 wt.% of CaF_2 showed the highest metal yield for AZ63 alloys.
- Fused salt increases the metal yield significantly.

Metal yield increased with increasing sphericity of droplets.

Author Contributions

The percentage of the author(s) contributions is presented below. All authors reviewed and approved the final version of the manuscript.

	P.Y.	M.G.
C	25	75
D	50	50
S		100
DCP	50	50
DAI	50	50
L	75	25
W	75	25
CR	25	75
SR	50	50
PM		100
FA		100

C=Concept, D= design, S= supervision, DCP= data collection and/or processing, DAI= data analysis and/or interpretation, L= literature search, W= writing, CR= critical review, SR= submission and revision, PM= project management, FA= funding acquisition.

Conflict of Interest

The authors declared that there is no conflict of interest.

Ethical Consideration

Ethics committee approval was not required for this study because of there was no study on animals or humans.

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References

Akbari S, Friedrich B. 2010. Salt-Metal interaction in magnesium recycling. In Proceedings of International Workshop on Metal-Slag Interaction, September 14-19, Yalta, Crimea, Ukraine, pp: 71.

Akbari S, Gökelma M, Friedrich B, Recycling M. 2009. Potential of minimizing magnesium losses in black dross through optimization of salt fluxes. In Proceedings of European Metallurgical Conference, June 28 - July 1, Innsbruck, Austria, pp: 1-19.

Çağlar Yüksel ÖT, Erzi E, Dışpınar D, Çiğdem M. 2017. Melt quality change with different fluxes in secondary A356 alloy. In Proceedings of European Congress and Exhibition on Advanced Materials and Processes, September 17-22, Athens, Greece, pp: 1-5.

Demirci G. 2006. Electrolytic magnesium production using coaxial electrodes. PhD thesis, Middle East Technical University, The Graduate School of Natural And Applied Sciences, Ankara, Türkiye, pp: 170.

Ding W, Gomez-Vidal J, Bonk A, Bauer T. 2019. Molten chloride salts for next generation CSP plants: Electrolytical salt purification for reducing corrosive impurity level. Solar Energy Mater Solar Cells, 199: 8-15.

Entr D. 2014. Report on critical raw materials for the EU. European Commission, Brussels, Belgium, pp: 124.

Filotás D, Fernández-Pérez B, Nagy L, Nagy G, Souto R. A novel scanning electrochemical microscopy strategy for the investigation of anomalous hydrogen evolution from AZ63 magnesium alloy. Sensors Actuat B: Chem, 308: 127691.

Lewicka E, Guzik K, Galos K. 2021.On the possibilities of critical raw materials production from the EU's primary sources. Resources, 10(5): 50.

Maksoud L, Bauer T. 2015. Experimental investigation of chloride molten salts for thermal energy storage applications. In Proceedings of 10th International Conference on Molten Salt Chemistry and Technology, May 22 - 25Seattle, USA, pp: 751-760.

Mendis CL, Singh A. 2013. Magnesium recycling: to the grave and beyond. Jom, 65: 1283-1284.

Nie H, Schoenitz M, Dreizin EL. 2016. Oxidation of magnesium: implication for aging and ignition. J Physical Chem, 120(2): 974-983.

Ostrovsky I, Henn Y. 2007. Present state and future of magnesium application in aerospace industry. In Proceedings of International Conference "New challenges in aeronautics", August 19-22, Moscow, Russia, pp: 19-22.

Sun H, Wang JQ, Tang Z, Liu Y, Wang C. 2020. Assessment of effects of Mg treatment on corrosivity of molten NaCl-KCl-MgCl2 salt with Raman and Infrared spectra. Corrosion Sci, 164: 108350.

Tan Q, Yin Y, Mo N, Zhang M, Atrens A. 2019. Recent understanding of the oxidation and burning of magnesium alloys. Surface Innovat, 7(2): 71-92.

Tenorio JAS, Espinosa DCR. 2002. Effect of salt/oxide interaction on the process of aluminum recycling. J Light Met, 2(2): 89-93.

Türe Y, Türe C. 2020. An assessment of using Aluminum and Magnesium on CO_2 emission in European passenger cars. J Cleaner Prod, 247: 119120.

Vidal JC, Klammer N. 2019. Molten chloride technology pathway to meet the US DOE sunshot initiative with Gen3 CSP. In AIP Conference Proceedings, 4–8 September, Bodrum, Türkiye, pp: 2126.

Yörük P. Gökelma M. Derin B. 2023. Effect of compaction and fluoride content on the remelting efficiency of pure magnesium chips. Canadian J Metallur Mat Sci, https://doi.org/10.1080/00084433.2023.2262189.