Investigation of Process Parameters in a Vacuum Distillation Setup to produce High Purity Magnesium

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Abstract

For its low density and high strength to weight ratio, magnesium usage in automotive and aerospace applications is highly appealing, as it drastically decreases the energy consumption, saving valuable resources as well as the environment. Moreover, magnesium has gained a lot of attention in the past few years as a suitable biodegradable metal for production of medical implants and also as a battery anode with superior properties to lithium. However, extensive usage of magnesium has been hindered by its low corrosion resistance, a problem that arises due to the presence of certain impurities inside the metal even with extremely low concentrations. In this study, experimental investigations focusing on magnesium refining with the aim of producing 4N (or higher) purity magnesium are conducted.

1 Introduction

Technological advances in research and development of magnesium has continued to grow in recent years in efforts to utilize it more in the transportation industry, as its low density has significant effects on fuel consumption [1]. Not only that, but various investigations have been reported to focus on the great potential of magnesium to replace titanium and polymer-based alloys as the main element in biomedical implants. That is due to its biodegradability, mechanical stability and enhanced stress shielding [2–4]. Moreover, its abundancy, price and non-toxicity compared to lithium, combined with a higher volumetric energy density and operational safety, makes magnesium a very attractive replacement for lithium as battery anodes [5, 6].

Despite the advantages, the application of magnesium and its alloys on an industrial scale is limited due to the poor corrosion resistance. Elements like Fe, Cu, Co and Ni even in very low ppm-concentrations have drastic influence on increasing magnesium's corrosion rate and hence negatively affecting its performance in the above mentioned applications [7]. The impurities, either in elemental form or as intermetallic phases, tend to act as cathodic sites in the magnesium matrix, thus forming micro-galvanic cells that results in rapid corrosion [8, 9].

Therefore, producing high "HP" (4N) as well as ultra-high purity grades "XHP" (5N or more) of magnesium is the main challenge facing the utilization of magnesium in various applications. Different methodologies including electro-refining, impurity precipitation or vacuum distillation have been investigated over the years, with vacuum distillation proving to be the only feasible technique for this task. In this paper, the vacuum distillation technique along with the process parameters determination have been demonstrated to show the effect of temperature and holding time on the refining percentage of selected impurities.

2 Vacuum Distillation

Vacuum distillation is the process of separating the components or substances from a liquid mixture by selective vaporization and condensation, based on different vapor pressures of different substances. As magnesium is normally more volatile than almost all of its common impurities (except for Zn), this method would be more than suitable to collect the purified magnesium from the condenser, while leaving most of the impurities in the crucible as residue [10, 11]. Figure 1 illustrates the vapor pressure of different elements, calculated in the simplest form, using the following equation [12]:

$$\log p^* = AT^{-1} + BlogT + CT + D \tag{1}$$

where p* is the vapor pressure of pure substances (Pa) and T is the absolute temperature (K). Regarding A, B, C, and D, they are evaporation constants for different elements that could be found in the literature [12].

Vacuum distillation has many advantages when metal's refining is considered. The lack of an oxidizing atmosphere is especially important in the case of magnesium as it prevents oxidation/burning of the material. Low pressures associated with the process allows for high rates of evaporation at significantly low temperatures, which decreases the energy consumption and operational costs. Additionally, vacuum distillation is considered to be an environmentally friendly process as it does not produce slags, waste water nor exhaust gases [13–15].

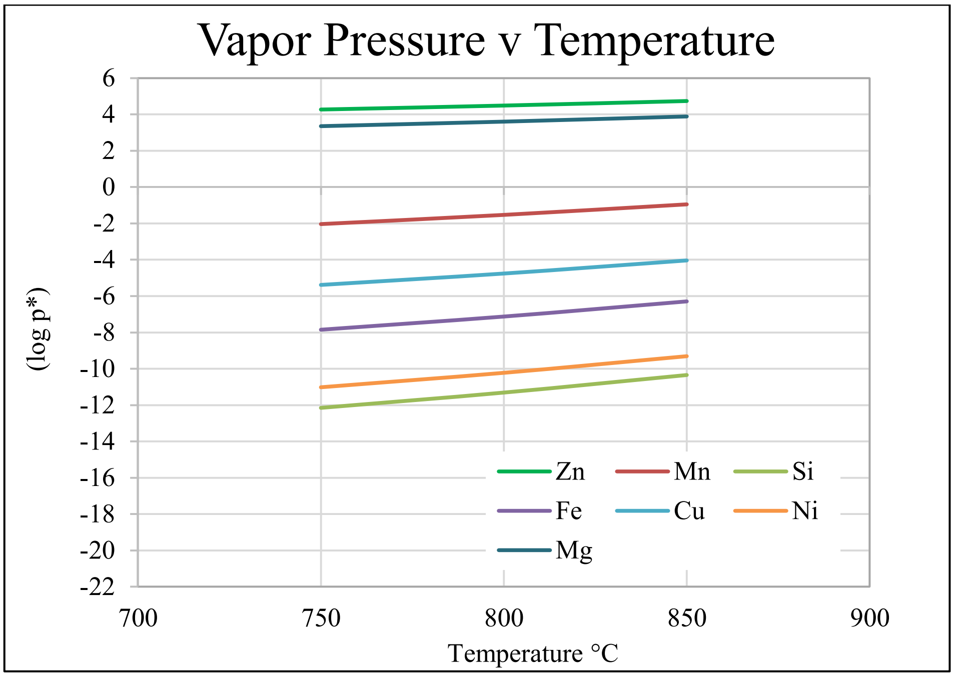


Figure 1: The variation of log p^* versus temperature for Mg and impurities

Over the years, the feasibility of vacuum distillation to produce HP and XHP magnesium has been investigated. Lam and Marx reported the production of 5N pure magnesium using a patented multi-zone vertical distillation retort in 1996, with their preferred temperature-pressure combination being 700 °C and 1.3×10^{-7} mbar respectively [16]. In other efforts to achieve the same goal, Tayama and Kimura devised a vertical retort with special vapor passage plates. They reported the optimum temperature-pressure combination to be 750 °C and 1.3×10^{-3} mbar. A purity level of almost 6N magnesium could be produced by this method [17]. More recently, Uggowitzer *et al.* developed a new retort that allows the collection of magnesium after processing as a bulk. This have a significant advantage over powders, as collecting magnesium in the form of fine crystals results in their oxidation (high surface/volume ratio and a highly reactive element), thus turning into non-metallic inclusions upon re-melting [18]. They produced 5N-pure magnesium using this technique [19]. In the following chapter, the experimental trials are discussed in details.

3 Experimental trials

The objective of these trials is to find the optimum temperature-pressure combination and the effect of temperature and holding time on the reduction percentage of selected impurities. An induction furnace with maximum power of 40 kW was used throughout the trials. An ingot of 3N (99.9 %) pure magnesium was used as the starting material for the experiments, whose chemical composition, analyzed through ICP-MS is represented in Table 1.

The surface of the ingot was initially cleaned mechanically by a milling machine to remove the oxide layer. The ingot was then cut into cubes and then the surface of these pieces was mechanically grinded by Al_2O_3 sand paper to get rid of the cooling fluid (needed during cutting) and any remaining defects in the charge material. Finally, these pieces were immersed in ethanol for a 3-hour ultrasonic bath to ensure no contamination from the sand paper. Through these preparation steps, the contamination from external sources was minimized, thus ensuring a chemically similar input material for each trial.

Table 1: Concentration of the impurity elements in the Mg-charge material

Element	Fe	Cu	Co	Ni	Mn	Zn	Al
Concentration (ppm)	15.31	9.61	0.46	<0.1	242.39	53.88	177.56

A vertical distillation reactor was used for the trials. The bottom part is composed of a high purity graphite crucible (less than 20 ppm ash content) with a lid, while the upper part of the setup is composed of a steel condenser/collecting plate system (as shown in Figure 2), and coated with pure Y_2O_3. This coating is essential to prevent any potential iron contamination into purified magnesium.

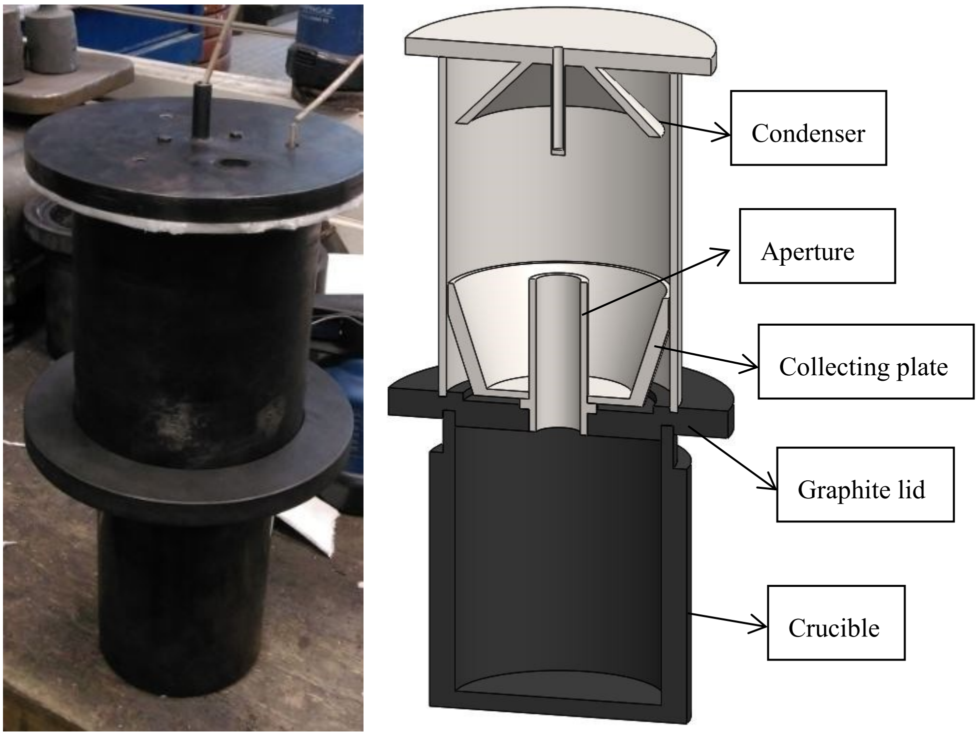


Figure 2: A simple sketch (right) and the actual external view of the vacuum distillation setup (left)

The parameters used for each trial are shown in Table 2. Two series of trials were conducted in this study. The first series was dedicated to assess the effect of the processing time on the purity of the product (from T1 to T3), while the second was dedicated to investigate the effect of the melt temperature on the purity of the condensed magnesium (from T4 to T6). Normally, a constant pressure should be chosen for the trials of series 2, in order investigate the effect of temperature. Choosing 1 mbar as the designated pressure for this series, it was observed during preliminary tests that decreasing the pressure below the level where the evaporation starts, results in splashing of the molten metal, especially due to the turbulent nature of induction heating. This could have a severely negative effect not only on the purity of the product, but could also cause a blockage in the setup due to magnesium condensing in the vapor path. To show the effect of this phenomena, an extra trial labelled T* with the exact parameters as T2, but at a lower pressure (1 mbar) was carried out. Moreover, it was decided to conduct each trial in series 2 at its optimum pressure, which is the pressure where evaporation starts.

Table 2: Parameters for conducted trials

Series 1 (Variable: Holding time)				**Series 2 (Variable: Temperature)**			
Trial	Temperature (°C)	Pressure (mbar)	Evaporation time (min)	Trial	Temperature (°C)	Pressure (mbar)	Evaporation time (min)
T1	750	15	30	T4	700	1	60
T2	750	15	60	T5	800	22	60
T3	750	15	90	T6	850	65	60

4 Results and Discussion

After all trials, almost all of the condensed magnesium was found in the form of small crystals in the condenser (see Figure 3). Samples from each trial were carefully taken to avoid any contamination and analyzed by ICP-MS. Nickel concentration remained below the detection limit after all trials, so it will not be mentioned from now on.

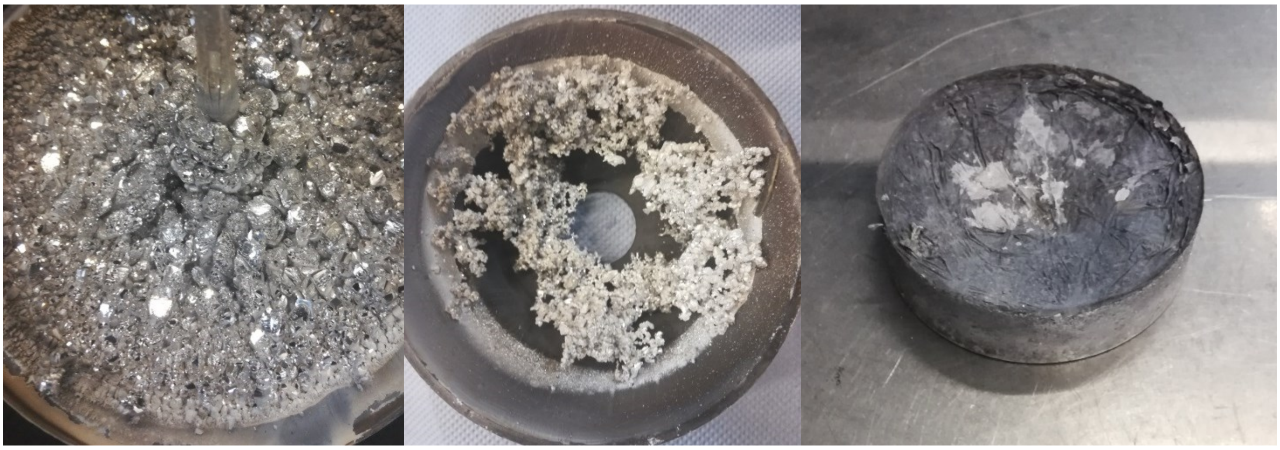
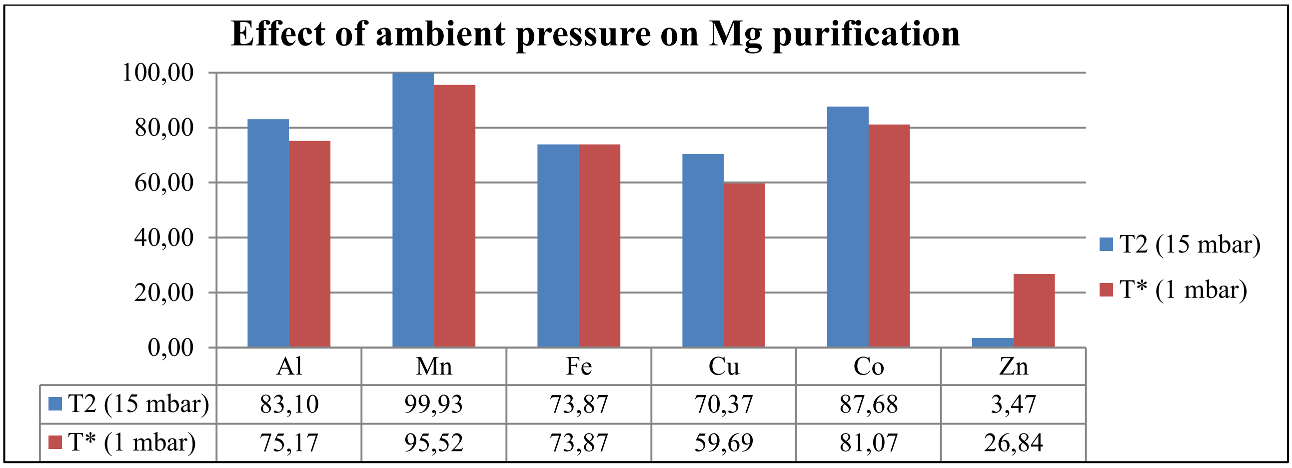


Figure 3: Condensed magnesium in the condenser (left) and in the collecting plate (middle) as well as the crucible residue (right)

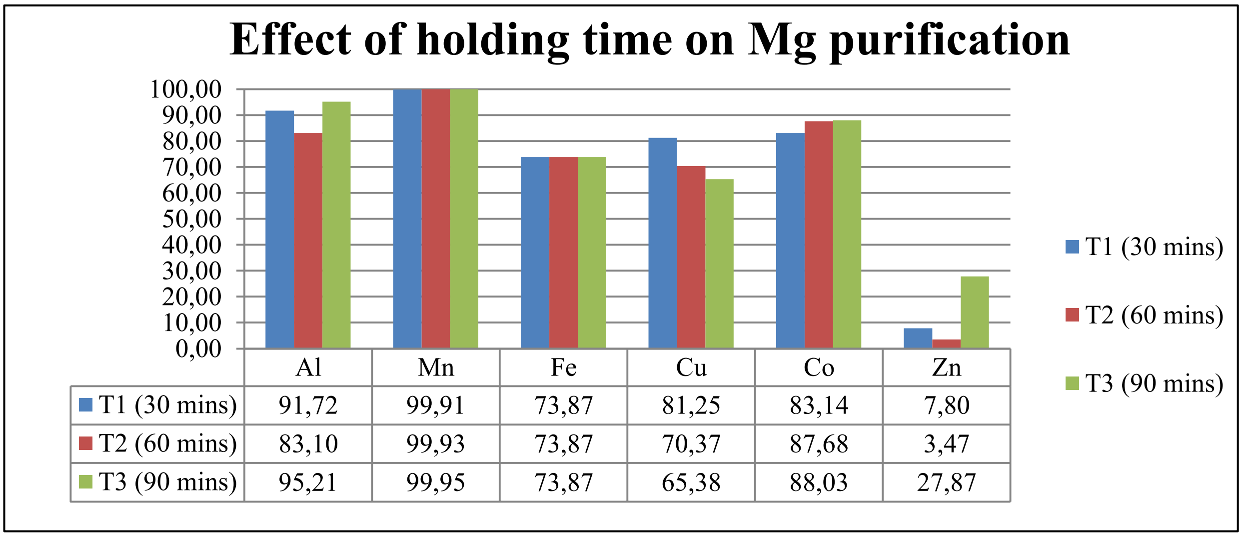
The results shown in Figure 4 show the significant difference in reduction percentages, which favors T2 over T* except in the case of Zn. The increased Zn concentration in T2 can be explained by the low concentrations of all other analyzed impurities. The decreased purification is attributed to the rapid violent evaporation (even to the extent of splashing from the melt, caused by the induction heating system) that occurs when the pressure is lowered further than the level, where the evaporation process initially started.



	Al	Mn	Fe	Cu	Co	Zn
🟦 T2 (15 mbar)	83,10	99,93	73,87	70,37	87,68	3,47
🟥 T* (1 mbar)	75,17	95,52	73,87	59,69	81,07	26,84

Figure 4: Comparison between reduction percentages achieved by T2 and T* for impurities

Regarding the first series of trials, the results show that the effect of holding time differs between two groups of impurities (see Figure 5). On one hand, the purification of magnesium from Mn, Fe and Co is not significantly dependent on the holding time. On the other hand, Al and Zn show an alternating tendency with time. The amounts of Al and Zn in the condensate increase throughout the first hour until their evaporation stop, so any further evaporated magnesium results in the dilution of these two impurities in the condensate, thus decreasing their concentration and increasing their reduction percentage. The opposite trend seen in the case of Cu could be simply explained by the extremely small amounts of Cu detected in all samples. The Cu concentration in the three trials is 1.8, 2.8 and 3.3 ppm for T1, T2 and T3 respectively, so it can be safely assumed that Cu belongs to the first group of metals that is not significantly affected by the holding time.



	Al	Mn	Fe	Cu	Co	Zn
🟦 T1 (30 mins)	91,72	99,91	73,87	81,25	83,14	7,80
🟥 T2 (60 mins)	83,10	99,93	73,87	70,37	87,68	3,47
🟩 T3 (90 mins)	95,21	99,95	73,87	65,38	88,03	27,87

Figure 5: Comparison between reduction percentages achieved by T1,T2,T3 for selected impurities

In Figure 6, a spider diagram is depicted to show the results of the second series. It is clear that no significant differences between the trials could be seen when it comes to the purity of the produced magnesium, with the best result being that of T4 at 700 °C. This chart also shows the increasing tendency of the pressure at which the evaporation process with the increase in temperature.

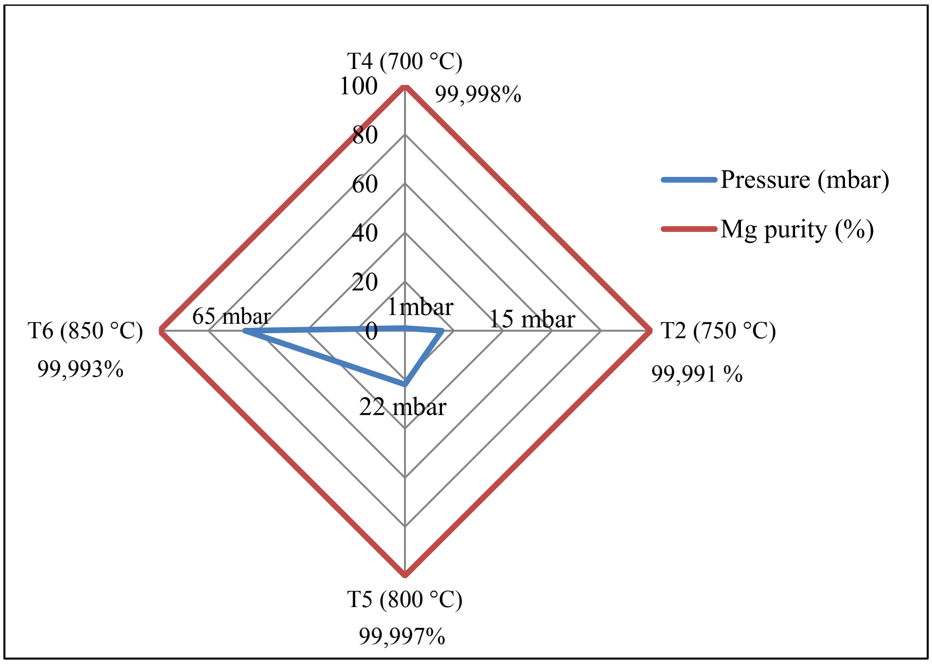


Figure 6: Effect of temperature on magnesium purity and optimum pressure

5 Overview

The effect of holding time and temperature on magnesium purification via vacuum distillation technique was investigated in this work. Based on the reduction percentages of the impurities, the holding time of 90 minutes is preferred. Regarding temperature, no significant effects were observed, with the best result being at 700 °C, the lowest of the investigated temperatures. In almost all conducted trials, the collected magnesium was successfully refined from 3N to 4N purity (except for T*), which confirms the importance of conducting the process with an optimum temperature-pressure combination. It was observed that when the pressure decreases below the level at which the evaporation starts, it can negatively affect the purity of the product. By combining this finding with the fact that during this study the evaporation started at much higher pressures (and considered optimum) than those reported by all previous studies (see chapter 2) that were all conducted in resistance furnaces. This generates an interesting future research area, which is the effect of induction heating (and also the setup itself) on the kinetics of the process, its optimum process window and the achievable purities in comparison to distillation processes conducted in resistance furnaces. Furthermore, in the current setup magnesium was not collected as bulk, as it condensed rapidly due to condenser's low temperature and formed fine crystals on the condensers wall with almost no liquid-condensed magnesium falling into the collecting plate. Therefore, different setup designs should be investigated with the aim of eliminating contamination and allowing the collection of magnesium as bulk material.

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