A Synopsis on

STUDY THE EFFECT OF "Mn" IN MAGNESIUM & MAGNESIUM BASED ALLOYS

Proposed to be submitted in partial fulfilment of the requirements for the award of the degree

DOCTOR OF PHILOSOPHY

in

METALLURGICAL AND MATERIALS ENGINEERING

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SYNOPSIS

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1. TITLE OF THE THESIS AND ABSTRACT

Title of the Thesis: Study the effect of "Mn" in Magnesium & Magnesium based Alloys

Abstract:

Magnesium and its alloys are extremely susceptible to oxidation and fire because of their reactivity with oxygen. Therefore, special care should be taken while melting them. In this research, nine magnesium melting and refining fluxes were studied by varying chlorides, fluorides, and oxide content. Decomposition behaviour, mass change, and fusing/melting of these nine fluxes were studied by TG/DTA technique. The surface morphology of these fluxes after fusing was studied by visual observation and scanning electron microscope. Magnesium was melted using these nine fluxes and for every flux weight loss of magnesium was calculated. From a thermal analysis study, it was confirmed that all the fluxes were fused before magnesium melting. Based on the flux layer and weight loss of cast magnesium calculations, flux 9 (23% KCl, 72% $MnCl_2$, 2.5% $BaCl_2$ and 2.5% CaF_2) was best compared to other fluxes.

Manganese solubility in magnesium mainly depends on temperature, its sources, and the presence of other elements. In this research, five different Mg-Mn systems were developed by the addition of different sources of manganese. To check the recovery of manganese in pure magnesium, each alloy was developed by adding the same weight % of the manganese-containing source (5 wt.%) at the same temperature (850°C). Among all manganese sources, the recovery of manganese was highest in the case of electrolytic manganese flakes containing the system. Optical pictures of all developed systems reveal the grain refinement of pure magnesium due the presence of manganese. The hardness and ultimate tensile strength of magnesium were increased by the addition of all sources of manganese. However, % elongation decreases as the wt. % of manganese increases like in the case of electrolytic manganese flakes containing system.

To check the solubility of manganese in pure magnesium, five Mg-Mn systems were also developed by varying the temperatures (750°C, 800°C, 850°C, 900°C, and 950°C). Results show that maximum manganese recovery is attained at 950°C temperature. It also found that manganese presence (up to 2.66 wt.%) refine the coarse grain of pure magnesium.

Mg-Cu, Mg-Cu-Mn, Mg-Ni, and Mg-Ni-Mn alloys were also developed and studied in this research. The effect of manganese variation on the microstructure and mechanical properties of Mg-Cu alloys and Mg-Ni alloys were studied using an optical microscope, scanning electron microscope, X-ray diffraction, and tensile test (room temperature), and Vickers hardness test. The corrosion rate of alloys was measured at 3.5 wt. % NaCl solution by immersion test. The result shows that the grain size of the Mg-Cu alloys was reduced by the addition of manganese. XRD analysis confirms the presence of main phases including α-Mg, Mg_2Cu, and Mn as minor phases. In 2 wt.% manganese-containing Mg-Cu alloys, the highest ultimate tensile strength (179 MPa) and hardness (55 HV) were achieved. The corrosion rates of the Mg-Cu alloys were drastically decreased due to the presence of manganese. On the other hand, the nickel and manganese presence refine the grain size of magnesium. However, the presence of manganese in Mg-Ni alloy shows an adverse effect on microstructure and corrosion behaviour. The corrosion rate of the Mg-Ni alloy was increased due to manganese. The ultimate tensile strength and hardness of all developed alloys are more compared to pure magnesium. Though mechanical properties of Mg-Ni and Mg-Ni-Mn alloys do not differ significantly. Overall, manganese addition is proper for Mg-Cu alloys but not appropriate for Mg-Ni alloy.

2. BRIEF DESCRIPTION OF THE STATE OF THE ART OF THE RESEARCH TOPIC

Magnesium alloys have been widely used in a variety of applications, from automobiles to electronics, due to its unique characteristics such as good damping capacity, high specific strength, excellent strength-to-weight ratio, good fatigue and impact strengths, relatively large thermal and electrical conductivities weld-ability under controlled atmospheres, and cast-ability. In certain applications where damping resistance is important, magnesium can substitute for conventional materials such as iron and aluminum. [1–9]. All above properties of magnesium alloys make it attractive for use in the automotive and aerospace industry to meet the requirements of weight reduction and higher fuel-efficient vehicles. [10] Magnesium is an excellent structural material due to its low cost, low density, and excellent machinability. [11,12] However, unalloyed magnesium is not widely used for structural purposes due to less corrosion resistance. [13]

Magnesium alloys have better solidification characteristics than copper and aluminum alloys; hence casting is one of the most important routes for its fabrication. [14] However, due to its high oxidation tendency, special care should be required while casting route. If magnesium oxidation is not controlled, a porous, non-sticky layer of MgO forms on the surface of the molten metal. This layer cannot be prevented and crates a passage of oxygen into magnesium melt. Additionally, magnesium and its alloys are evaporating easily so extremely fine powder will form around the colder areas of the melt. This magnesium dust easily ignites due to the high surface-to-volume ratio. Therefore, preventing the melt from oxidation and controlling magnesium from evaporation is very crucial.[15–18]

2.1 Casting Techniques

The casting of magnesium consists of a fluxing technique or a flux-less technique (in presence of a gas or vacuum) because it oxidizes and contains non-metallic inclusions. [19]

Flux-less Method:

In the flux-less method, nonreactive gases such as nitrogen, argon, and oxide film modifiers such as sulphur hexafluoride (SF_6), and sulphur dioxide (SO_2) are used as a cover gas. Sulphur hexafluoride provides an effective barrier due to the formation of a dense magnesium oxide and magnesium fluoride film. This film protects magnesium from oxidation and evaporation. However, SF_6 has a warming potential, 23,900 times greater than carbon dioxide (CO_2) and is progressively expensive so it is banned in many countries. The gases used to cover the surface of molten magnesium must be continuous, fresh, and free of moisture. Because of the high cost and environmental pollution, the alternative fluxing method is also preferred by the magnesium casting industries.[20–23]

Fluxing Method:

Each type of flux plays an important role in the magnesium melting and refining process. The main characteristics of the covering fluxes are to protect the magnesium melt against oxidation, melt before melting of magnesium, cover the surface properly, and form a dense strong film that is easily separable during pouring. As per individual characteristics, a combination of chlorides, fluorides, and oxides is used as a flux that is shown in table 1. [24–30]

Table 1 Characteristics of various chemicals used to synthesis the flux

Chemicals	Characteristics
Chlorides	• The higher density of the chlorides causes the impurities to sink to the bottom of the melt as sludge. So, a combination of $MgCl_2$ and KCl was used to provide the low melting point eutectic. • $MgCl_2$ minimizes surface oxidation by creating a thin-film layer on the metal surface. • $MnCl_2$ is also used as an effective and economical additive in flux for the removal of iron in the production of magnesium alloys. • $BaCl_2$ was added to adjust the melting point. Due to its high density, encourage the flux and the flux-oxide particulates to settle at the bottom.
Fluorides	• Fluorides are added due to their better wet-ability and chemical reactivity with magnesium oxide. • The barium, strontium, and calcium fluorides provide the density required for the salt to effectively mix with the magnesium and then settle out at the bottom of the crucible by making high-density inclusions like MgF_2.
Oxides	• MgO absorbs the chlorides. • It also offers typical density to cover and refine the metal.

2.2 Effect of Manganese on Magnesium Alloys

Manganese is an important addition to many magnesium alloys to improve corrosion and creep resistance (with a rare earth addition). It is added in Mg-Al alloys, Mg-rare earth alloys, Mg-Zn alloys, and with many other elements to lower the effect of the iron (Fe) impurity content to control the overall corrosion of that alloys. [13,31–33] Manganese addition decreases the solubility of iron in magnesium drastically and therefore leads to the precipitation of iron, which settles down in the magnesium melt. The excess iron is removed by precipitation and settling of intermetallic particles containing iron and manganese in combination with other alloying elements. Moreover, Manganese forms a protecting layer during the oxidation of magnesium. For these reasons, manganese is added to commercial Mg alloys in small amounts. [34]

Manganese additionally assumes a significant job in the control of the microstructure. For instance, it controls the crystal grain size of magnesium while solidification and refines the grains. Manganese presence prevents unusual germination, which happens during heat treatment. [35] It is by and large added with around 0.34% to change the iron and other heavy metal elements by converting into moderately harmless inter-metallic compounds.[32]

Pure magnesium-manganese alloys such as Mg-1.5Mn and Mg-2Mn are counted as alloys for general use with medium strength values. The alloying content is limited to a maximum of 2.2% manganese. The influence of the manganese content on the mechanical properties is rather low (figure 1). In rolled condition alloys with more than approximately 1.5% manganese, offers higher strength. [36]

In the presence of other alloying elements, the level of manganese additions varies which depends on the mutual solubility of iron and manganese. The solubility of manganese is less than 1% at 482 °C and 2.2% at 653°C temperature. [31,32]Solubility of manganese decreases with decreasing temperature causing more precipitation of manganese. As shown in figure 2, the Mg-Mn system is described by a wide miscibility gap in the liquid state and very less experimental information is accessible on this system. [37]

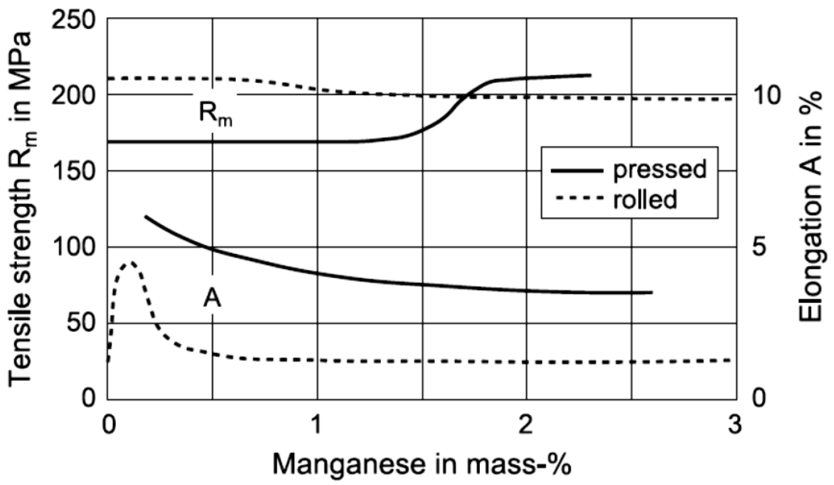


Figure 1: Effect of additions of manganese on the mechanical properties of magnesium [36]

Phase diagram

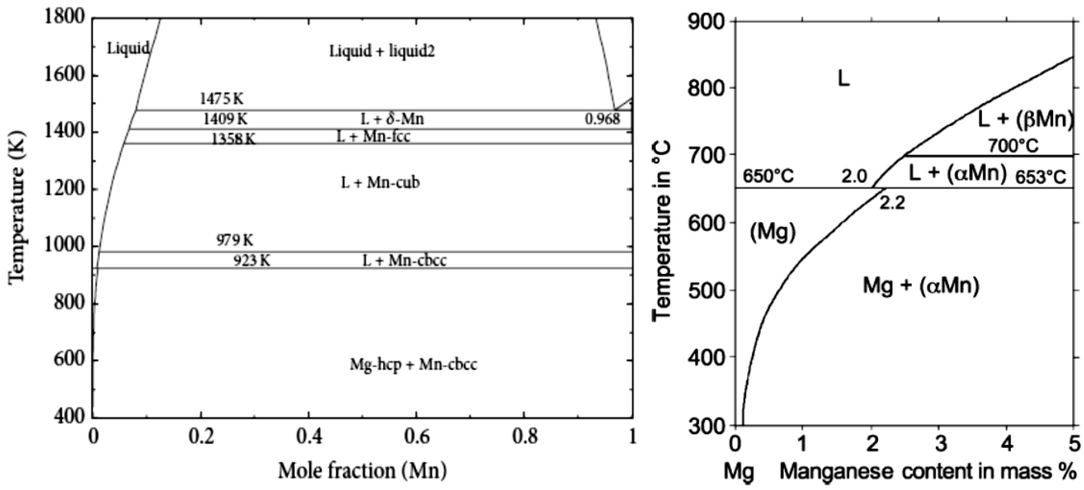


Figure 2: Mg-Mn binary phase diagram [36–38]

2.3 Effect of Copper on Magnesium Alloys

As per literature, copper, nickel, and iron elements increase the corrosion rate of magnesium. If copper presents greater than 0.05 wt. %, it reduces corrosion resistance and ductility of magnesium. Copper has a detrimental effect on corrosion in AZ and AM alloys, but comparatively, it is less harmful than nickel and iron. However, in addition to this copper is also useful for improving, room temperature and high-temperature strength of magnesium alloy, hence it is added as an alloying element in Mg-Mn-Zn alloy.[32,36,39–41]

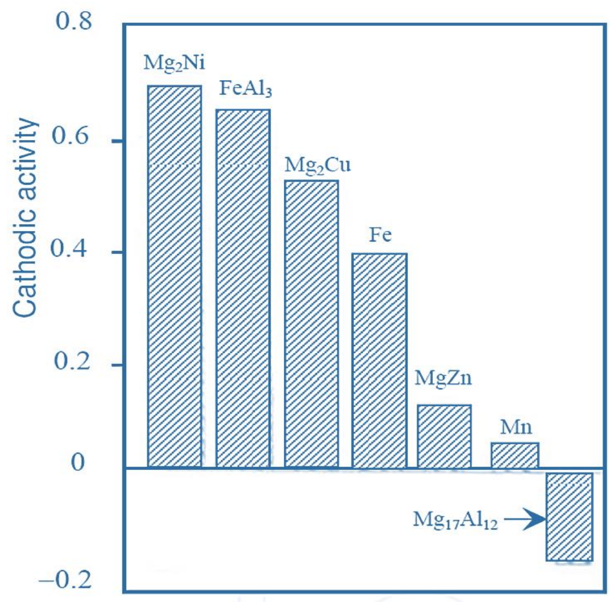


Figure 3: Cathodic activity of precipitated phases in Mg alloys in salt water relative to their alloy matrix [41]

2.4 Effect of Nickel on Magnesium Alloys

The solid solubility of nickel in magnesium is limited.[42] The cathode activity of nickel in Mg alloys is greater than that of iron in pure Mg and Mg alloys, because, as indicated in figure 3, nickel precipitates in magnesium alloys as Mg_2Ni, which is more cathodically active than $FeAl_3$ and Fe. [41] Hassan et al. [43] reported that the formation of Mg_2Ni intermetallic increases room temperature yield strength and ultimate tensile strength. However, the addition of nickel to magnesium alloys has adverse effects on corrosion resistance, even in very minute amounts. Due to this reason, the use of nickel is limited in magnesium alloys. [44]

3 DEFINITION OF THE PROBLEM

As per the literature, a major challenge for the designer of the 21st century is to design and develop lightweight and energy-efficient materials. Magnesium can substitute steel, aluminum alloys, and plastics. However, molten magnesium is extremely susceptible to oxidation so melt-protection during melting and alloying are necessary. Molten magnesium is protected by the flux process and flux-less process. Both processes have their merits and demerits but due to the environmental and cost factors fluxing technique is still used in many foundries. In the fluxing process, melt loss and the presence of inclusions is the major problem. To overcome this problem, nine magnesium melting and refining fluxes were studied. Dow fluxes compositions were taken as a base to prepare five fluxes and another four fluxes were developed by varying chlorides, fluorides, and oxide content.

Magnesium alloys are used in numerous applications due to their unique characteristics (discussed in 2) but their poor strength and corrosion resistance property (compare to aluminum alloys) limits their use particularly outdoors. To improve little strength, and corrosion resistance and lower the iron (Fe) impurity in many magnesium alloys, manganese is added as an alloying element. However, its solubility in magnesium is less than 1% at 482 °C and 2.2% at 653 °C temperature only. There is not enough literature available to increase the concentration of manganese in magnesium and its alloys. To achieve highest recovery of Mn from its various sources are studied and included as a part of the present research activity.

In most of the literature, it was reported that iron, copper, and nickel are responsible for increasing the corrosion rate of magnesium and its alloys. Therefore, to improve corrosion resistance they should be kept below a threshold value. However, hardly a few researchers worked on the effect of copper and nickel on the mechanical properties of magnesium. So, in this research, the effect of various amounts of copper and nickel on microstructure, mechanical properties, and corrosion behaviour of magnesium alloys are also included. Also, Mg-Cu-Mn alloys (CM alloys) and Mg-Ni-Mn alloys (NM alloys) were developed and studied which are still unexplored by the researcher.

4 OBJECTIVE OF THE WORK

The present research work has been planned with the following objectives considering the research gap and key issues as discussed above:

- Synthesis and characterization of magnesium melting fluxes
- Increase the amount of manganese by addition of various sizes and forms of Mn sources like manganese coarse powder, manganese chloride, manganese oxide, manganese fine powder, and manganese flakes and finally studied their behavior in magnesium.
- Develop Mg-Mn alloys by varying temperatures and study their effect on the solubility of manganese in magnesium
- Develop Mg-xCu and Mg-xCu-yMn alloy (where x=1,2,3 and y=1,2,2) and study the microstructure, mechanical property, and corrosion behavior of them
- Develop Mg-xNi and Mg-xNi-yMn alloy (where x=1,2 and y=2,2,3) and study the microstructure, mechanical property, and corrosion behavior of them.

5 ORIGINAL CONTRIBUTION BY THE THESIS

The major research contributions are discussed below.

1) Nine magnesium melting fluxes were developed and identified the best flux among them.
2) Using best flux magnesium melting is done and develop various Mg-Mn, Mg-Cu-Mn, and Mg-Ni-Mn alloys.
3) Higher manganese-containing alloys were developed.

4) Refine the microstructure of magnesium, Mg-Cu alloys, and Mg-Ni alloys
5) Increase ultimate tensile strength and hardness of pure magnesium
6) The corrosion rate of Mg-Cu alloys was reduced by adding manganese to it
7) Microstructure, mechanical properties, and corrosion behavior of pure magnesium, Mg-Mn, Mg-Cu-Mn, and Mg-Ni-Mn alloys were studied.

6 METHODOLOGY OF RESEARCH AND RESULTS & DISCUSSION

This research work is divided into 5 phases.

Phase I: Develop magnesium melting fluxes and identify the best among them

Phase II: Effect of addition of various manganese sources on magnesium metal

Phase III: Effect of temperature on solubility of manganese in magnesium

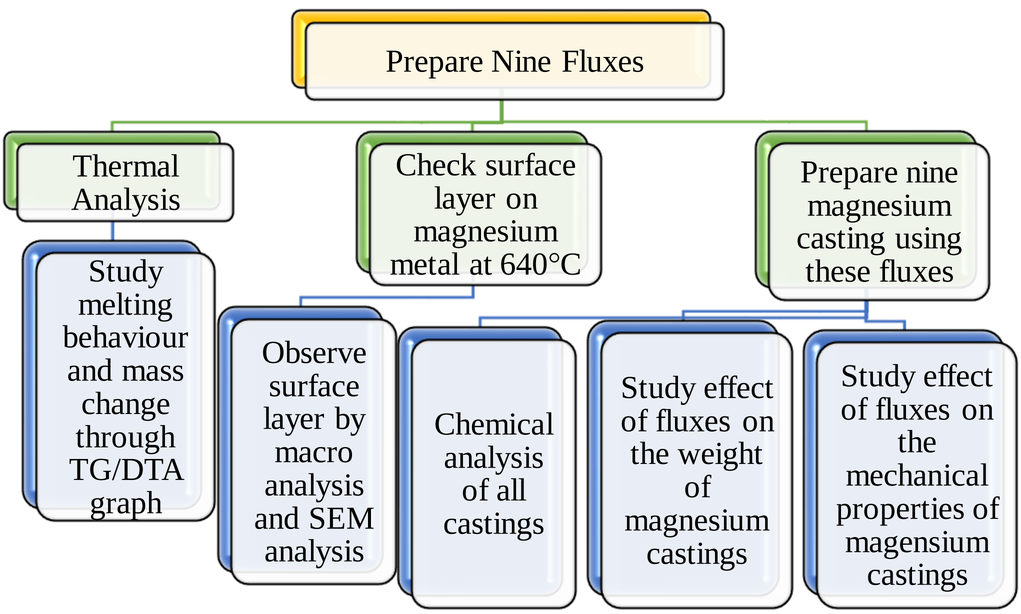
Phase IV: Develop and study the Mg-Cu and Mg-Cu-Mn system

Phase V: Develop and study Mg-Ni and Mg-Ni-Mn alloys

6.1 Phase I

Develop magnesium melting fluxes and identify the best among them

Magnesium melting can be possible by using a different flux, but the amount of magnesium metal recovery varies from flux to flux. The present research work focuses on magnesium melting because once the burning of molten magnesium is controlled then alloying can be possible. Following flow chart include Experimental work.



Results and Discussion:

a) Thermogravimetric/Differential Thermal Analysis of All Fluxes:

In this study, nine types of fluxes were prepared by varying the amount of $MgCl_2$, KCl, and $CaCl_2$. $BaCl_2$, NaCl, MgO and CaF_2. By varying the amount of chemicals (salts), the melting behavior of all fluxes was different, and finally, to understand it, thermal analysis has been carried out. For reference, TG/DTA graph of flux 1 is shown here in figure 4. All thermal analysis results indicate that the proper covering layer of fluxes was started before the actual melting of magnesium metal. Thus, magnesium melting can be possible by using a different flux, but the amount of magnesium metal recovery varies from flux to flux.

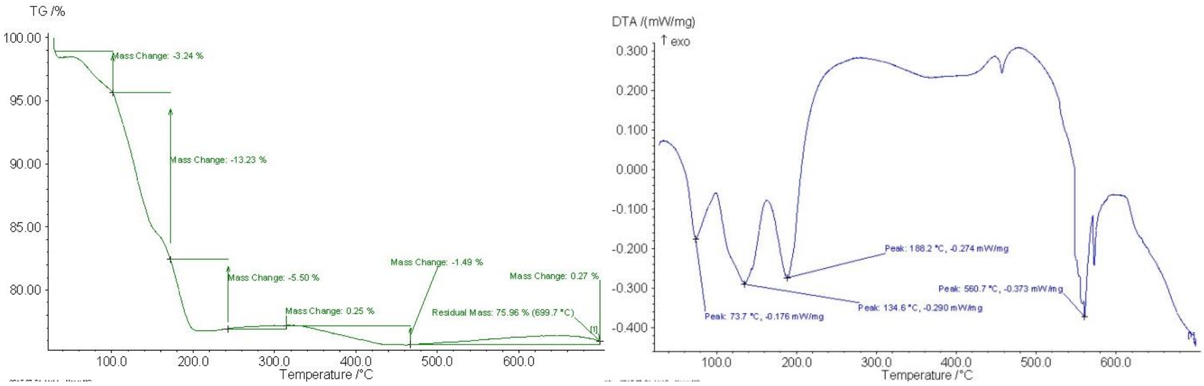
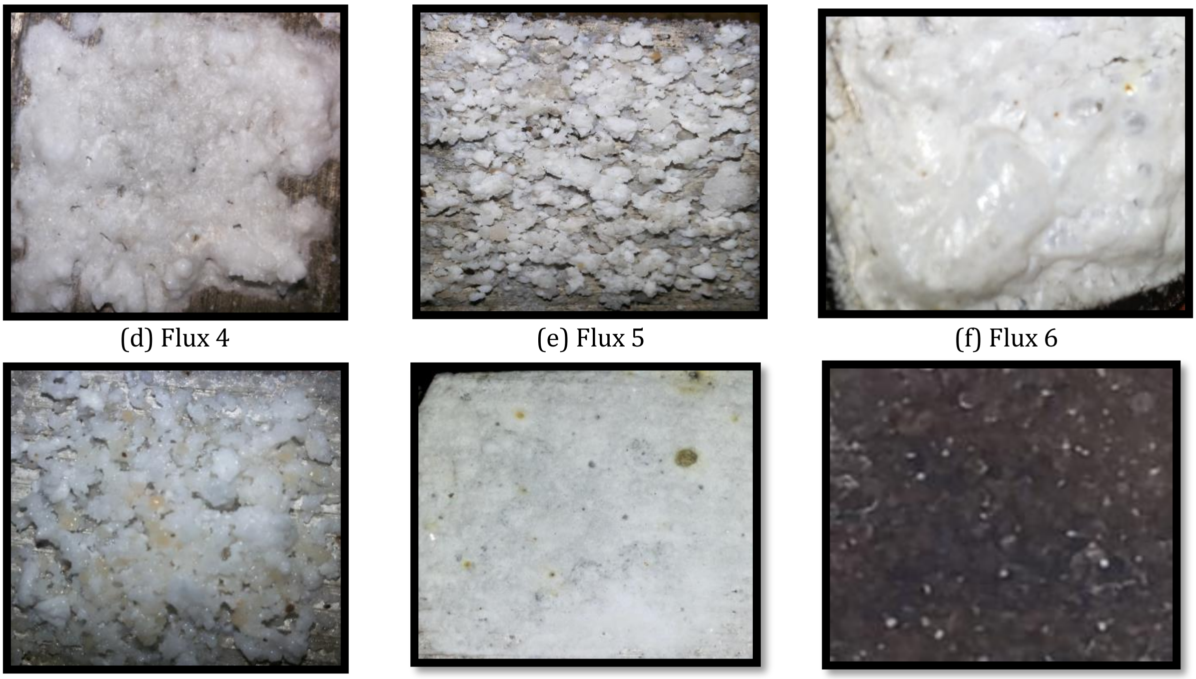


Figure 4: TG/DT analyses of flux 1

b) Observation of Surface Layer of Flux on Magnesium:

Figure 5 indicates a micrograph of a fused flux layer on a solid magnesium surface at 10X magnification. Figure 6 indicates a scanning electron micrograph at 100 X magnification.

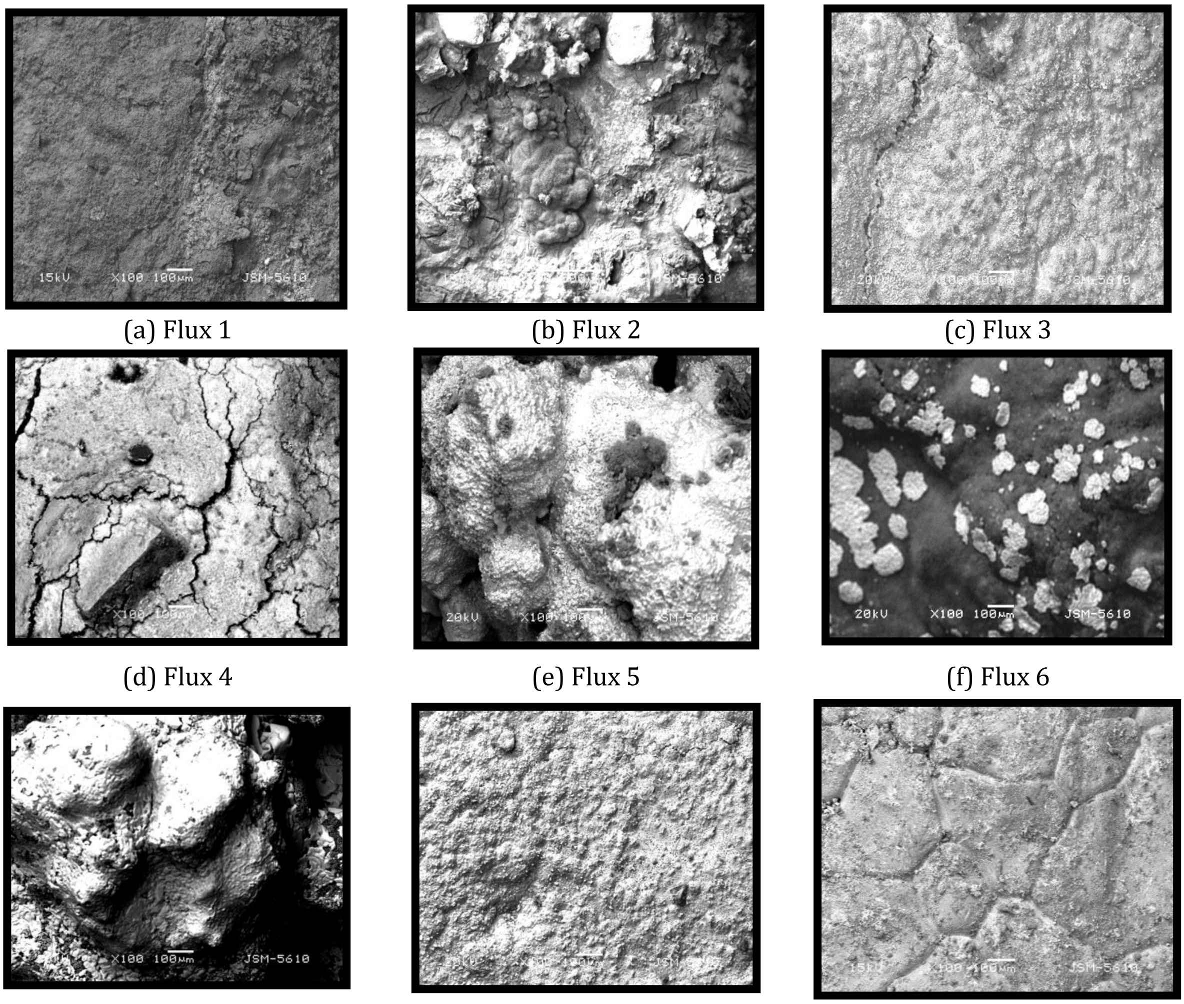
(a) Flux 1 (b) Flux 2 (c) Flux 3



(d) Flux 4 (e) Flux 5 (f) Flux 6

(g) Flux 7 (h) Flux 8 (I) Flux 9

Figure 5: Macro Photographs of fused fluxes (10X)



(a) Flux 1 (b) Flux 2 (c) Flux 3

(d) Flux 4 (e) Flux 5 (f) Flux 6

(g) Flux 7 (h) Flux 8 (I) Flux 9

Figure 6: SEM analyses of all fused fluxes at 100X magnification

c) Chemical analysis of all Castings:

To verify the presence of magnesium and other elements, a chemical analysis of all castings is carried out using EDS analysis, as shown in Table 2.

Table 2 Composition of raw material and cast products

Material	Flux used for casting	Mg	Mn	Ca	K	Na	O
Raw Material (Pure Mg)	-	98.68	0.08	-	-	-	1.24
Mg Casting	Flux 1 (320)	98.51	0.16	-	-	-	1.33
	Flux 2 (220)	99.75	0.08	0.01	0.16	-	-
	Flux 3	97.91	0.03	0.01	0.05	0.02	1.98
	Flux 4 (230)	98.70	-	0.03	-	-	1.27
	Flux 5 (310)	99.87	0.04	-	0.09	-	-
	Flux 6	97.86	0.04	0.04	-	-	2.06
	Flux 7	97.82	0.08	-	0.02	-	2.08
	Flux 8	97.48	0.03	0.16	-	0.01	2.33
	Flux 9 (250)	97.89	0.32	0.04	-	-	1.75

d) Effect of fluxes on the weight of magnesium castings:

The weight loss of cast products was calculated as per formula 1.

$$\text{Weight loss } (\%) = \frac{(\text{Weight of pure magnesium before casting} - \text{Final weight of casting}) \times 100}{\text{Weight of pure magnesium before casting}} \quad (1)$$

For fluxes 1 to 5, weight loss is quite high and it is approximately around 12 wt. % while for fluxes 6 to 9 it decreases. In the case of flux 9 weight loss is only around 6 %.

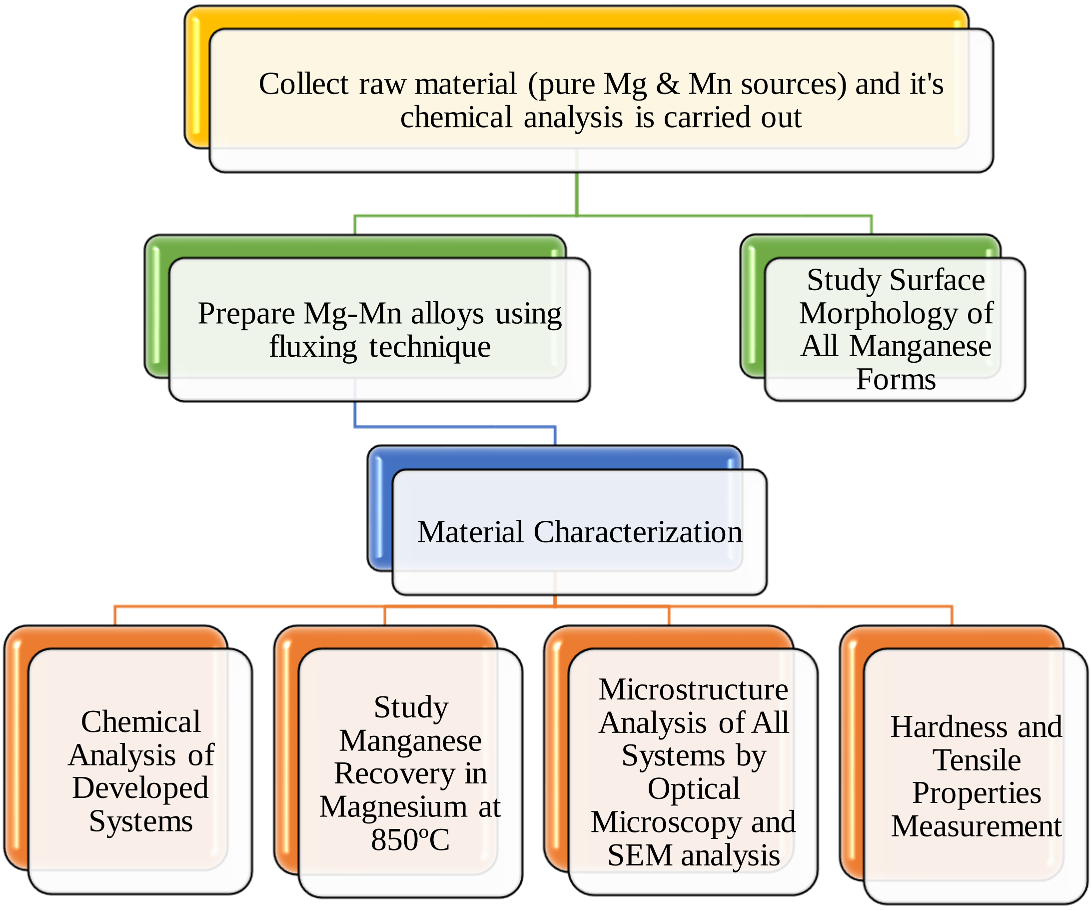
e) Effect of fluxes on the mechanical properties of magnesium castings:

In all magnesium castings, a negligible difference is observed in hardness and ductility value. Hardness is lying between 36 - 40 HV and ductility value is around 8 – 10 %. The ultimate tensile strength of all castings is varying between 96 to 111 MPa. [32]

6.2 Phase II

Effect of addition of various manganese sources on magnesium

- **Flowchart of Experimental Work:**



a) <u>Chemical Analysis of Developed Systems:</u>

The chemical composition of all developed systems was determined by the Energy Dispersive Spectroscopy technique and the results for the same are shown in table 4.

Table 3 Chemical analysis of all Mg-Mn systems

System	System	Mg	Mn	O
System 1	Mg –5wt% Mn coarse powder	97.14	0.38	2.48
System 2	Mg –5wt% $MnCl_2$	97.90	0.79	1.31
System 3	Mg –5wt% MnO_2	94.35	0.85	4.80
System 4	Mg –5wt% Mn fine powder	97.11	1.05	1.84
System 5	Mg –5wt% Mn electrolytic flakes	95.89	2.66	1.45

b) Surface Morphology of All Manganese Forms:

The shape and size of all manganese forms were studied in a scanning electron microscope. This analysis was done at 35 X, 50 X or 100 X magnifications to properly analyze the size and shape of manganese particles.

c) Manganese Recovery in Magnesium at 850°C:

Researchers have a different opinion about the solubility of manganese in magnesium. The greater part of the accessible data is on the Mg-rich side describing the limited solid solubility of manganese in magnesium. According to Tiner [45], the maximum solid solubility of manganese in magnesium is 2.0 at. % at 650 °C, as per Petrov et al. [46] 1.03 at. % and according to Nayeb-Hashemi and Clark [47] solubility limit of manganese in magnesium is 0.996 at.%. [45–48]Figure 7 shows manganese recovery in magnesium from different sources at 850°C.

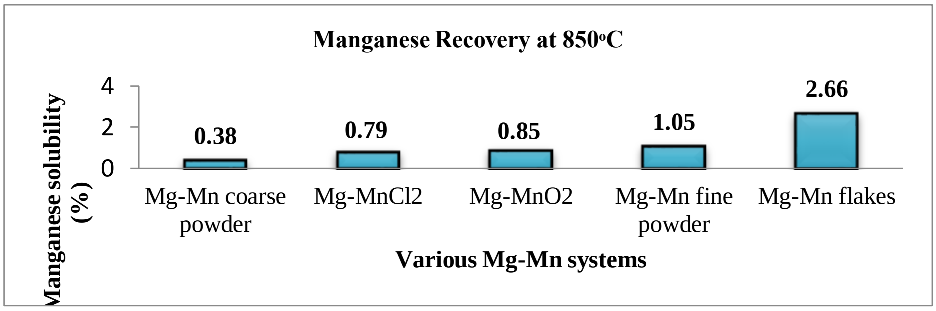


Figure 7: Recovery of Manganese from its different sources at 850°C in Pure Mg metal

d) Microstructure Analysis of All Systems:

Pure magnesium structure was changed from coarse-grained to fine-grained due to the presence of manganese and superheating. Original pure magnesium sample has always a big size grain structure but as the amount of manganese changes, structure refines. (Figure 8)

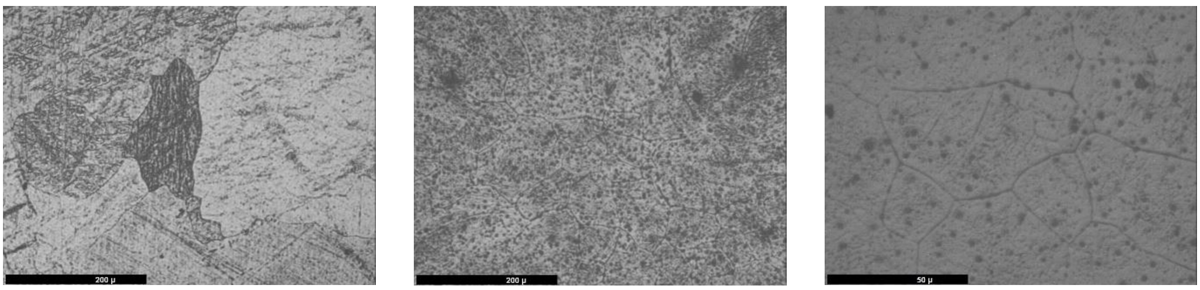


Figure 8: Optical Micrograph of magnesium & Mg-Mn flakes (a) Pure Mg (b) Mg-Mn flakes system at 100 X and (c) Mg-Mn flakes system at 400X

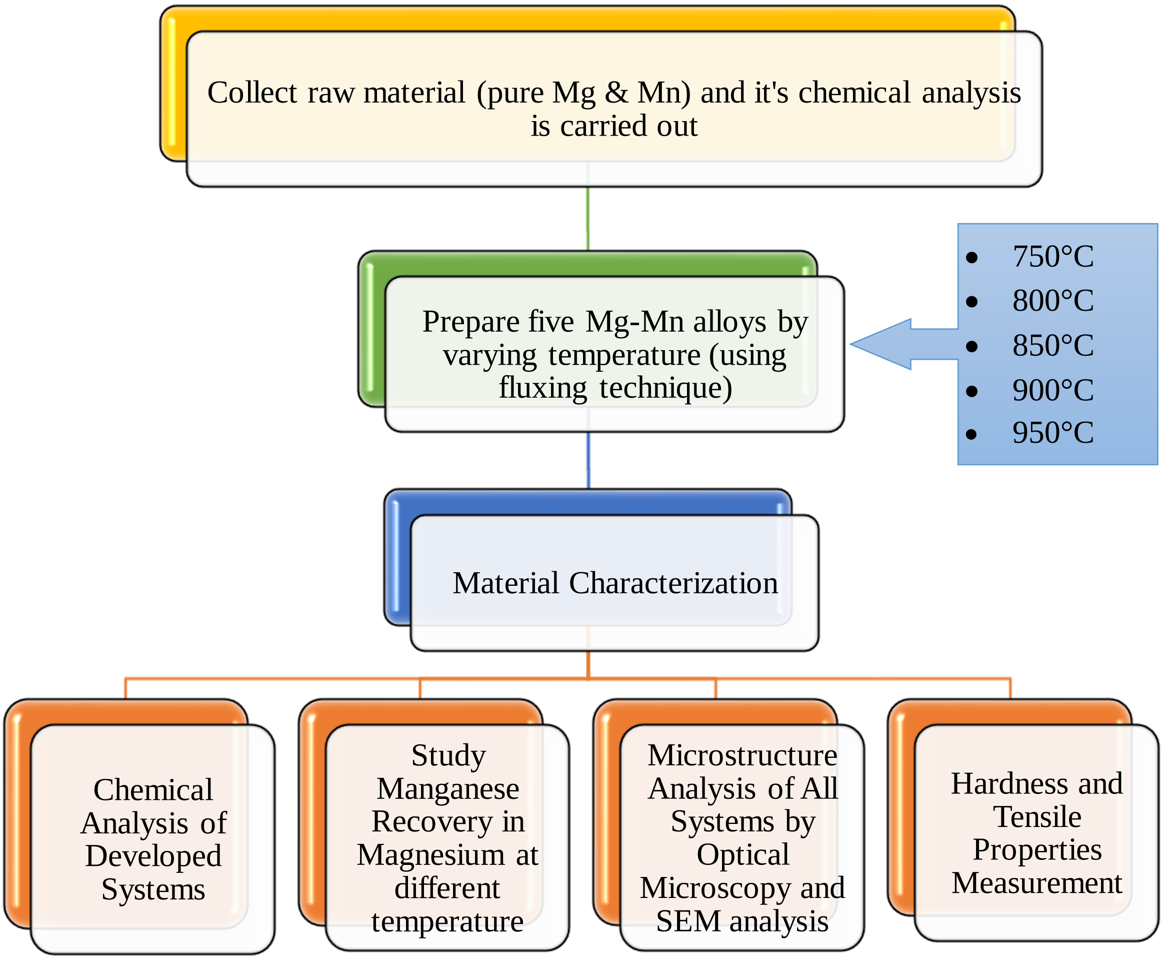
e) Hardness and Tensile Properties Measurement:

The hardness value of Mg-Mn systems is more compared to pure magnesium. It increases from 38HV to 58HV due to the solid solutionizing effect and beyond its solubility making precipitation of Mg-Mn phases. Up to 1% manganese, the ultimate tensile strength value is nearly the same. Maximum UTS is achieved in manganese flakes containing system 5 i.e. 140 MPa. There is negligible change in % elongation is observed up to 1% manganese.

6.3 Phase III

Effect of temperature on solubility of manganese in magnesium

Flowchart of Experimental Work:



a) Chemical Analysis of Developed Systems:

The chemical composition of all developed is shown in table 5.

Table 4 Chemical analysis of all Mg-Mn systems at different temperature

System	System	Temperature	Mg	Mn	O
System 6	Mg –5wt% Mn flakes	750 °C	91.43	0.3	8.27
System 7	Mg –5wt% Mn flakes	800 °C	92.57	1.7	5.73
System 8	Mg –5wt% Mn flakes	850 °C	95.89	2.66	1.45
System 9	Mg –5wt% Mn flakes	900 °C	90.38	3.01	6.61
System 10	Mg –5wt% flakes	950 °C	90.03	3.46	6.50

b) Manganese Recovery in Magnesium at Different Temperatures:

The maximum manganese amount is found at 950°C temperature.

c) Microstructure Analysis of All Systems:

As discussed in phase II, the presence of manganese refines the grains of pure magnesium and it is observed in systems 6, 7, and 8 (figure 9 a, b, c). In more than 3 % manganese-containing Mg-Mn alloy, a bigger grain size is observed compared to other systems (figure 9 d, e).

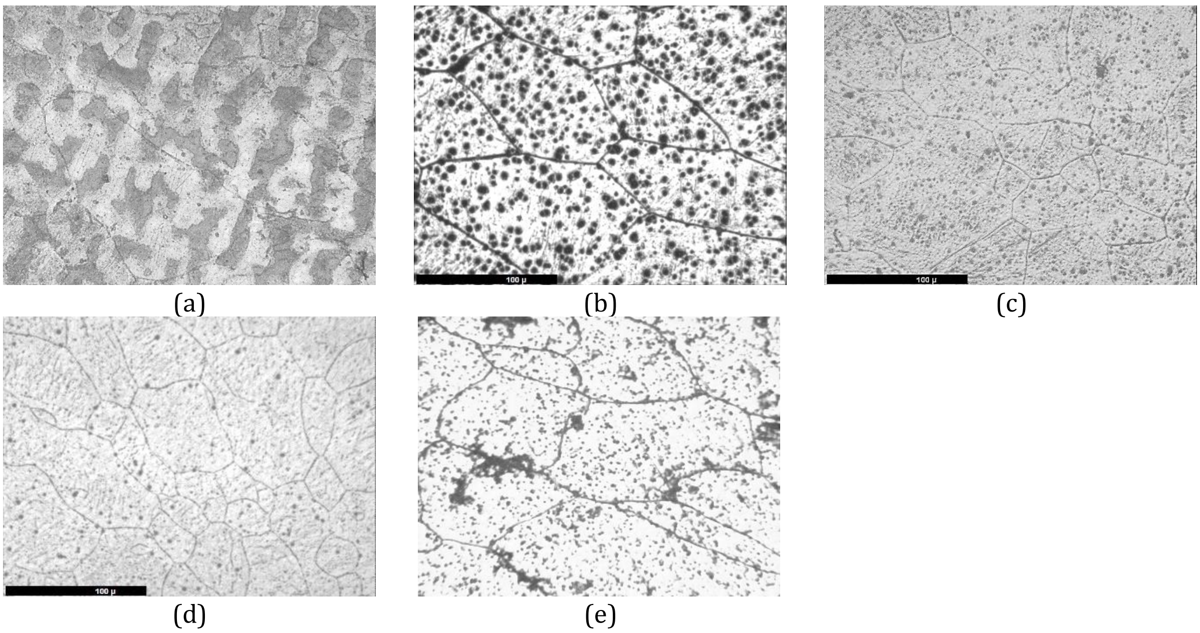


Figure 9: Optical Micrograph of all Mg-Mn systems at (a) 750 °C (b) 800 °C (c) 850 °C (d) 900 °C (e) 950 °C (at 200 X)

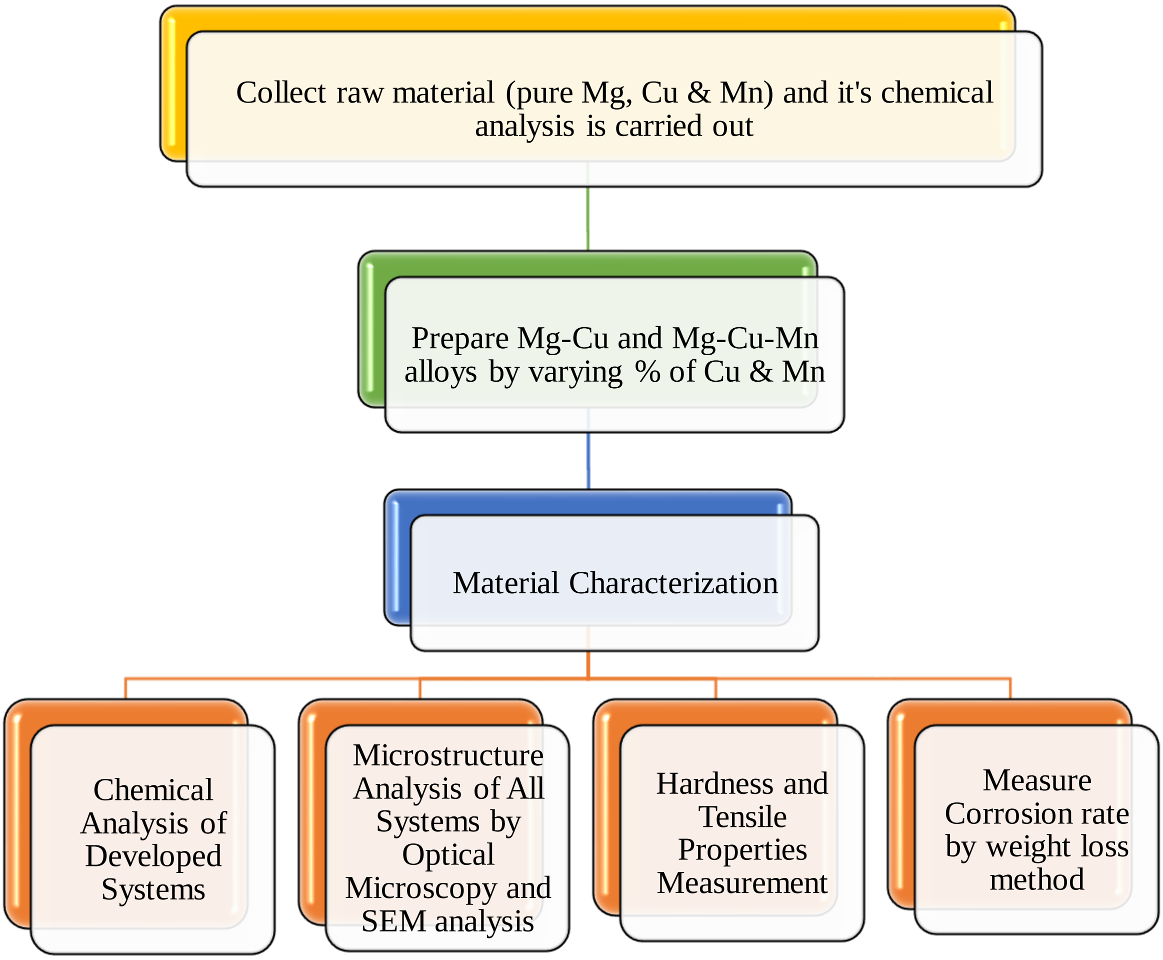
d) Hardness and Tensile Properties Measurement:

The presence of manganese increases the hardness and ultimate tensile strength of pure magnesium and decreases the % elongation. Maximum UTS and hardness are observed in Mg-2.66%Mn alloy (system 8) i.e. 140 MPa and 58 HV0.1 respectively.

6.4 Phase IV

Develop and study the Mg-Cu and Mg-Cu-Mn alloys

- **Flowchart of Experimental Work:**



a) Chemical Analysis of Developed Systems:

The chemical composition of all developed is shown in table 6.

Table 5 Chemical analysis of CM alloys

System	Alloy	Cu	Mn	O	Mg
System 11	Mg-1Cu (CM10)	0.91	0.45	2.92	Balance
System 12	Mg-2Cu (CM20)	1.87	0.61	4.73	Balance
System 13	Mg-3Cu (CM30)	2.57	0.47	3.33	Balance
System 14	Mg-1Cu-1Mn (CM11)	0.76	1.12	3.58	Balance
System 15	Mg-2Cu-2Mn (CM22)	1.83	2.54	5.13	Balance
System 16	Mg-3Cu-2Mn (CM32)	2.79	2.32	4.47	Balance

b) Microstructure Analysis of All Systems by Optical Microscopy and SEM analysis

Figure 10 shows the optical microstructures of the Mg-Cu and Mg-Cu-Mn alloys. The microstructure is composed of α – base magnesium, eutectic compounds, and some isolated particles dispersed inside the grains. It is visible that the microstructures of manganese-containing Mg-Cu alloys are more refined compared to only copper-containing alloys. The XRD results of CM22 and CM32 alloy consists of Mg(2H), (Mg_2Cu)48S, and (Mn)20C phases.

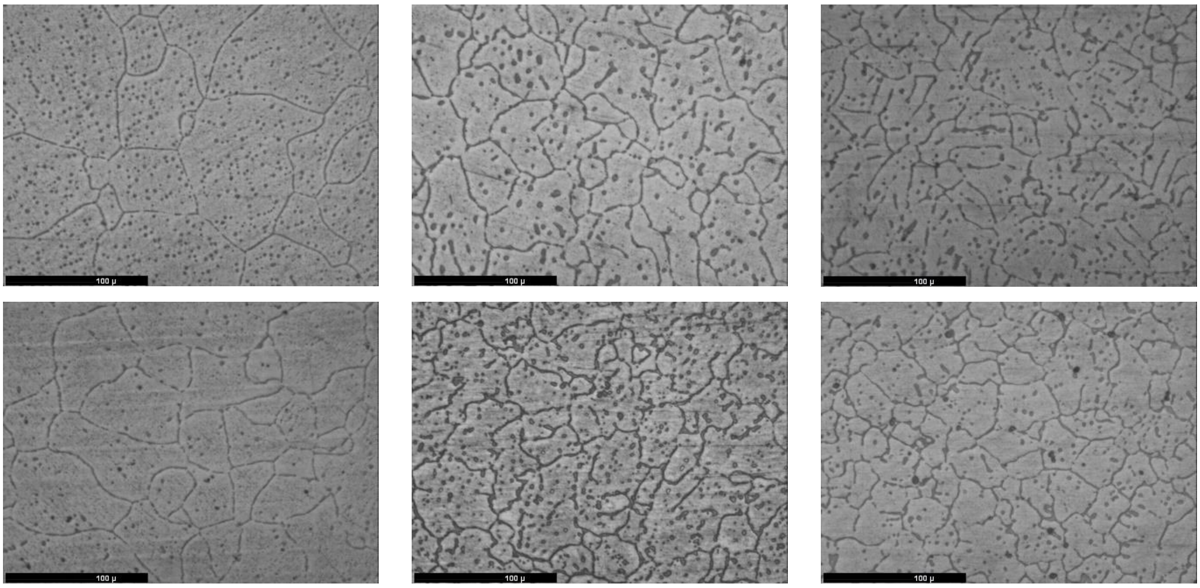


Figure 10: Optical Micrographs of the as cast alloys at 200 X (a) CM10 (b) CM20 (c) CM30 (d) CM11 (e) CM22 (f) CM32

c) Hardness and Tensile Properties Measurement

2 % Manganese containing Mg-Cu alloys have more ultimate tensile strength compared to only Mg-Cu alloys. Vicker's hardness of Mg-Cu and Mg-Cu-Mn alloys are lying between 20 to 55 HV. Maximum hardness is achieved in CM32 alloy i.e. 55 HV. % Elongation of 1 wt. % Cu containing alloy is 11 % which is the highest among the other alloys. With the addition of more amount of Cu and Mn % elongation is decreased.

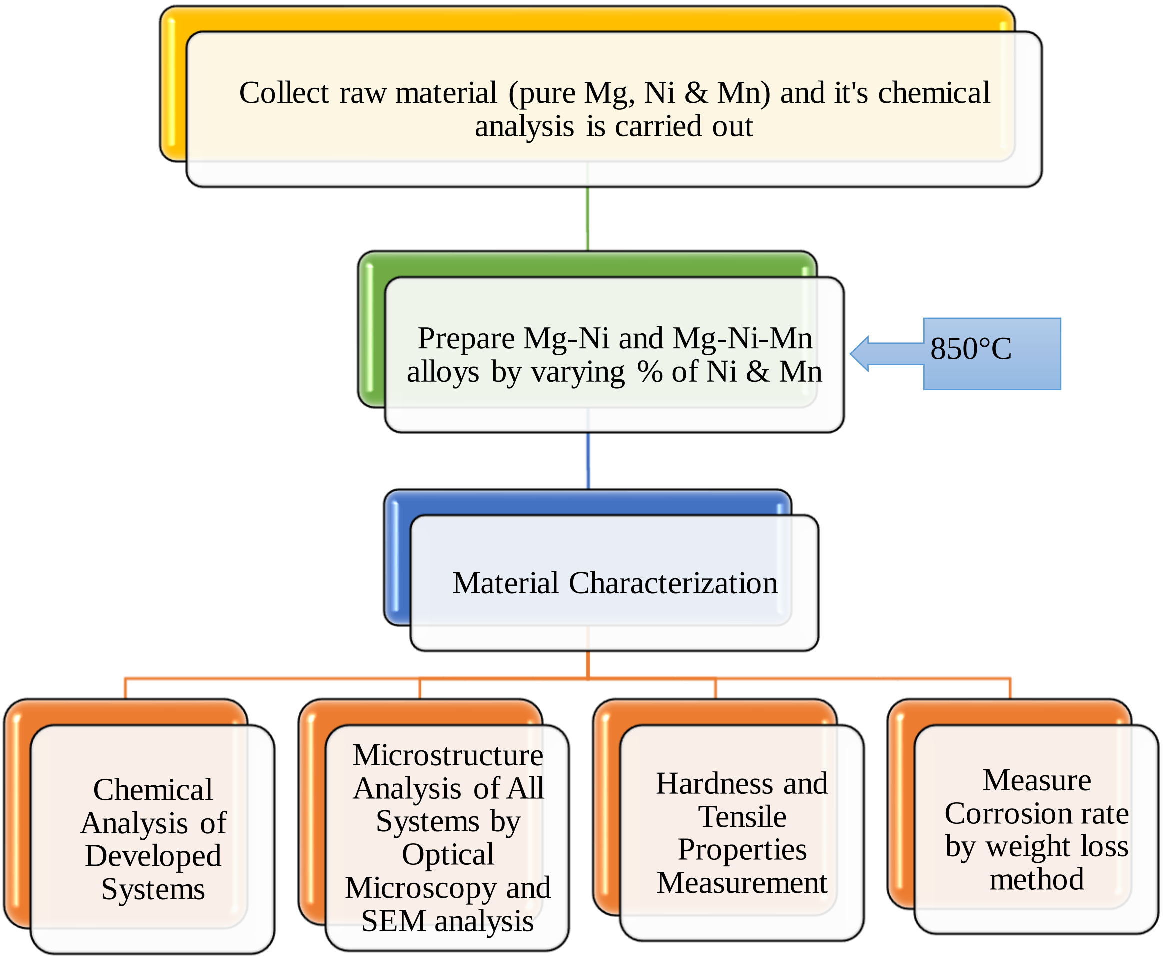
d) Measure Corrosion rate by weight loss method

Corrosion rate of the Mg-1Cu and Mg-2Cu alloy is increasing after 6 hrs and 12 hrs. Most severe corrosion is observed in Mg-3Cu alloy. Many corrosion pits are observed and they are increasing by increasing copper content. It is observed that more amount of Cu content can accelerate the corrosion rate significantly.

6.5 Phase V

Develop and study Mg-Ni and Mg-Ni-Mn alloys

- **Flowchart of Experimental Work:**



a) <u>Chemical Analysis of Developed Systems:</u>

The chemical composition of all developed is shown in table 8.

Table 6 Chemical analysis of NM alloys

System	Alloy	Ni	Mn	O	Al	Mg
System 17	Mg-0.7Ni	0.72	0.37	4.44	0.17	Balance
System 18	Mg-1.4Ni	1.39	-	3.50	0.31	Balance
System 19	Mg-1.7Ni	1.74	0.45	3.33	-	Balance
System 20	Mg-0.7Ni-2.33Mn	0.72	2.33	3.50	-	Balance
System 21	Mg-1.7Ni-3.15Mn	1.79	3.15	2.96	0.15	Balance
System 22	Mg-2.3Ni-1.96Mn	2.27	1.96	3.34	0.13	Balance

b) Microstructure Analysis of All Systems by Optical Microscopy and SEM analysis

Figures 11 shows the optical images of the Mg-Ni and Mg-Ni-Mn alloys. The microstructure is composed of α – base magnesium, eutectic compounds, and some isolated particles dispersed inside the grains. The eutectic compound is distributed along the grain boundaries.

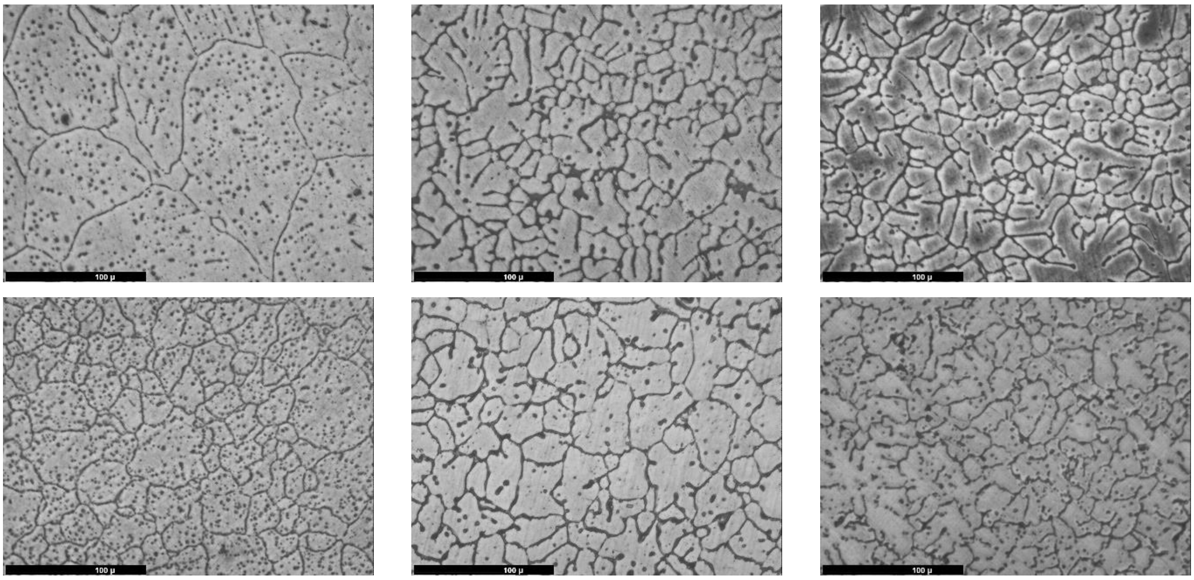


Figure 11: Optical Micrographs of the as cast alloys at 200 X (a) Mg-0.7Ni (b) Mg-1.4Ni (c) Mg-1.7Ni (d) Mg-0.7Ni-2.33Mn (e) Mg-1.7Ni-3.15Mn (f) Mg-2.3Ni-1.96Mn

c) Hardness and Tensile Properties Measurement

Ni and Mn-containing alloys have more ultimate tensile strength and hardness compared to pure magnesium. The ultimate tensile strength of more than 1% nickel-containing alloy is around 160 MPa. Vicker's hardness of Mg-Ni and Mg-Ni-Mn alloys are lying between 47 to 59 HV. Maximum hardness is achieved in Mg-2.3Ni-1.96Mn alloy i.e. 59 HV. There is a negligible difference is observed in % Elongation of different alloys.

d) Measure Corrosion rate by weight loss method

The corrosion rate of most of the alloys are increasing after 1.5 hrs and 2 hrs. Most severe corrosion is observed in Mg-1.4Ni alloy. Many corrosion pits are observed and they are increasing by increasing nickel content. It is observed that manganese is giving an adverse effect on corrosion rate. Mn containing Mg-Ni alloys shows more corrosion rate compare to only Mg-Ni alloy.

7 CONCLUSIONS

1. Decomposition of all fluxes is started between 450 to 635°C, and it protects the molten magnesium from oxidation.
2. 23% KCl, 72% $MnCl_2$, 2.5% $BaCl_2$ and 2.5% CaF_2containing Flux 9 is best for magnesium melting compare to other fluxes.
3. Maximum manganese recovery found in electrolytic flakes forms i.e., 3.46 wt. % at 950°C temperature.
4. Manganese addition refines the grain of pure magnesium and increases hardness and ultimate tensile strength.
5. 2 wt. % Manganese addition is more effective to improve UTS and hardness of Mg-Cu alloys. Maximum UTS and hardness are achieved in CM32 alloy i.e. 179 MPa and 55 HV respectively.
6. Mg-2.3Ni-1.96Mn alloy has achieved maximum hardness i.e. 59 HV. There is negligible change in % Elongation is observed.
7. The corrosion resistance of Mg-Cu alloys is increased by manganese addition. However, in the Mg-Ni system, manganese presence accelerates the corrosion rate so it can't use in this system.

8 LIST OF PUBLICATIONS ARISING FROM THE THESIS

Sr. No.	Name of Author	Title of Paper	Journal Name/Conference Proceeding Name	ISSN/ISBN No. Page No. and Year	Publisher	Status	Other Details
1	Sonam M. Patel, Vandana J. Rao	Study the Effect of Different Types of Fluxes Used For Magnesium Melting	National Seminar on Recent Scenario in science and technology, RSST – 2016 **Organized by:** FTE, The M.S. U. of Baroda	**Year:** 2016	-	Paper presented on 27th Feb 2016	Best Oral Presentation
2	Sonam M. Patel, Vandana J. Rao	Study the Influence of MnO_2 and $MnCl_2$ on Microstructure and Mechanical Properties of Pure Magnesium	**Conference Name:** Proceedings of International Conference on Recent Advances in Metallurgy for Sustainable Development	**ISBN:** 978-93-88879-64-4 pp. 136 - 138 **Year:** 2018	New Delhi Publishers	Paper presented on 1-3 Feb, 2018 and published	

			(IC-RAMSD 2018) **Organized by:** The M. S. University of Baroda, Vadodara, India				
3	Sonam M. Patel, Vandana J. Rao	Effect of Various Forms of Manganese and Its Recovery in Pure Magnesium Metal	**Conference Name:** International Conference on Recent Advances in Mechanical Engineering Research and Development (ICRAMERD_2020) **Organized by:** Department of Mechanical Engineering, Institute of Technical Education & Research, Siksha 'O' Anusandhan	**ISSN:** 2195-4356, **ISBN**: 978-981-33-4794-6 **pp.** 929 - 938 **Year:** 2021	**Springer Proceeding:** Current Advances in Mechanical Engineering, Lecture Notes in Mechanical Engineering	Paper presented on 25/07/2020 And published in 2021	https://doi.org/10.1007/978-981-33-4795-3
4	Sonam M. Patel, Mehul M. Patel, Vandana J. Rao	Synthesis and characterization of magnesium melting fluxes	Materials Research Express **Impact Factor:** 1.620	8 (2021) 116503 **Year:** 2021	IOP Publishing	Published on 15 November 2021	https://doi.org/10.1088/2053-1591/ac30b2
5	Sonam M. Patel, Vandana J. Rao	Microstructure, Mechanical Properties and Corrosion Behaviour of Mg-Ni and Mg-Ni-Mn Alloys	26th Int. Conf. Nonferrous Metals, 2022, Nagpur, India	8-9 July **Year:**2022	Pursuing	Paper accepted	-
6	Sonam M. Patel, Vandana J. Rao	Microstructure, Mechanical Properties and Corrosion Behaviour of Mg-Cu and Mg-Cu-Mn Alloys	In process	-	-	-	-
7	Sonam M. Patel, Vandana J. Rao	Study the recovery of manganese at various temperatures and its influence on microstructure and properties of pure magnesium	In process	-	-	-	-

9 REFERENCES

[1] B.L. Mordike, T. Ebert, Magnesium: Properties — applications — potential, Materials Science and Engineering: A. 302 (2001) 37–45. https://doi.org/10.1016/S0921-5093(00)01351-4.

[2] C. Blawert, N. Hort, K.U. Kainer, Automotive applications of magnesium and its alloys, Trans. Indian Inst. Met. 57 (2004) 397–408.

[3] A.A. Luo, Magnesium casting technology for structural applications, Journal of Magnesium and Alloys. 1 (2013) 2–22.

[4] T. Zhu, P. Fu, L. Peng, X. Hu, S. Zhu, W. Ding, Effects of Mn addition on the microstructure and mechanical properties of cast Mg–9Al–2Sn (wt.%) alloy, Journal of Magnesium and Alloys. 2 (2014) 27–35.

[5] Q. WANG, Y. CHEN, S. XIAO, X. ZHANG, Y. TANG, S. WEI, Y. ZHAO, Study on microstructure and mechanical properties of as-cast Mg-Sn-Nd alloys, Journal of Rare Earths. 28 (2010) 790–793. https://doi.org/https://doi.org/10.1016/S1002-0721(09)60202-7.

[6] M.K. Kulekci, Magnesium and its alloys applications in automotive industry, The International Journal of Advanced Manufacturing Technology. 39 (2008) 851–865. https://doi.org/10.1007/s00170-007-1279-2.

[7] G.L. Song, A. Atrens, Corrosion Mechanisms of Magnesium Alloys, Advanced Engineering Materials. 1 (1999) 11–33. https://doi.org/10.1002/(SICI)1527-2648(199909)1:1<11::AID-ADEM11>3.0.CO;2-N.

[8] R. Gradinger, P. Stolfig, Magnesium wrought alloys for automotive applications, Proceedings of the Minerals, Metals & Materials Society. (2003) 231–236.

[9] M.O. Pekguleryuz, Current developments in wrought magnesium alloys, Advances in Wrought Magnesium Alloys. (2012) 3–62. https://doi.org/10.1533/9780857093844.1.3.

[10] J. Zhang, Z.X. Guo, F. Pan, Z. Li, X. Luo, Effect of composition on the microstructure and mechanical properties of Mg–Zn–Al alloys, Materials Science and Engineering: A. 456 (2007) 43–51. https://doi.org/https://doi.org/10.1016/j.msea.2006.11.089.

[11] P. Aroule, IMA-55, a global vision for magnesium, International Magnesium Association, Washington, DC. (1998) 36–46.

[12] H. Hu, A. Yu, N. Li, J.E. Allison, Potential magnesium alloys for high temperature die cast automotive applications: a review, Materials and Manufacturing Processes. 18 (2003) 687–717.

[13] B.A. Shaw, Corrosion resistance of magnesium alloys, ASM Handbook. 13 (2003) 692–696.

[14] A. Kumar, S. Kumar, N.K. Mukhopadhyay, Introduction to magnesium alloy processing technology and development of low-cost stir casting process for magnesium alloy and its composites, Journal of Magnesium and Alloys. 6 (2018) 245–254. https://doi.org/https://doi.org/10.1016/j.jma.2018.05.006.

[15] Z. Xiaoqin, W. Qudong, L. Yizhen, Z. Yanping, D. Wenjiang, Z. Yunhu, Influence of beryllium and rare earth additions on ignition-proof magnesium alloys, Journal of Materials Processing Technology. 112 (2001) 17–23. https://doi.org/10.1016/S0924-0136(00)00854-2.

[16] J.A.S. Tenório, D.C.R. Espinosa, High-Temperature Oxidation of Al–Mg Alloys, Oxidation of Metals. 53 (2000) 361–373. https://doi.org/10.1023/A:1004549522648.

[17] A.W. Brace, F.A. Allen, Magnesium casting technology, Chapman & Hall, 1957.

[18] N. Hort, B. Wiese, H. Dieringa, K.U. Kainer, Magnesium melt protection, Materials Science Forum. 828–829 (2015) 78–81. https://doi.org/10.4028/www.scientific.net/MSF.828-829.78.

[19] KABLOV Y.N., K.V.A. MUKHINA I.YU., Additive Materials for Molding Sands Used in Magnesium Alloy Casting, Lit. Proizvodstvo. (2007) 15–18.

[20] S. Lun Sin, A. Elsayed, C. Ravindran, Inclusions in magnesium and its alloys: A review, International Materials Reviews. 58 (2013) 419–436. https://doi.org/10.1179/1743280413Y.0000000017.

[21] S.P. Cashion, N.J. Ricketts, P.C. Hayes, The mechanism of protection of molten magnesium by cover gas mixtures containing sulphur hexafluoride, Journal of Light Metals. 2 (2002) 43–47. https://doi.org/10.1016/S1471-5317(02)00012-3.

[22] S.-M. Xiong, X.-L. Liu, Microstructure, composition, and depth analysis of surface films formed on molten AZ91D alloy under protection of SF 6 mixtures, Metallurgical and Materials Transactions A. 38 (2007) 428–434.

[23] M. Maiss, C.A.M. Brenninkmeijer, Atmospheric SF6: trends, sources, and prospects, Environmental Science & Technology. 32 (1998) 3077–3086.

[24] C.E. Nelson, The melting and refining of magnesium, Trans. AIME. 159 (1944) 392.

[25] M.M. Avedesian, H. Baker, ASM specialty handbook: magnesium and magnesium alloys, ASM international, 1999.

[26] H. Antrekowitsch, G. Hanko, P. Ebner, Recycling of different types of magnesium scrap, Magnesium Technology. 39 (2002) 321–328.

[27] G. Hanko, H. Antrekowitsch, P. Ebner, Recycling automotive magnesium scrap, JOM. 54 (2002) 51–54. https://doi.org/10.1007/BF02701075.

[28] A.A. Leonov, V.A. Duyunova, Z.P. Uridiya, N. V Trofimov, New Universal Flaky Flux for Cast Magnesium Alloys, Russian Metallurgy (Metally). 2019 (2019) 268–272.

[29] A. Ditze, C. Scharf, Recycling of magnesium, Ditze & Scharf, 2008.

[30] A. Lipnitsky, The Melting of Cast Iron and Non-Ferrous Alloys, 1960.

[31] E. Aghion, G. Golub, Friedrich · Mordike Magnesium Technology, 1996. https://doi.org/10.1007/3-540-30812-1.

[32] Frank Czerwinski, Magnesium Injection Molding, Springer, 2008.

[33] D. Gandel, N. Birbilis, M.A. Easton, M.A. Gibson, Influence of manganese, zirconium and iron on the corrosion of magnesium, Proceedings of Corrosion & Prevention. (2010) 875–885.

[34] K.U. Kainer, Magnesium: Proceedings of the 6th International Conference-Magnesium Alloys and Their Applications, John Wiley & Sons, 2006.

[35] Y. Tamura, T. Haitani, N. Kono, Liquid solubility of manganese and its influence on grain size of Mg-Al alloys, Mater Trans. 47 (2006) 1968–1974.

[36] H.E. Friedrich, B.L. Mordike, Magnesium technology, Springer, 2006.

[37] M. Mezbahul-Islam, A. Mostafa, M. Medraj, Essential magnesium alloys binary phase diagrams and their thermochemical data, Journal of Materials. 2014 (2014).

[38] M. Asgar-Khan, M. Medraj, Critical evaluation and thermodynamic modeling of the Mg-Mn, Al-Mn and Mg-Al-Mn systems, in: Proceedings of the Materials Science and Technology (MS&T) Conference, Pittsburgh, PA, USA, 2008: pp. 5–9.

[39] C. Moosbrugger, Engineering Properties of Magnesium Alloys, ASM International. (2017) 1–12.

[40] F. Kaiser, K.U. Kainer, Magnesium alloys and technology, John Wiley & Sons, 2003.

[41] H. Hu, X. Nie, Y. Ma, Corrosion and surface treatment of magnesium alloys, Magnesium Alloys-Properties in Solid and Liquid States. (2014) 67–108.

[42] H.E. Friedrich, B.L. Mordike, Technology of magnesium and magnesium alloys, Magnesium Technology: Metallurgy, Design Data, Applications. (2006) 219–430.

[43] C.S. Goh, M. Gupta, J. Wei, L.C. Lee, Characterization of high performance Mg/MgO nanocomposites, J Compos Mater. 41 (2007) 2325–2335.

[44] M. Gupta, S.N.M. Ling, Magnesium, magnesium alloys, and magnesium composites, John Wiley & Sons, 2011.

[45] N. Tiner, The solubility of manganese in liquid magnesium, Metals Technology. (1945) 1–7.

[46] D. Petrov, M. Mirgalovskaya, I. Strelnikova, E. Komova, The Constitution Diagram for the Magnesium-Manganese System, Institute of Materials Science, Academy of Sciences of the Ukrainian SSR. 1 (1958) 142–143.

[47] A.A. Nayeb-Hashemi, J.B. Clark, The Mg– Mn (Magnesium-Manganese) system, Bulletin of Alloy Phase Diagrams. 6 (1985) 160–164.

[48] E. Karakulak, A review: Past, present and future of grain refining of magnesium castings, Journal of Magnesium and Alloys. 7 (2019) 355–369.