SOME CRITICAL ISSUES IN THE PROCESSING OF MAGNESIUM ALLOYS AND COMPOSITES

P.K. BISWAS, S.C.DEV AND C.S.S.KRISHNAN
National Metallurgical Laboratory, Jamshedpur.

Abstract

Handling of molten Mg alloys and composite slurries is risky due to the danger of explosion and oxidation in contact with O_2 of the atmosphere and water. Hence special attention is to be taken for safety and quality in all steps of processing—melting, moulding, casting, heat treatment and mechanical working. The limitations and specialities are in respect of alloying (viz. with Zr,Mn,Ca,Be), removal of non-metallic and metallic impurities (viz.Fe,Ni etc), grain refinement, degassing, choice of fluxes and the manner of its addition, die design for extrusion, selection of temperature and time in melting, pouring and heat treatment, selection of stirrer rpm, its geometry and location in the bath for composite making by stir casting including rheocasting methods etc. These issues are reviewed in this paper.

1.0 Introduction

Mg based alloys and composites are attractive to aerospace and automobile applications for their high strength-to-weight ratio [1] compared to the common engineering materials. Although their processing technologies are similar to those of Al counterparts, it is essential to take special attention for the former with respect to melting, moulding, casting and mechanical processing, since Mg is highly reactive to O_2 that causes rapid oxidation, flare and sometimes even explosion. Of various techniques, liquid metallurgy technique is the most economic for large scale production. However non-uniformity of mixing of dispersoids (viz. SiC particles or fibres) in the melt is a major problem which deteriorates the mechanical and other properties of the final product due to segregation. One advantage of Mg composite over Al composite is that the wettability of liquid Mg with ceramic phase is better. However appropriate design of blades is needed to get uniform dispersion of dispersoids in the liquid state. Some of the above issues and their remedies together with some case studies conducted at NML are highlighted in this paper.

2.0 Melting

Unlike Al, speciality of Mg melting is that at all stages, appropriate fluxes must

be used whether it be charging, degassing. grain refining or casting. Of late fluxless melting [2.3] under protective inert gas cover is being practiced. But both the methods have certain merits and demerits. In the former, materials handling and removal of dross is easier, yield of clean metal is about 80-90%; while the latter is expensive and suitable for bottom pouring mainly where the remnants of the drosses formed if any is difficult to remove: however yield is slightly better than the former.

The behaviour of Mg in melting differs from that of Al in two fundamental ways which are the basis of selection of melting pot for magnesium.

Firstly. Mg reacts exothermally with various ceramic materials particularly silica and silicates such as fire clay and so such materials are not used in contact with molten Mg metal. Thus Mg and its alloys are never melted in ordinary clay bonded plumbago crucible.

Secondly, Mg does not exert a solvent action on iron, so the metal can be melted in unprotected iron pot.

Hence melting and refining of Mg and Mg alloys are generally done in wrought or cast-steel pots. CI pots are also used. However, the use of heat resisting metal pots containing Ni and Cr is not permissible owing to the dissolution of Ni and Cr by the molten Mg which reduce corrosion resistance.

The above facts hold good for composite making by stir cast method. Since melting of Mg alloys precedes preparing composite slurry, the melting aspect is dealt first.

2.1 Fluxing

Fluxes are used (1-3%) primarily to protect from oxidation of molten metal) and secondly to remove non-metallic inclusions. One important issue in fluxing is the right choice of fluxes. Further, one must know when and how it should be used.

Types of Fluxes :

Fluxes used during melting fall into two groups:

1. Fluxes containing $MgCl_2$ — used for melting alloys of systems like Mg-Al-Zn, Mg-Zn, Mg-Zn-RE;
2. Fluxes free from $MgCl_2$ — used for alloys containing Ca, La, Ce, Nd etc.

With respect to nature of fluidity, there are two types of fluxes viz. fluid and

stiff. By varying the flux composition, degree of fluidity can be varied. During the initial stages of melting, very fluid fluxes are used. Very stiff fluxes are suitable for final pouring operation as they are easier to be separated from the molten metal thus preventing fluxes from entering into the mold.

Modern fluxes consist of mixed chlorides of K, Ba, Ca, Na, Mg. Magnesium and calcium fluorides may be included in the stiffer fluxes. $MnCl_2$ is also used not only to protect the melt but also to control the level of Mn in the alloy. Again with respect to functioning, fluxes are classified into two types—protective and refining fluxes. The refining action of fluxes is brought about by the removal of insoluble non-metallic impurities such as oxides and chlorides from the molten metal. Refining fluxes are added in powder form or lumped form. The protective flux consists mainly of chloride and fluoride salt of eutectic composition or nearly so, including compounds of double salt e.g. Karnallite (KCl, $MgCl_2$) with unavoidable impurities.

Stages and manner of application of fluxes :

At charging stage, a little flux is sprinkled around the sides and bottom of the preheated crucible and the metal charge added. When the melting is about to begin fluxes are sprinkled over the charge and subsequently added as required to prevent or check burning. After melting is over, the metal surface is covered with a thick layer of flux.

During casting, SO_2 gas, S powder or borax is applied to avoid oxidation or burning.

2.2 Alloying

Common alloying elements for Mg are Al, Zn and Mn. Sometimes Ca is added to improve rollability and traces of "Be" may be added to increase oxidation resistance in the molten state. "Be" however coarsens the grain and so it must be limited. Zr should not be used when Al is present with Mg since it forms intermetallic compounds with liquid Zr [4]. The method of alloying also differs depending upon whether it is for Zr containing alloy or Zr free alloy

Al (6-9.5%) and Zn (0.5-2.0%) are added without difficulty for strengthening. These are solid solution hardeners. For corrosion resistance, Mn is added in the form of powdered $MnCl_2$ at about 750°C by plunging or sprinkling over the skimmed and cleaned surface followed by stirring when some of the liberated Mn dissolves in Mg.

$$MnCl_2 + Mg = MgCl_2 + Mn$$

Electrolytic Mn is added directly to Mg and the melt stirred for some time at 750-

800°C. For best results, the size of the Mn flakes should be controlled. The finer flakes should be rejected or compacted and used. There is not much to choose between $MnCl_2$ and electrolytic Mn from the economic point of view.

For adding Mn to alloys containing Al, it is convenient to use Al-5% Mn as hardener alloy which is readily available commercially. Where Mn is added as a precipitant for iron and melts are held for a period at relatively low temperatures, some settlement of Mn occurs. Mn additions must therefore exceed the amounts desired in the final alloy to the extent based on experience and depending upon the settling condition.

Ca is added (0.05-0.3%) as metal or as a hardener alloy with Mg eg. Mg-15%Ca or Ca-20%Mg. Since the fluxes normally used with Mg alloys contain $MgCl_2$, it is customary to add the Ca to the melt shortly before pouring. Ca addition is fixed by experience or checked by rapid analysis e.g. with a direct reading spectrograph. To end up with 0.05% Ca in the final melt, nominal addition of about 0.1% is usually required. Ca is a good de-oxidiser.

"Be" is added as hardener alloy with Al eg. Al-5%Be. Such an alloy can readily be added to Mg-Al alloys and no special precautions against toxicity are required. Recovery of "Be" depends upon the amount of Al in the melt, Be-hardener, iron content and settling conditions. The liquid solubility of "Be" in pure Mg is only 0.005% approx., but increases with increasing Al content. It is difficult to introduce more than about 0.002% Be into Mg using "Be" metal.

2.3 Removal of Impurities

Although iron does not alloy appreciably with molten Mg and its alloys as mentioned earlier, the danger of iron contamination (from melting pot) cannot be overlooked. The presence of small amount of Mn in the bath is known to take care of metallic contamination particularly when a small amount of Mn is taken into solution before the addition of Al. Under this condition a certain portion of Mn is immediately precipitated in the form of $MnAl_3$ which sinks to the bottom and takes metallic impurities like iron etc. with it. For this purpose, an excess amount of Mn is always added to control the level of Mn. This can control iron level upto 0.003-0.005% which is acceptable.

2.4 Grain Refining

One of the difficulties encountered with Mg alloys is its coarse columnar grains which deteriorate the mechanical properties. Unlike Al or other common metals grain

refining techniques of Mg alloys have some speciality. Generally superheating of the melt is deleterious to melts like that of Al, it coarsens the grain by remelting of the dendrites and nucleating embryos. But in the case of Mg, superheating to 830-870°C followed by rapid cooling to pouring temperature 700-750°C brings about grain refinement.

During cooling, it is customary to make the usual addition of Ca upto 0.25% to act as a de-oxidiser prior to pouring. However this method is now obsolete.

Grain refinement is also done by minor additions of the following :

(1) Anhydrous $FeCl_3$ in powder form; 0.2% added before pouring.
     (Elfinal process)

(2) Zr (0.002%) added for alloys without containing Al

(3) C-compounds viz. hexachloroethane (0.05-0.10%), paraffin wax, CaC_2 at about 750°C (practiced in UK & USA)

(4) MgF_2 (0.10%) and metallic Ca (0.05-0.3%) (Michael process—practiced in   France & Germany)

Out of the above processes, grain refinement by hexachloroethane is now most popular owing to its dual action — refining as well as degassing.

Failure of grain refinement occurs in presence of inhibiting elements.

2.5 Degassing

Degassing is done by the addition of hexachloroethane or by passing Cl_2 or Freon gas into the melt through C-tube to get sound castings.

3.0 Preparation of Composite Slurry & Casting

Mg based composite slurries are prepared by similar process as Al based composites by liquid metallurgy technique (also called vortex method or stir casting) [2,5,6]. This technique is generally used not only for gravity die casting but also for pressure die casting, rheocasting and centrifugal casting. Here the chemically and/or thermally treated dispersoids are added to the clean molten metal while stirring by a stirrer. Suitable design of blades, its location in the vessel and the rpm of the stirrer are critical for uniform mixing. The degree of mixing of the solids with the liquid also depends upon viscosity and surface tension of the liquid and the size, shape and size distribution of the particles. Since dispersoids like SiC particles or fibres are heavier

than molten Mg-alloy, there will be a tendency of the dispersoids to sink to the bottom of the vessel. Hence although very low rpm is desirable to avoid turbulence and air-entrainment that cause oxidation, rpm should not be too low, to avoid particle settling at the bottom of the vessel. Modelling studies [7] have shown that air-entrainment generally occurs when depth of pipe profile touches or goes below the impeller level at high rpm. Normally an rpm of 250-500 is found to be suitable. However the correct rpm primarily depends upon liquid viscosity, relative density between the particle and the liquid and also the slurry concentration.

The composite thus prepared homogeneously is cast into preheated metallic mould and S powder, borax or SO_2 gas is blown onto the melt poured to avoid oxidation.

4.0 Heat Treatment

Solution heat treatment (345-420°C for 16 to 24 hrs) followed by quenching in still or moving air is done both for Mg alloy and its composite. Liquid quenching is not done ordinarily.

Direct gas fuel furnace should never be used. Inert atmosphere should be maintained in the furnace using inhibitor (SO_2), the concentration of which must be maintained from 0.7-1.0% especially at the high temperature where hazard of burning is greater.

5.0 Extrusion

The hexagonal nature of the Mg crystal limits the amount of deformation at room temperature and can not be worked readily by all the usual forming processes.

Mg alloy extrude readily and less control on homogeneity and grain size is required than is demanded for the more exacting process of rolling and forging.

During the extrusion processes the surface of Mg alloy product is apt to show defects in the form of tears (patterned disruptions), which is designated as "surface rippling". The occurrence of this defect is more frequent in lower alloys. The surface rippling may be reduced to a minimum or completely through the correct choice of technological parameters viz.,

(1) increase in the degree of deformation upto 98%

(2) increase in run-out velocities during extrusion

(3) modifying the shape of the working face of the die.

Conical die with the cone, facing the run-out side is best to completely remove rippling. Cylindrical shape of the working face of the die without due radius of curvature promotes formation of disruptions.

Extrusion ratio ranges from 10 to 60 at run-out velocities from 5-40 m/min and at temperature of the billet and of the container in the range of 230-400°C [8,9].

Extrusion of Mg-SiC particle is somewhat difficult when SiC wt% >15. The temperature of the billet should be slightly on the higher side for easeness of operation and good product quality. Properties of composites are enhanced a lot due to extrusion.

6.0 NML Work

(1) Mg alloys and dispersoids used for composite making

Mg alloys of types AZ61 and AZ91 (Table-1) & SiC_p of 15-75 microns size were used for composite making.

(2) Melting, mixing and casting

Mg was melted in an electrical resistance pot type furnace in a mild steel crucible with a cover of chloride and flouride flux ($MgCl_2$ + CaF_2). The flux, about 1% by weight, of the total charge, was added in instalments starting from the initial heating of the charge so that the free Mg surface was never exposed to the atmosphere.

The required quantity of Al was added as soon as the Mg was melted and the temperature was raised to 850°C. The desired level of Mn was introduced through the addition of electrolytic Mn metal as well as dehydrated $MnCl_2$ additions. Normally direct addition of Mn metal is not very satisfactory as some passive layers are formed which prevent further dissolution [10]. After the melt attained homogenisation, a calculated quantity of Zn metal was added and the melt was stirred, precaution being taken to cover the surface with flux. The surface of the melt was then cleaned, degassed and grain refined with hexachloroethane and dehydrated $FeCl_3$.

In the experiment vortex method of mixing solid particle with liquid was used. Propeller type of stirrer system optimally designed by water modelling was used in the actual metallic system. The speed control of the stirrer was initially done by a step cone pully. However for satisfactory results it was done through a variac.

The preheated (700-800°C) SiC particles were then introduced into the melt

through a specially designed cup while the melt was being stirred at a rpm of 250-350. The composite slurry was then cast into the preheated permanent mould. During pouring S-powder was sprinkled to the melt to prevent oxidation and burning. All the tools used in the preparation of the Mg alloys and composites were of mild steel coated with lime and properly dired.

(3)   Heat Treatment of Cast Billets :

Prior to extrusion, the cast Mg alloy/composite billets were machined and solution treated at 360°C for 24h in normal atmoshphere. Since the heat treatment was done in normal atmosphere for a long time, special care against oxidation and fire hazards were taken. The billets were heated slowly at an uniform rate in a sufficiently wide furnace keeping the billets away from the heating element so that the temperature of the billet in any way did not rise above the required level. The heat treatment schedule of the alloy is shown in Fig.1.

(4)   Extrusion of the Alloys/Composites :

The heat treated Mg alloy billets were soaked at preselected temperature in an electric resistance furnace for different periods of time. The extrusions were carried out in a 500T capacity horizontal extrusion press having a minimum ram speed of 19 mm/s to various sections. The extrusion of Mg-Al-SiC particulate composites to round shape was also done successfully.

The details of the extrusion trials and results are given in Table.2. This table also shows the effect of extrusion parameters such as extrusion temperature, speed, extrusion ratio as well as the type of lubricant used for extrusion. The adverse effect of high temperature extrusion and improper lubrication on the extruded section are shown in Fig.2. Some important results on tensile properties of the Mg alloys and composites are given in Table.3.

7.0 Conclusion

Processing of Mg alloys and composites require adequate attention specially due to the problems associated with the high reactivity of Mg with O_2.

Melting should always be done under protective flux cover. Special care should be taken during alloying, grain refining, removal of non-metallic and metallic impurities, degassing, heat treatment for extrusion compared to Al.

For composite making by liquid metallurgy technique suitable stirrer design and optimisation of process parameters, heat treatment of particles are needed in order to get casting with uniform dispersion of dispersoid particles.

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Table 1
Chemical Composition of Alloys used

	Al	Zn	Mn	Fe	Ni	Cu	Si	Mg
AZ61	6.5	0.85	0.25	0.005	0.003	0.10	0.10	Balance
AZ91	9	1	0.15	0.005	0.003	0.10	0.10	Balance

Table 2
Extrusion parameters of Alloy (A) and Composites (B)

A. ALLOY (AZ61)

Expt No.	Soaking Temperature (°C) Time (min)	Container Temperature (°C)	Ratio	Speed m/min	Pressure kg/mm²	Extruded Shape	Remarks
1.	340, 60	300	17:1	18	45	19mm dia.	High temperature failure (Fir tree)
2.	300, 180	280	-do-	18	40	-do-	High temperature defects
3.	280, 180	270	-do-	18	45	-do-	Surface cracks
4.	280, 60	260	-do-	12	56	-do-	Very good products
5.	270, 75	260	-do-	12	52	-do-	-do-
6.	320, 60	300	25:1	24	55	32x6mm rectangular	Failed at high temperature
7.	280, 30	280	-do-	24	-do-	-do-	Good product
8.	250, 60	250	-do-	24	-do-	-do-	-do-

B. COMPOSITES

1.	AZ61	280,60	250	17:1	18	45	19mm dia	Good
2.	AZ61+5%SiCp	280,60	250	-do-	18	50	-do-	-do-
3.	AZ61+10%SiCp	270,60	260	-do-	18	55	-do-	-do-
4.	AZ61+15%SiCp	280,60	270	-do-	15	60	-do-	Surface crack
5.	AZ91	280,75	250	-do-	18	50	-do-	Good product
6.	AZ91+5%SiCp	280,75	250	-do-	18	53	-do-	-do-
7.	AZ91+10%SiCp	270,75	260	-do-	18	60	-do-	-do-
8.	AZ91+15%SiCp	280,75	270	-do-	14	63	-do-	Serration

Table 3
Tensile properties of extruded Mg alloys and composites

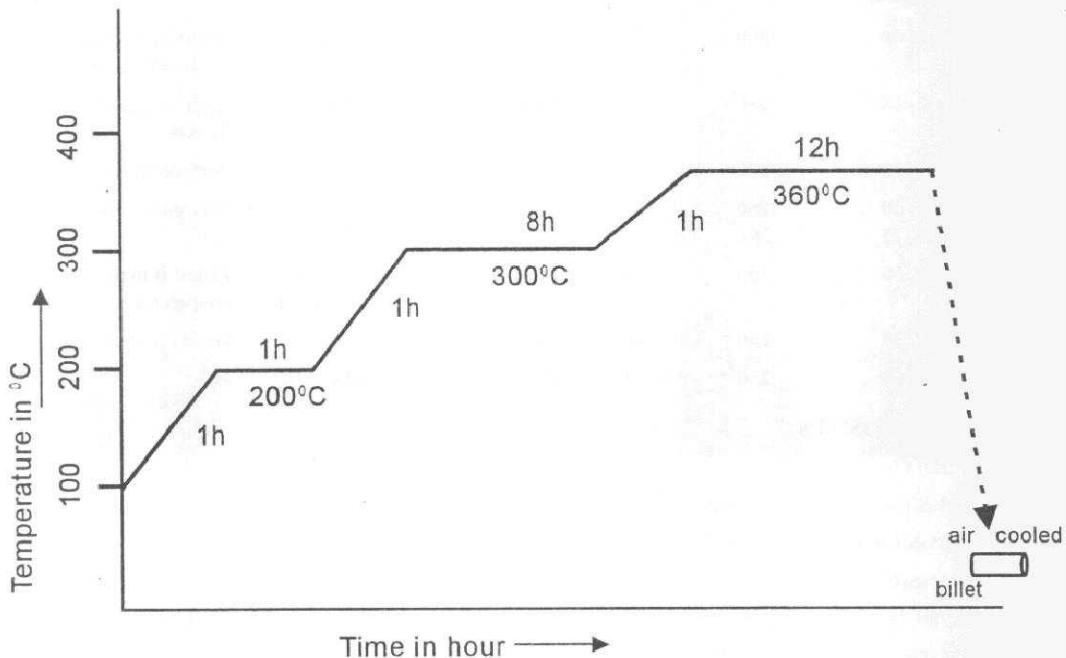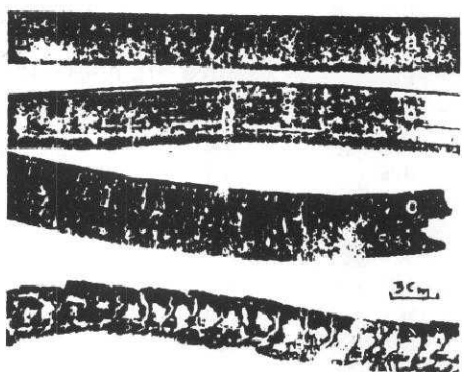| Alloy	UTS MPa	YS MPa	%Elongation	Youngs Modulus, GPa
AZ61	260	170	12	42
AZ61+5% SiCp	260	180	8	45
AZ61+10% SiCp	270	190	6	50
AZ61+15% SiCp	280	210	4	55
AZ91	285	180	16	44
AZ91+5% SiCp	285	225	10	50
AZ91+10% SiCp	290	250	5	55
AZ91+15% SiCp	280	215	3	60

Fig. 1- Solution Heat-treatment schedule

Fig. 2- Shows the effect of lubricant and extrusion temperature
(a) grease + MoS_2 (b) inadequate lubrication (c) high extrusion temperature.