POSSIBILITIES OF MAGNESIUM RECYCLING

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Abstract

Manufacturing of magnesium products is connected with environmental point of view. A large amount of waste in the form of chips and discards is produced in the machining process of castings and sheets. Approx. 1/3 of magnesium used to fabricate structural products (castings and wrought products) ends as new scrap, so it is really inevitable to find ways for its efficient recycling in order to keep the use of primary Mg and thus price at reasonable level. The motivation of this work was to find and investigate some reasonable possibility (though challenging) for recycling of class 5B magnesium scrap. As testing material a mixture of contaminated chips machined from die cast engine block made of AJ62 (MgAl6Sr2) + A390 (AlSi17Cu4) alloys was selected. Extrusion, separation, salt treatment purification and distillation were used as recycling techniques.

Key words

Magnesium, Recycling, Extrusion, Separation, Purification, Distillation

INTRODUCTION

Magnesium alloys are lighest metals (magnesium is one third lighter than aluminum) used for structural applications. They are mainly used in automotive industry for its capability of weight reduction and resulting improvement of fuel economy and reduction of harmful emissions. These properties are derived from high specific strength and specific stiffness, low density, good thermal conductivity, good vibration damping and good castability. Despite relatively low cold formability, temperature stability (low high temperature strength), unfavorable creep properties, problematic corrosion resistance, weldabilty and rather high price the demand for magnesium alloys is increasing rapidly [1]. The most critical drawback of magnesium alloys in the past, i.e. low corrosion resistance, has already been successfully solved by limiting the amount of impurities like Fe, Ni, Cu, Si etc. at the ppm level. Nowadays so called HP – high purity magnesium alloys are mostly alloyed by Al, Zn, Mn, Sr and rare elements.

The high price of magnesium is derived from an energy-consuming winning process. There are only few main processes used for magnesium production. Electrolysis of fused magnesium chlorides (1) from brines and sea water and silicothermic Pidgeon (2) process which is a reduction of dolomite at high temperatures using ferrosilicium. Energy consumption for winning of one kg primary magnesium is about 35 kWh, which makes an extraordinary impetus for its reuse after efficient recycling.

Winning of magnesium with electrolysis [2]:

$$\begin{aligned} cathode &: Mg^{2+} + 2e^{-} \rightarrow Mg^{0} \\ anode &: 2Cl^{-} \rightarrow Cl_{(g)} + 2e^{-} \end{aligned} \quad (1)$$

Winning of magnesium with thermal process [3]:

$$2MgO.CaO + Si \rightarrow 2Mg + Mg_2SiO_4 \quad (2)$$

According to literature [4] the consumption of magnesium alloys can be divided into these groups: 40% is used for alloying of aluminium, 38% for production of die cast parts and wrought products (sheets and profiles), 16% for steel desulphurization, and about 6% for other uses. The production stands for approximately 1 milion ton of magnesium alloys and this number has risen from 1998 more than three times [5]. It is interesting to mention than China takes 84 % portion in world magnesium production but consumes only small part of it. The production of magnesium in Western countries covers only 20 % of their needs.

Nowadays the mostly used industrial manufacturing processes for parts production are die-casting (high pressure die casting – HPDC), sand casting, rolling and extrusion. The research tendencies are to implement advanced casting technologies [6] like thixocasting, thixomolding, rheocasting etc. Casting still accounts for the majority of applications of magnesium alloys although efforts to develop adequate wrought alloys have increased. The various manufacturing processes and alloy compositions result in specific microstructures and properties which determine the potential use of these materials. Today, the spectrum of available alloys covers standard MgAlZn or MgAlMn alloys (AZ, AM) as well as alloys for use at elevated temperatures (creep-resistant alloys) mostly alloyed by Si and Sr. The trend will be to further diversify the alloy compositions and to improve the alloy properties.

Also environmental point of view is connected with manufacturing of magnesium products. A large amount of waste in the form of chips and discards is produced in the machining process of castings and sheets. For example about a half of the total weight of rough castings goes into scrap until final part is machined. generated in the die-casting process Approximately 80% of the scrap arises from trimmings, 8% ends as dross, 7% as chips, 4,5 % as rejected parts, 0,5 % as a slurry. From magnesium extrusion, approx. 75% is used in product and approx. 25% is new scrap. It means that approx. 1/3 of magnesium used to fabricate structural products (castings and wrought products) ends as new scrap, so it is really inevitable to find the ways for its efficient recycling in order to keep the use of primary Mg and thus price at reasonable level. It should be noted that the recycling of Mg needs only 3 kWh per kg, what is 10 times less then required for primary Mg production.

However magnesium alloys recycling is a challenging process. There are only few ways, mostly based on scrap remelting, unfortunately a lot of them are not economically and environmentally acceptable. One reason is high affinity of Mg to oxygen or nitrogen, which makes oxide decomposition in reduction atmospheres almost impossible, another one is strictly limited amount of impurities such as Fe, Si, Cu, Ni which often contaminate the scrap and are difficult to remove. Reduction of MgO and impurities thus usually requires usage of large amounts of chlorides or other environmentally harmful chemicals (not acceptable slag storage and gas development).

Magnesium alloy chips form another of the big recycling problems. They have very large specific surface covered with MgO, which is additionally polluted with lubrication emulsion and often are also mixed with chips made of other metals like Al alloys mostly containing alloying elements extremely unsuitable for magnesium corrosion resistance (like Si or Cu). Reactions of chips with humidity (3) (4) lead to considerable oxidation, which results in loss of a lot of metal. On the other side accompanying exothermic reaction can cause fire (ignition temperature is below 450°C) during which chips burn at 1000 °C and are difficult to extinguish. During this reaction hydrogen is liberated and entails another safety problem.

$$Mg + H_2O \rightarrow MgO + H_2 \quad (3)$$
$$MgO + H_2O \rightarrow Mg(OH)_2 \quad (4)$$

According to different literature sources industrial magnesium scrap can be sorted into following groups (Table 1) [4, 7].

MAGNESIUM SCRAP CLASSIFICATION Table 1

Class of scrap	**1A**	**1B**	**2**	**3**	**4**	**5A**	**5B**	**6A**	**6B**
Definition	Clean scrap	Clean scrap with high surface	Clean scrap with steel, Al (No Cu)	Scrap castings, painted, without Al, Fe	Unclean metal scrap - oily, wet, contains Si,Al, sweepings	Clean - chips, swarfs, machinings	Contaminated - chips, swarfs, machinings	Flux free residues	Flux containing residues

From these groups only first one is relatively easy recyclable. The recycling difficulties increase with increasing group number, whereas recycling of last groups is economically not feasible at all. Therefore only small amount of strictly sorted scrap is recycled (only one third) while the rest is burned or buried in the ground [8]

MATERIAL AND RECYCLING METHODS

The motivation of this work was to find and investigate some reasonable possibility (though challenging) for recycling of class 5B magnesium scrap. As testing material a mixture of contaminated chips machined from die cast engine block made of AJ62 (MgAl6Sr2) + A390 (AlSi17Cu4) alloys was selected. Their chemical composition is in Table 2. For these scrap any remelting processes are inadmissible because of dominant intense creation of Mg_2Si Laves phase, which strictly impede melting process. Moreover high level of impurities like Fe, Cu, Si (coming from A390) is detrimental for any Mg alloy, while high content of potentially formed Mg_2Si for aluminum one.

CHEMICAL COMPOSITION OF AL AND MG MIXED SCRAP Table 2

Fraction	**Alloy**	**Chemical composition**	*Al [%]*	*Zn [%]*	**Mn [%]**	**Fe [%]**	**Cu [%]**	**Ni [%]**	**Si [%]**	**Ti [%]**	**Ba [%]**	**Sr [%]**	**Ca [%]**	**Mg [%]**
Fraction 1	AlSi17Cu4	A390	***75,3-79,5***	***<0,1***	<0,1	<0,4	4,0-5,0	-	16 - 18	<0,2	-	-	-	0,5-0,65
Fraction 2	MgAl6Sr2	AJ62	***6,1***	***-***	0,34	-	-	-	-	-	-	2,1	-	rest

Following alternative methods were investigated to recycle this mixed scrap:

First one was ***direct extrusion*** of this mixture with an aim to obtain lightweight magnesium profile. There are few operations connected with chips pretreatment before extrusion: deoiling, decoating (in case of coatings), crushing (in case of agglomerates) and drying. These steps help to avoid hazardous situations which may result from dangerous nature of magnesium chips. Washing-deoling should be made with non-water based solutions and emulsions to avoid hydrogen liberation. Drying temperatures can not overcome 300 °C to avoid spontaneous ignition.

Tests were carried out on extrusion machine at various temperatures and extrusion ratios. Table 3 is showing extrusion parameters and results of extrusion.

Although the mutual compaction of chips was quite satisfactory (see Fig. 2), the surface of obtained profile always exhibited hot cracks caused by severe mismatch in formability of both alloys. Some cracks were often observed in the brittle AlSi17Cu4 grains, while grains of AJ62 chips were deformed profoundly, confirming acceptable plasticity of this alloy. Optimization of processing parameters may lead to acceptable profile surface quality especially for low-cost lightweight applications.

EXTRUSION PARAMETERS AND RESULTS OF EXTRUSIONS Table 3

Extr. temperature [°C]	**Extrusion ratio**	**Extrusion result**
280	1:11	hot cracks
350	1:11	hot cracks
350	1:20	hot cracks
350	1:40	hot cracks

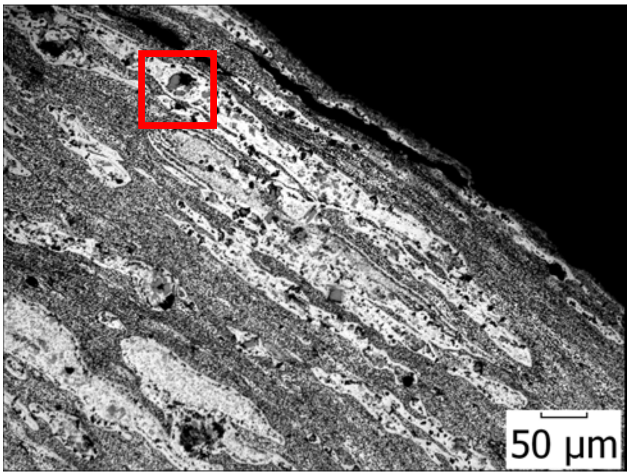

Fig. 2. *Crack sources in AlSi17Cu4 region*

Another investigated recycling possibility was based on separation of both alloys from the mixture via ***flotation method***. This approach is based on different densities of magnesium and aluminum. Magnesium chips flows on the surface of liquid which density lies between magnesium and aluminum (1,7 – 2,7 g.cm^{-3}) while aluminum chips settle at the bottom of the tank, as is shown on Figure 2.

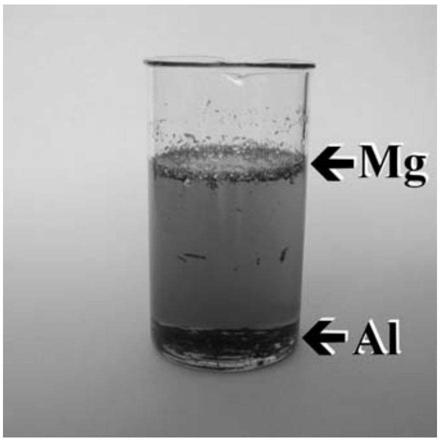

Fig. 2. *Separated Mg and Al chips*

This floatation technique enabled successful separation of magnesium and aluminium chips thus allowing individual recycling of both alloys via standard recycling techniques without danger to bring Mg and Si into mutual reaction. Floatation liquids should be based on non-water solutions to secure the safety of this process.

After separation AJ52 fraction was melted and purified via standard ***salt treatment***. The tests showed that Sr can be effectively removed from the melt using both EMGESAL FLUX 5 and KF salts, however the reaction with later was very intense and exothermic and therefore it cannot be recommended for this type of recycling.

Last approach was gaseous state recycling – vacuum distillation. Vacuum distillation allows to win HP magnesium (99,999%) and to process unclean magnesium scrap, especially machining chips, oily magnesium, smelting sludge, dross or the scrap mixture [8]. Compounds and crucial impurities of magnesium (Al, Fe, Mn, Si, Cu, Ni and oxides) have a higher boiling point, which means that these elements cannot be distilled under the temperatures when magnesium is already evaporated. Magnesium vapor pressure is function of specific vacuum and temperature. The distillation was successful on samples made of mixed trimmings, dross, rejected parts at 650 – 800 °C for more than 6 hours in vacuum < 100 Pa (industrial scale). If the cooling zone is 800 K or lower the magnesium vapors can be collected in a crystal crown, as it is shown in Figure 3.

Distillation of floated Mg chips fraction of AJ62 alloy (chemical composition is in table 1) proved that all elements (including Sr) with the exception of Zn (Zn is acceptable alloying element) can be successfully removed from the alloy (Table 4). The distillation of 30 g of the alloy took 60 minutes in vacuum < 100 Pa at 650 – 700 °C, the undistilled rest represented 2,5 g. It means that nearly all Mg was distilled from the alloy at these conditions. The structure of obtain metal is illustrated in Figure 4.

Fig. 3. *Collected magnesium crystal*

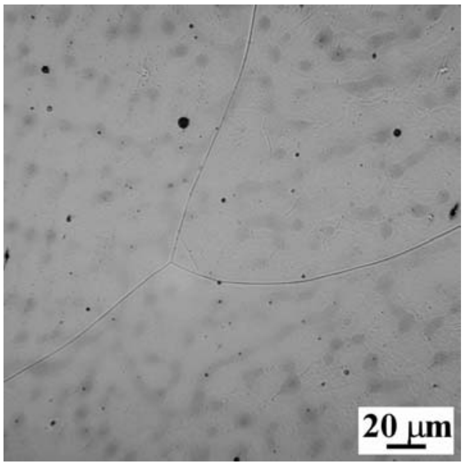

Fig. 4. *Structure of the distilled metal*

CHEMICAL COMPOSITION OF DISTILLED MATERIAL Table 4

Samp. **No.**	*Al [%]*	*Zn [%]*	*Mn [%]*	*Fe [%]*	*Cu [%]*	*Ni [%]*	*Si [%]*	*Ti [%]*	*Ba [%]*	*Sr [%]*	*Ca [%]*
1	***< 0,01***	***0,02***	***< 0,01***	***< 0,01***	***< 0,01***	***<0,001***	***< 0,01***	***< 0,01***	***< 0,01***	***<0,001***	***< 0,01***

CONCLUSION

Four recycling techniques were used to investigate the possibilities of magnesium scrap class 6 recycling: direct extrusion, separation, salt treatment purification and distillation. The most promising recycling method is extrusion technique and the most effective is distillation. Within the extrusion optimization of processing parameters may lead to acceptable profile surface quality. Therefore additional test should be carried on magnesium scrap chips ranging various chemical compositions and testing extrusion parameters.

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