

OPTIMIZATION OF THE RECYCLING PROCESSES FOR MAGNESIUM FROM A HIGHLY CONTAMINATED WASTE

OPTIMIRANJE POSTOPKA RECIKLIRANJA MAGNEZIJA IZ MOČNO KONTAMINIRANIH ODPADKOV

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Prejem rokopisa – received: 2013-07-30; sprejem za objavo – accepted for publication: 2013-10-04

With the recently increased use of magnesium alloys, especially in the automotive industry, a large quantity of generated waste, based on magnesium alloys, is expected. Such a waste often contains many impurities such as oil, paint, moisture, non-metallic fractions, oxides, Cu, Fe, etc. In this paper, two different methods for extracting magnesium from a highly contaminated waste are presented: the recycling of magnesium with flux and with the vacuum-distillation process. In addition, we present the process of pre-treating the contaminated magnesium waste that has proved to be a very important step in the recycling process for both economic and environmental reasons. The processing of post-consumer and contaminated magnesium scrap is described with a diagram, providing a sustainable and environmentally friendly procedure for the treatment of such wastes.

Keywords: recycling, magnesium waste, vacuum distillation, flux, contaminated, impurities

Z naraščanjem uporabe magnezijevih zlitin, posebno v avtomobilski industriji, se pričakujejo velike količine odpadkov na osnovi magnezijevih zlitin. Taki odpadki pogosto vsebujejo številne nečistoče, kot so olja, barve, vlaga, nekovinske frakcije, oksidi, Cu, Fe in drugo. V tem članku sta predstavljeni dve različni metodi za ekstrakcijo magnezija iz močno onesnaženih odpadkov: recikliranje magnezija s talilom in z vakuumsko destilacijo. Dodatno je prikazan še postopek predobdelave kontaminiranih magnezijevih odpadkov, ki se je izkazal za pomembnega pri recikliranju, tako iz ekonomskih kot tudi okoljevarstvenih razlogov. Obdelava iztrošenega in kontaminiranega odpadnega magnezija je opisana z diagramom, ki zagotavlja trajnosten in okolju prijazen postopek obdelave takih odpadkov.

Ključne besede: recikliranje, magnezijevi odpadki, vakuumaska destilacija, talilo, kontaminiran, nečistoče

1 INTRODUCTION

Magnesium alloys, being the lightest metals, are used widely for many parts in the automotive industry.¹ Such a trend is mainly a consequence of increased fuel prices, leading to a decrease in the total mass of a vehicle. Furthermore, many environmental regulations require the use of lightmass materials in transport to reduce harmful emissions. The European guideline on car usage has enforced the trend of using parts of lightmass metals.^{2,3}

Due to their poor corrosion resistance, magnesium automotive components exposed to a corrosive atmosphere must be coated (paint and lacquer). Oily and coated magnesium car components, at the end of their life cycle, make the recycling process very difficult because of the contamination of magnesium melts with a lot of impurities. There are several characterizations of magnesium scrap, but the most referenced is the one using eight classes of scrap. Class 1 of magnesium scrap represents high-grade clean scrap without any impurities; Class 2 is clean scrap with aluminium or steel inserts; Class 3 includes clean, dry and uncontaminated turnings and swarfs; Class 4 includes flux-free residues such as dross and sludge; Class 5 refers to painted coated scrap

with/without aluminium or steel inlays and with no copper or brass impurities; Class 6 includes oily and/or wet turnings, swarfs, etc.; Class 7 includes unclean and contaminated metal scrap, e.g., the post-consumer scrap that may contain silicon (Al-alloys, shot blasting), Cu-contaminated alloys, iron inserts, Ni-coatings and non-magnesium sweepings; Class 8 includes the flux-containing residues from Mg recycling, high amounts of oxides, chlorides, fluorides (Mg amount < 30 %) and Fe.⁴⁻⁶

Only the first-class scrap is relatively easy to recycle. The recycling difficulties increase with the increase in the class number of magnesium scrap. At present, only a small amount of magnesium-alloy scrap is recycled (only one third), while the rest is burned or buried in the ground.^{3,7,8} Magnesium-alloy chips represent a big recycling problem, caused by a very large specific surface covered with MgO. Reactions of the chips with humidity lead to a considerable oxidation, resulting in a loss of a lot of metal.^{9,10} On the other hand, the accompanying exothermic reaction can cause fire (the ignition temperature is 450 °C) during which the chips burn at 1000 °C and they are difficult to extinguish. Hydrogen is liberated

during this reaction causing small explosions and entailing another safety problem.^{1,5}

The elements such as Ni, Cu, Fe, and Si have a crucial influence on decreasing the magnesium-alloy corrosion resistance, so the amount of these impurities must be limited to the ppm level. It is very difficult to recycle "old" scrap (especially from a shredder plant), because it always contains a certain amount of these impurities.^{4,9,11-13} A removal of Ni and Cu from a magnesium melt with additives is practically impossible due to strong interactions in the Mg-Ni and Mg-Cu systems.^{6,9} Only the distillation process is an effective way to separate Ni and Cu from magnesium alloys.

The recycling of magnesium must be, above all, economically reasonable. The average price of primary magnesium metal (99.9 %) has been about 3.1 \$/kg in the past five years.¹⁴ Different recycling methods for magnesium scrap have been developed. The most common method for recovering clean scrap (classes 1, 2 and 3) involves flux. The recycling of magnesium scrap classes 4, 5, 6, 7 and 8 is not practical due to the increased impurities (Cu, Ni, Fe, Si) and the dirtiness of the starting material that decrease the economic efficiency of the recycling process. The most efficient process for the treatment of these classes of waste is the vacuum-distillation process.^{5,6,10}

2 EXPERIMENTAL PART

The first part of the experiment covers the most common method of magnesium recovery, the recycling with flux. A pre-treatment was conducted in order to improve both the economy and the technology of the process. The second part of the experiment refers to the most efficient method for recycling contaminated magnesium scrap, the vacuum-distillation process.

In the experiments with the flux treatment of the waste, two types of the samples were used. The first type of the samples mostly included the parts from the automotive industry and the casting process without any oil contaminations, with different thicknesses of the oxide layer on the surface as well as different sizes and shapes. The second type of the samples included oil-contaminated parts with oxides, dust and other inorganic impurities. The dimensions and descriptions of the samples are shown in **Table 1**.

Table 1: Characteristics and dimensions of the samples

Tabela 1: Značilnosti in dimenzije vzorcev

Sample		Characteristics	Dimensions, (<i>a</i> · <i>h</i>) mm ²
Without oil (Classes 4 and 7)	1	Compact parts from the auto industry and parts of a gating system. A thin oxide layer is noticeable.	from 15 · 20 to 90 · 200
	2	Spongy, loose parts; mostly casting slag. A 1–3 mm oxide layer is noticeable on the surface.	from 20 · 30 to 30 · 100
Oil contaminated (Class 6)	3	Irregular biconcave parts with oil, oxides, dust and other inorganic impurities.	from 10 · 2 to 60 · 5

The pre-treatment of samples 1 and 2 was conducted in the following four steps:

- mechanical treatment in a rotating drum;
- dust separation;
- chemical treatment in a solution of sulfuric acid;
- washing and drying.

The mechanical treatment was performed in a laboratory rotating drum with a volume of 6 dm³ and rotation of 150 r/min. In this drum, the light fraction containing dust was separated from the massive fraction. The mass of the solid samples in the drum was (2000 ± 10) g. The chemical treatment of the massive fraction was conducted at the temperatures from 45–50 °C with an addition of a solution with mass fractions, *w* = 5–10 % H₂SO₄. After the chemical treatment, the metal fraction in the lattice basket was washed with water. The drying process was performed in a furnace at the temperature of about 100–200 °C for a period of 6–8 h.

The smelting of prepared Samples 1 and 2 was conducted in an induction 25 kVA furnace with a graphite crucible of 1 dm³ and with additional mechanical stirring. A commercial smelting-salt mixture with the following composition was used: 76 % emgesal, 18 % dekamag and 6 % CaF₂. Since Sample 3 was contaminated with oil, the degree of oil contamination had to be determined. The oil removal was carried out with a prepared water solution of water glass (sodium silicate, 18.3 %), dode-

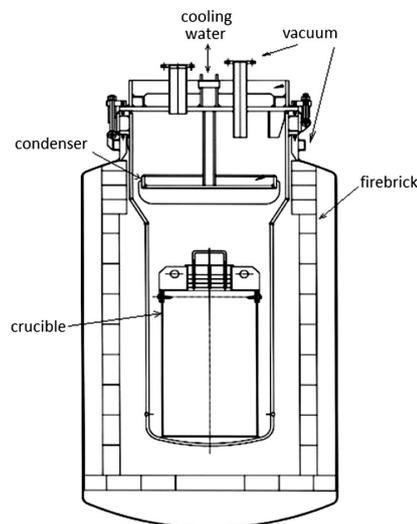


Figure 1: Vacuum-distillation furnace

Slika 1: Vakuumska destilacijska peč

cybenzenesulfonate (DBS, 6.7 %) and sodium hydroxide (NaOH, 5.0 %).

For the processing of the contaminated magnesium scrap with the vacuum-distillation process, highly contaminated magnesium scrap was used, belonging to Classes 5, 6 and 7. The waste was briquetted and its content was determined with a chemical analysis. The vacuum-distillation furnace is shown in **Figure 1**.

A batch of (400 ± 5) kg was melted in the electric-resistance furnace with two chambers under the vacuum of 0.5 bar. In the lower part of the furnace, the temperature was around 840–950 °C and in the upper part it was from 650–680 °C. The temperature of the condenser was about 135 °C. The times of the distillation process for magnesium from the waste were from 24–48 h.

3 RESULTS AND DISCUSSION

The processing of the magnesium waste, of Classes 4, 5, 6 and 7, was conducted with the flux-recycling process and the vacuum-distillation process. In the first part of the experiment, the importance of the waste pre-treatment was shown. The smelting process of Samples 1 and 2 was conducted with different pre-treatment combinations in order to indicate how each step affects the magnesium recovery rate. In addition, smelting salt was added in different amounts. The results are shown in **Table 2**.

Table 2: Magnesium recovery rate of Samples 1 and 2 in dependence of different combinations of the pre-treatment process and smelting salt

Tabela 2: Stopnja pridobitve magnezija v vzorcih 1 in 2 pri različnih kombinacijah predobdelave in talilne soli

Sample	Pre-treatment	Smelting salt, g	Mg recovery rate, %
1	Without pre-treatment, direct smelting	–	71 ± 2.5
	Mechanical treatment, 1 h, dust separation	50	91 ± 0.5
	Chemical treatment with 5% H ₂ SO ₄ , drying at 100 °C	50	81 ± 1.5
	Mechanical treatment, 1 h, dust separation, chemical treatment with 5 % H ₂ SO ₄ , drying at 100 °C	50	94 ± 0.8
2	Mechanical treatment, 1 h, dust separation	–	44 ± 1.5
	Mechanical treatment, 1 h, dust separation	60	47 ± 1.5
	Chemical treatment with 5 % H ₂ SO ₄ , drying at 100 °C	60	46 ± 1.5
	Mechanical treatment, 1 h, dust separation, chemical treatment with 5 % H ₂ SO ₄ , drying at 100 °C	60	49 ± 1.5

By processing Sample 1 (belonging to Class 7), it was shown that it is possible to achieve a utilization of up to 94 % with a pre-treatment. Without the pre-treatment, the utilization is only 71 %, which indicates the importance of the pre-treatment step in the recycling

process of this type of magnesium scrap. The maximum utilization after the processing of Sample 2 (the Class 4 scrap) is about 49 %, which is a consequence of a relatively thick oxide layer of 3 mm and a sponge structure of the waste, i.e., a relatively high surface/volume ratio. The Sample 2 pre-treatment does not significantly increase the recovery of magnesium from the waste due to the thick oxide layer.

The time for removing the oil from Sample 3, with a constant stirring, was 5 min at the temperature of 60 °C, while the sample mass was (1000 ± 10) g. The average degree of oil contamination with powder impurities for Sample 3 was (17 ± 0.5) %. It was shown that the optimum share of the water solution for an efficient removal of oil contamination (about (96 ± 1.5) %) is 10 %. When oil was removed from the surface, the scrap was smelted in an induction furnace. The total metal-recovery rate for Samples 4 was (93 ± 1.8) %. The results for Sample 3 (the Class 6 scrap) showed an effective way to remove oil from the waste, with a high recovery rate.

A pre-treatment of magnesium waste has a significant influence on:

- the utilization of magnesium from the waste,
- the reduction of slag amounts,
- a better economy,
- a better ecology and safety of the process.

It should be noted that same experiments with the flux were done in industrial conditions in the factory Bela stena in Boljevac, Serbia, with the batches of the total mass of 157 t (Samples 1, 2 and 3). The total utilization of magnesium from the waste, in industrial conditions, was (75 ± 0.5) % (118 t of magnesium).

In the second part of the experiment, the vacuum-distillation process was employed for the extraction of magnesium from the contaminated waste (Classes 5, 6 and 7). The share of impurities was about 10 % (7 % moisture and 3 % oil, paint, oxides) and the rest was the magnesium alloy (mostly from the automotive industry). The experiments were conducted in different ranges of temperature and time in order to obtain the optimum parameters of the process. The results are shown in **Table 3**.

Table 3: Parameters for the vacuum-distillation process

Tabela 3: Parametri pri vakuumskem destilacijskem procesu

Sample	Temperatures down/up the furnace, °C	Time of distillation process, h	Metal in crown, kg	Residue, kg	Metal recovery rate, %
v1	840/650	24	200.2	170.5	55.5
v2	840/650	30	201.1	169.7	55.7
v3	840/650	40	203.6	170.3	56.2
v4	840/650	48	206.9	167.9	57.0
v5	900/670	24	207.5	162.4	57.4
v6	950/680	24	212.1	163.7	58.2

The chemical compositions of distilled magnesium crowns are shown in **Table 4**. Since zinc has a lower

vapor pressure than magnesium, the zinc in a crown required higher temperatures and longer times, but, in general, high-purity magnesium was obtained.

Table 4: Chemical composition of the magnesium crown

Tabela 4: Kemijska sestava magnezijeve krone

Sample	Chemical composition of the magnesium distillate						
	Al	Zn	Mn	Fe	Si	Cu	Mg
v1	0.02	0.04	0.005	0.001	0.003	0.001	99.93
v2	0.03	0.05	0.003	0.001	0.003	0.001	99.91
v3	0.03	0.05	0.005	0.001	0.002	0.002	99.91
v4	0.02	0.08	0.002	0.002	0.004	0.001	99.89
v5	0.03	0.14	0.004	0.001	0.003	0.0005	99.82
v6	0.04	0.34	0.005	0.002	0.004	0.001	99.61

The waste in the form of pressed briquettes was contaminated with oil, oxides, paint and dust. The oxides of magnesium and aluminium (MgO and Al_2O_3) contained in a batch cannot be converted to their elementary state; instead, they form a foamed slag along with the impurities and inter-metallic compounds. The distillation residue, besides the foamed slag, consists of a metal fraction that has a chemical composition of 35 % Al, 0.2 % Zn, 1.2 % Mn, 0.03 % Fe, 0.05 % Si, and the rest is magnesium and impurities. During the process, the amount of the magnesium in the metallic fraction of the batch was decreased and the amounts of the slag and aluminium in the batch were increased. Consequently, the utilization of magnesium is at a low level due to the difficulties in the movement of magnesium atoms through the oxides and alloys in the batch at the end of the process.

According to the results from **Tables 3** and **4**, it can be concluded that the duration of the process does not significantly affect the extraction of magnesium from the waste. However, by increasing the temperature, while keeping the same duration of the process, the magnesium recovery was increased by 2–3 %, which is a low rate with respect to the increment of the energy consumption of 7–8 %. In addition, with an increase in the operating temperature, the impurity amount in the distillate increased due to an intense evaporation of the impurities from the batch surface.

The residue from the vacuum-distillation process can be used for a recovery of aluminium, but a large amount of impurities must be taken into consideration. Although the recovery of magnesium from the waste is at a low level (about 58 %), pure magnesium was obtained (up to 99.93 %), justifying the economy of the process. For the industrial use, it is necessary to construct less expensive and more mobile equipment for the vacuum-distillation process. In addition, further research should focus on the combination of pre-treatment and vacuum-distillation process, which should increase the extraction of magnesium from the waste.

To remove an organic coating/paint and oil/moisture the pre-treatment step was used as a very effective

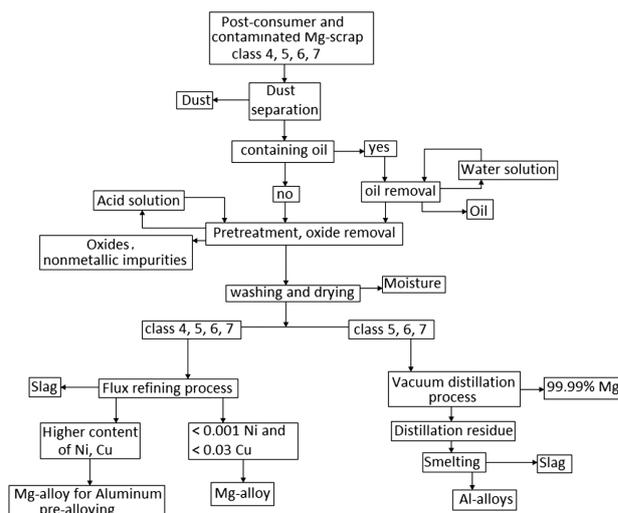


Figure 2: Processing of post-consumer and contaminated magnesium scrap

Slika 2: Obdelava izrabljenih in kontaminiranih odpadkov magnezija

method. The removal of these contaminations is essential for decreasing the dross formation and harmful gas exhaust and, thereby, reducing the loss of magnesium through the dross. Besides, if not removed they can significantly influence the vacuum-equipment lifetime when there is a direct contact. If there is a filter in the vacuum equipment for a disposal of harmful gases it will increase the price of the investment and make it difficult to create a vacuum, so a pre-treatment is a much better solution.

In the post-consumer scrap, the main impurities such as Ni, Cu, Fe and Si are always expected due to the complexity of the waste structure, particularly in the shredder process, where many materials are involved. In the vacuum-distillation process, impurities are easily separated from magnesium due to a different vapor pressure, which is a noticeable advantage of this process. In the process with flux, it is advisable to produce magnesium pre-alloys for the aluminium-alloy production rather than neutralizing it with Zn or Mn, especially at higher levels of Ni and Cu in the alloys (greater than 0.002 % for Ni and 0.03 % for Cu).

A recommended scheme for processing post-consumer and contaminated magnesium scrap is shown in **Figure 2**.

In **Figure 2**, we can see that the by-products such as oil, slag, dust, metallic oxides and non-metallic impurities are obtained. Dust, slug and non-metallic impurities can be used as additions to asphalt and oil can be used as a fuel. The Al-alloy from the vacuum-distillation process can be used for steel desulphurization.

4 CONCLUSION

In this paper two different methods for recycling magnesium waste were investigated: recycling with flux and recycling with the vacuum-distillation process. Mag-

nesium waste with oil, moisture and other non-metallic impurities was used in these processes. On the basis of the presented results, we can conclude that a pre-treatment has a significant role in the recycling process. The main advantages of the pre-treatment step applied to contaminated magnesium waste in the recycling process are the following:

- a significant increase in the recovery of magnesium from the waste (up to 94 %);
- an improvement in the economy of the process;
- a reduced share of the slag in the flux-recycling process;
- a removal of the moisture and oil from the waste enables a proper storage of the waste, without any safety risks;
- elimination of environmental problems (an emission of harmful pollutants into the air is prevented);
- an improved diffusion throughout the batch in the vacuum-distillation process, increasing the intensity of the process;
- prevention of contamination and vacuum-equipment damage.

In addition, a recommended scheme for processing contaminated magnesium waste was given, whereby several semi-products were obtained. In the case of higher proportions of Ni and Cu contained in a magnesium alloy, it is recommended to use these alloys for aluminium pre-alloying. If high-purity magnesium has to be obtained, the vacuum-distillation process is inevitable. By-products such as oil, slag, dust, metallic oxides and non-metallic impurities can be used as a fuel and as building-material components.

Acknowledgement

The authors wish to acknowledge the financial support from the Ministry of Education and Science of the Republic of Serbia within projects TR34002 and TR34033.

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