

## Purification of Highly Contaminated Magnesium Melt

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### Abstract

The steering wheel core is chosen as the first target for the development of a purification technology for highly contaminated magnesium melt, because it contains abundant foreign matter such as polyurethane, copper electrodes, and steel inserts, which have high potential to form non-metallic inclusions and to deteriorate the corrosion resistance of recycled alloys. Various melt treatment technologies have been investigated for refining AM50 magnesium alloy contaminated with polyurethane. The NMI content in magnesium alloy scrap contaminated with polyurethane was effectively reduced by a sequential refining process consisting of filtration, fluxing, and gas bubbling treatments. The filtration step reduced most large inclusions such as carbon residues from the decomposed polyurethane. The subsequent fluxing and gas bubbling treatments effectively removed the small inclusions such as carbonates and oxides.

### Introduction

The application of magnesium in the automotive industry has been expanded by the growing necessity of automotive weight restrictions and reduction [1-4]. For example, individual automotive components such as steering wheels, gear boxes, instrument panels, seat components, wheel rims, rear flaps, reflectors, door frames, oil pans, and crank cases have been made of magnesium alloys. The European directive on end-of-life vehicles demands that by 2015 95% of the total car weight must be reused and recovered [5]. The rates specified for reuse and recycling are 85%, excluding energetic recovery. This means that by 2015 85% of the parts from a car of average weight must be “used for the same purpose for which they were conceived” or that they must be “reprocessed in a production process of the waste materials for the original purpose or for other purposes” [5-6]. The Korean Government also launched a directive on end-of-life vehicles according to which 95% of the vehicle’s weight will have to be reused and recycled by the beginning of 2015, keeping pace with the EU’s legislation. Therefore, with the increased use of magnesium for automotive components, the development of more effective magnesium recycling technology for all types of scrap becomes more important. Thus far, magnesium recycling for magnesium alloy production is done only for clean scrap, which is also referred as Class-1 scrap, consisting of sprues and runners from magnesium die casters. Most end-of-life scrap has been used for desulphurization of steel and the alloying of aluminum [2,7]. There is significant motivation to investigate recycling technology of end-of-life magnesium scrap.

Among the automotive components using magnesium alloys in the Korean automotive industry, the steering wheel has the longest history of magnesium alloy use. The steering wheel contains abundant foreign matter such as a polyurethane cover, copper electrodes, and steel inserts, which have high potential to form

non-metallic inclusions (NMIs) and to deteriorate the corrosion resistance of recycled alloys. In this research, a purification technology for highly contaminated magnesium melt was developed. Various melt treatment technologies for refining AM50 magnesium alloy scrap contaminated with polyurethane were investigated.

### Experimental procedures

By analyzing steering wheel assemblies collected from various ELVs, the mass percentages of foreign matters in AM50 magnesium alloy frame were determined as 28.7%, 10.8%, and 0.5% for the polyurethane (PU) cover, steel hub, and copper electrode, respectively. The mass percentage of the PU cover in the U-shaped groove (Fig. 1) relative to the whole magnesium alloy frame reached 7.5%. Because of the existence of adhesive bonding between the magnesium alloy frame and the PU cover as well as the structural joining by a U-shaped groove, it is difficult to separate the PU cover from the magnesium frame by the crusher. To simulate the refining process with similar conditions to the actual situation, the mixing ratios of PU to the magnesium alloy were determined as 1, 4, 7, and 10%.

In order to estimate the amount of thermally reduced PU and to eliminate ignition risk, the mass reduction of PU by heating was measured using a thermal gravity analyzer (TA Instrument SDT2960). 2kg of a mixture of AM50 magnesium alloy scraps and a predetermined weight of PU scraps was melted in a crucible electric resistance furnace under the protection of a mixed gas atmosphere of SF<sub>6</sub> (50 cc/min) and CO<sub>2</sub> (500 cc/min). Before melting the metal, slow heating between 300°C and 550°C was carried out until fume discharging was completed. The furnace was then heated to 730°C followed by various melt treatments as shown in Table 1: (1) filtering with a stainless steel mesh (D<sub>wire</sub>=0.45 mm, hole=2mm x 2 mm); (2) flux treatment with a

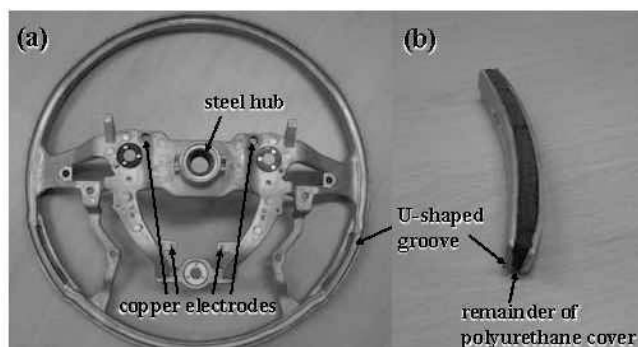


Fig. 1. Dismantled magnesium alloy steering wheel frame (a) and fractured rim with U-shaped groove filled with the remainder of the polyurethane cover.

commercial flux RJ-5 (amount of flux=1% of metal weight, rotational speed of impeller=120 rpm, stirring time=30 min, holding time=30 min) as shown in Table 2; and (c) gas bubbling with 99.9% argon (rotational speed of impeller=120 rpm, gas flow rate=0.5 and 1.0 liter/min, stirring time=30 min, holding time=30 min).

After each melt treatment, a small quantity of melt was poured with a ladle into a coupon-shaped steel mold of 50 mm diameter and 15 mm height. The shapes and compositions of NMIs were analyzed using scanning electron microscopy and energy dispersive X-ray spectroscopy (JSM-6610 LV), and the area fraction of NMIs was evaluated using image analyzing software (i-Solution DT) on optical micrographs sequentially obtained 150 times with 100 magnification from each polished specimen. In order to verify the NMI content, analyses by an optical emission spectroscopic (OES) method and by a particle analyzer using Oxford INCAFeature software in conjunction with scanning electron microscopy (JSM-6480 LV) were also performed.

### Results and discussion

Because the PU is a thermoset polymer, the PU covering the magnesium alloy frame cannot be removed by melting. The PU mixed with magnesium scraps consequently causes serious melt contamination during the refining process. Fig. 2 shows the mass changes of the PU collected from the steering wheel scrap by heating at a rate of 10°C/min and isothermally holding at 300°C and 400°C, respectively. The decomposition of PU began and finished at 267°C and 365°C, respectively, and the weight of remaining material decreased to 20% of the initial mass at 500°C. However, slow heating of the mixed scrap is necessary, as fast heating can cause ignition of the magnesium. By isothermal holding at 300°C, the weight of the PU remainder decreased to about 30% of the initial mass after holding for 50 min, and no

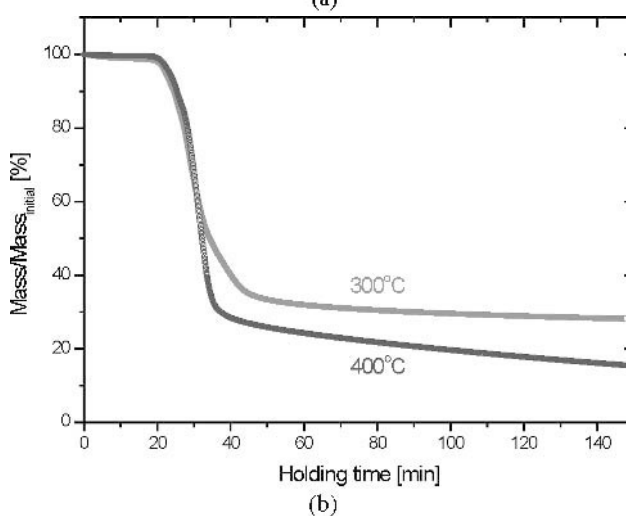
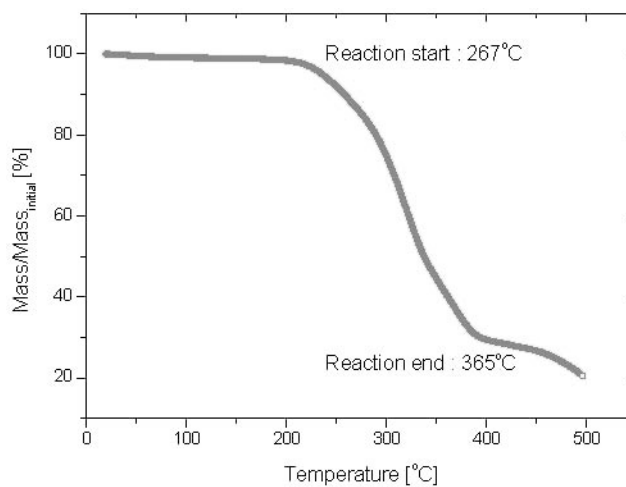


Fig. 2. The mass change of polyurethane by heating at a rate of 10°C/min (a) and isothermal holding at 300 and 400°C (b).

Table 1. Processing conditions used for remelting and refining AM50 magnesium alloy scrap containing polyurethane.

Sample code	PU addition (%)	Filtration	Flux addition (%)	Gas flow rate (ℓ/min)
P1-R	1	×	0	0
P1-F	1	○	0	0
P1-FX	1	○	1	0
P1-FX-B0.5	1	○	1	0.5
P1-FX-B1.0	1	○	1	1.0
P4-R	4	×	0	0
P4-F	4	○	0	0
P7-R	7	×	0	0
P7-F	7	○	0	0
P7-FX	7	○	1	0
P7-FX-B0.5	7	○	1	0.5
P7-FX-B1.0	7	○	1	1.0
P10-R	10	×	0	0
P10-F	10	○	0	0

Table 2. The chemical composition of the RJ-5 flux.

Component	MgCl <sub>2</sub>	KCl	BaCl <sub>2</sub>	CaF <sub>2</sub>	MgO	H <sub>2</sub> O	Insoluble
Amount (%)	30±3	26±3	22±3	22±3	<1.5	0.5	<1.5



Fig. 3. The remaining tar and char on the surface of magnesium alloy scraps during decomposition of polyurethane scraps by heating at 400°C in air.

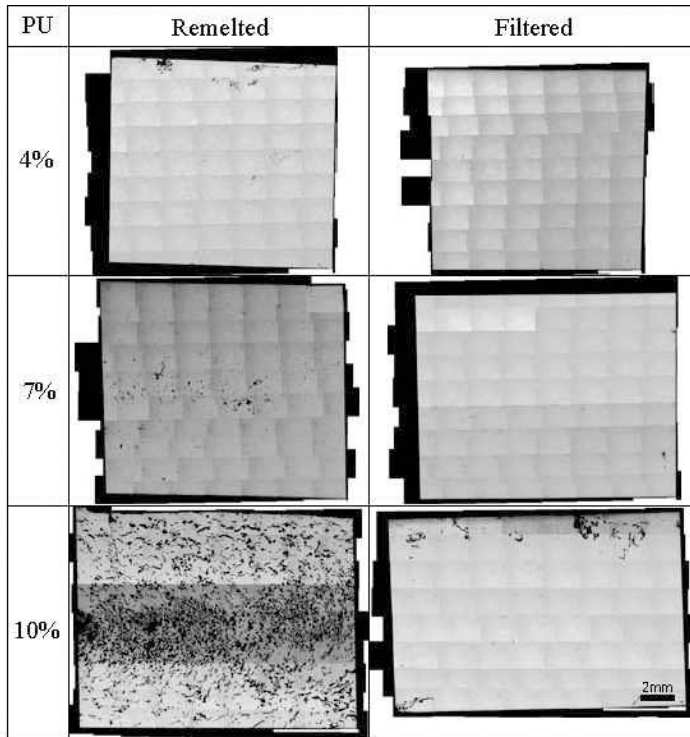


Fig. 4. Optical microscopic images of remelted and filtered ingots made of AM50 magnesium alloy scraps initially containing 4, 7, and 10% of polyurethane scraps.

further decrease was achieved. On the other hand, the weight decrease of the PU remainder to 20% of the initial mass after holding for 60 min was achieved by isothermal holding at 400°C. Therefore, preheating at 400°C for more than 60 min is suitable for decomposing the PU before melting the magnesium alloy. Fig. 3 shows the mixed scrap during heating at 400°C for decomposing the PU. Tar and char, which are residues of PU, cover the surface of the magnesium alloy scrap. They discharge a huge amount of fume which may contain harmful gasses such as dioxin, NO<sub>x</sub>, HCN, and NH<sub>3</sub> [8]. Most of the remaining material was mixed with the magnesium melt during the remelting process, and caused serious contamination of solidified ingots.

Fig. 4 shows the microstructure of remelted and filtered ingots made of AM50 magnesium alloy scraps initially containing 4, 7, and 10% of PU scraps. The filtered ingots show large differences from the remelted ingots. Most large inclusions were removed from the ingot initially containing 4% of PU scrap by filtration, whereas the ingots initially containing more than 7% of PU scrap had a considerable amount of large inclusions. In order to classify the NMIs, SEM and EDS analyses were carried out. Fig. 5 shows SEM images and EDS results for the NMIs in remelted ingot of AM50 magnesium alloy scrap containing 7% of PU scrap (P7). The large inclusions as shown in Fig. 5 (a) were mainly composed of carbon, which originates from the remaining char of PU. Some carbon inclusions were found as carbonate, as shown in Fig. 5 (b). Also, typical inclusions found in magnesium alloy such as fluoride and oxide films, oxide clusters, and small oxide particles were detected as shown in Fig. 5 (c), (d), (e) and (f), respectively. From these results, it was concluded that the remaining tar and char after decomposition of PU were not eliminated from the magnesium melt by heating up to 730°C, and they were present in

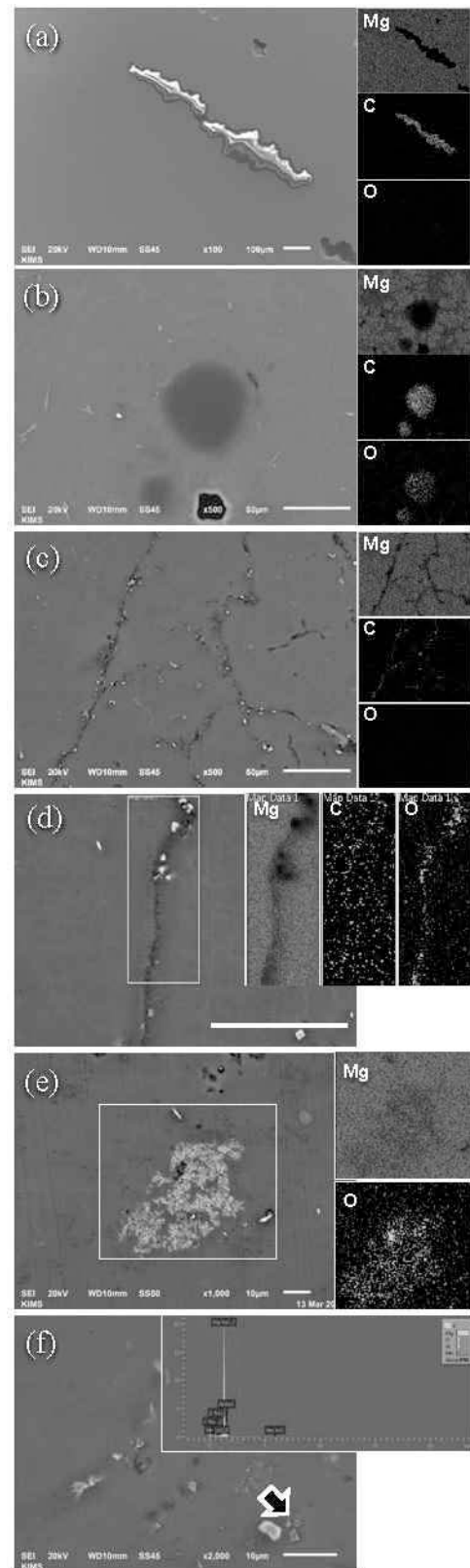


Fig. 5. SEM images and EDS analysis results on the second phases in remelted ingot of AM50 magnesium alloy scrap initially containing 7% of polyurethane scrap representing carbon residues (a), carbonate inclusions (b), fluoride films (c), oxide films (d), oxide clusters (e), and oxide particles (f).

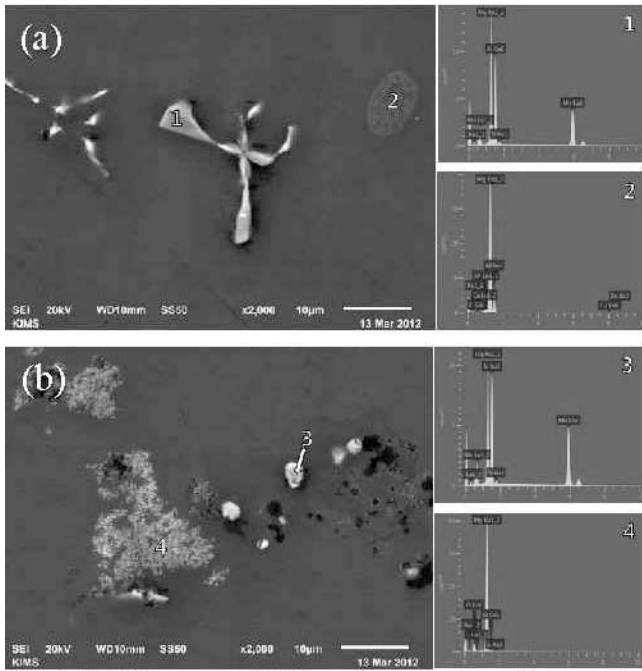


Fig. 6. SEM images and EDS analysis results on the second phases in filtered ingot of AM50 magnesium alloy scrap initially containing 7% of polyurethane scrap: (a) Al-Mn intermetallics and (b) oxide inclusions in the forms of cluster and particle.

the forms of carbon and carbonate inclusions in the solidified ingot. Fig. 6 shows SEM images and EDS results for the NMIs of filtered ingots of the same scrap (P7-F). By means of filtration of the contaminated melt, the amount of large inclusions was considerably reduced. Most of the inclusions after filtering were oxides in the forms of lumps and particles. Although they could be expected to improve the filtration effect on smaller inclusions, filters with smaller openings were not used in this study in order to avoid plugging and choking by metal [9].

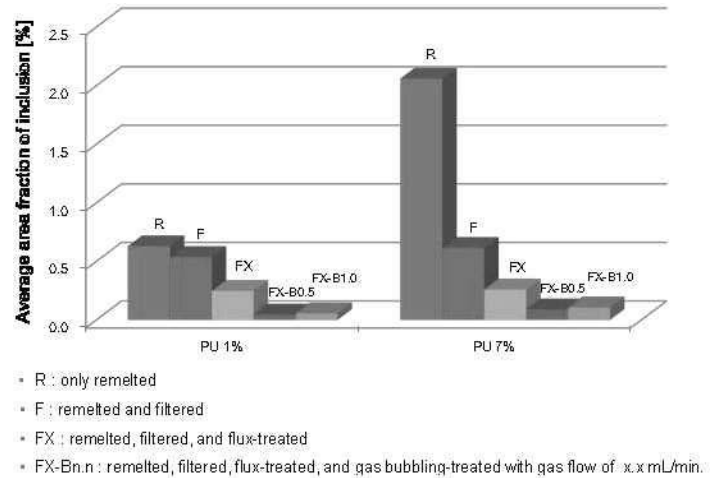


Fig. 8 shows the variation in the average area fractions of NMIs in remelted and refined AM50 ingots initially containing 1 and 7% PU according to the refining process. In the case of 1% PU specimens, the filtration was not effective in terms of decreasing the amount of NMIs, whereas the followed fluxing and gas bubbling treatments showed better refining effects. In the case of 7% PU specimens, the filtration was more effective than in the former case, and the effects of subsequent treatments were similar to observations made in the former case. In order to verify the type of inclusions that were mainly reduced by each refining treatment, other NMI analysis methods were introduced. Fig. 9 (a) shows the variation in the weight percentages of NMIs according to the refining process in refined ingots initially containing 7% PU, which were measured using an OES method. Fig. 9 (b) shows the

PU	Remelted	Filtration	Fluxing	Gas Bubbling (0.5/1.0 L/m)
1%				
7%				

Fig. 7. Variation in microstructures of remelted and refined ingots of AM50 magnesium alloy scraps initially containing 1 and 7% of polyurethane scraps according to the melt treatment.

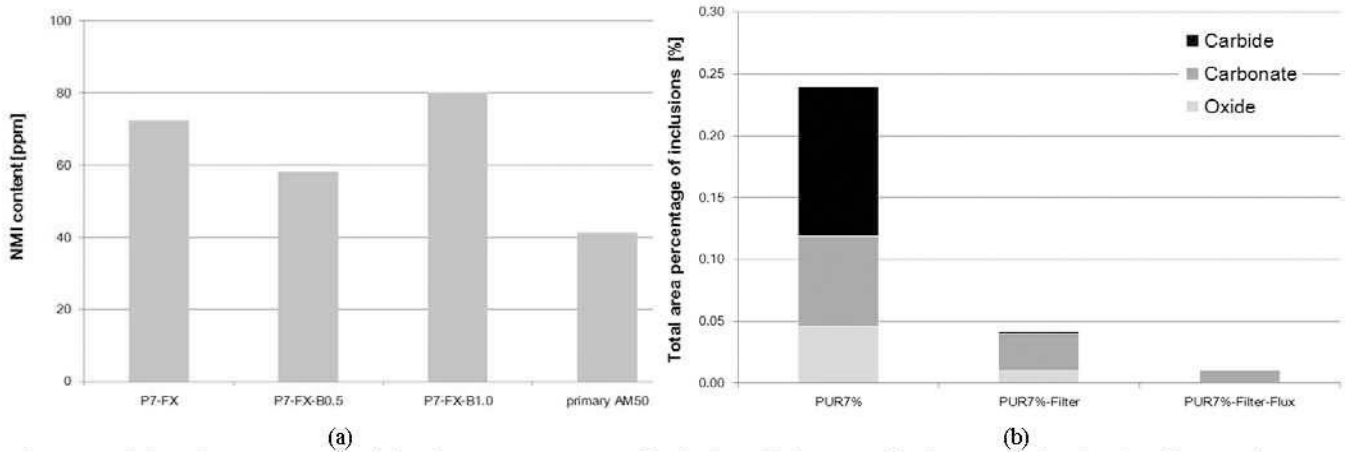


Fig. 9. Variations in NMI contents (a) and area percentages of inclusions (b) by types in the remelted and refined ingots of AM50 magnesium alloy scraps initially containing 7% of polyurethane scrap according to the melt treatment.

variation in the average area fractions of NMIs according to the refining process in the same ingots, which were measured using an automated particle analyzer on the EDS mapping images. From the OES analysis results, it was concluded that the NMI contents did not show a significant change according to the refining treatment. Also, the NMI content of refined ingots was slightly higher than that of the remelted AM50 primary ingot. Because the OES equipment used in this study can distinguish oxide-type inclusions only, the carbon, carbide, or carbonate content were not included in these results. On the other hand, the results from a particle analyzer include the classification of NMIs according to the chemical composition regardless of the type. However, carbon residues could not be distinguished from carbides due to the inherent limit of the EDS analysis and particles smaller than 3  $\mu\text{m}$  could not be identified due to the resolution limit of the 100 times magnified EDS mapping image. Therefore, it can be concluded that most of the carbon or carbide inclusions were reduced by filtration, whereas the carbonate and oxide inclusions were gradually reduced by the sequential refining processes.

### Conclusions

The NMI content in magnesium alloy scrap contaminated with polyurethane was effectively reduced by a sequential refining process consisting of filtration, fluxing and gas bubbling treatments. The filtration could reduce most large inclusions such as carbon residues originating from the decomposed polyurethane. The following fluxing and gas bubbling treatments effectively removed the small inclusions such as carbonates and oxides. However, a separation process before the remelting and refining process should be employed to avoid discharging a huge amount of fume which may contain harmful gasses such as dioxin during the remelting process of polymer-contaminated scrap.

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