

Recycling of Magnesium Alloy Scrap by Remelting and Chemical De-coating Process

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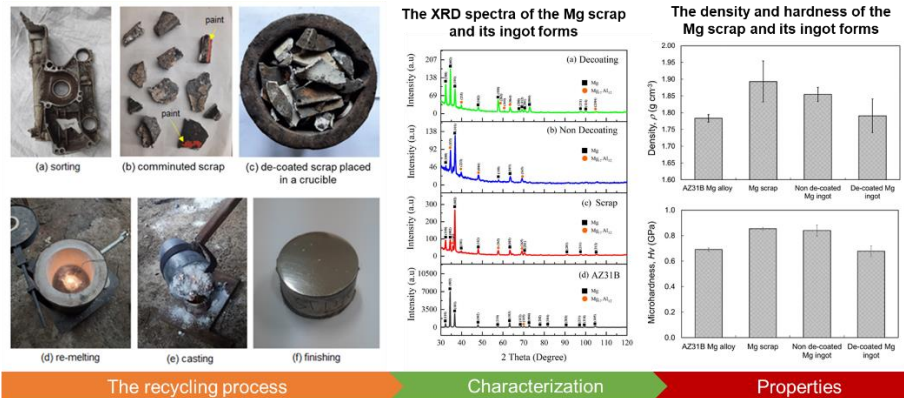
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Abstract: The growing demands of magnesium (Mg) based materials had risen new challenges related to disposal of unused parts and a huge amount of waste made by such metals. Attempts to recycle the scrap of these materials through remelting had become one of the preferred choices. However, a series of preliminary steps should be carried out to reduce the impurities as well as to maintain the quality of the casted ingot, for instance, by applying de-coating for removing paints or coating substrates at the scrap surface prior to remelting. In this research, the effects of chemical reagent de-coating on the properties of ingot obtained from recycling Mg scrap were studied. A commercial paint removal liquid was preferred as the reagent for removing paint layers over the Mg scrap surface. The de-coated scrap was then remelted in a conventional furnace with NaCl powder as the fluxing layer. The results of this study noticed the importance of chemical de-coating process to reduce the impurity contents in the ingot which might be originated from the coating or paint substrates covering the Mg scrap. Meanwhile, the density and hardness of the Mg ingot processed without de-coating were obviously higher than that had been cleaned previously with paint removing agent.

Keywords: chemical de-coating; magnesium; recycling; remelting; properties.

Graphical abstract

RECYCLING OF MAGNESIUM ALLOY SCRAP BY REMELTING AND CHEMICAL DE-COATING PROCESS



1. Introduction

Since 1990s, magnesium (Mg) and its alloys have been increasingly used as a promising metallic material for automotive components owing to its low specific gravity but having appropriate mechanical properties required for several automobile parts, such as powertrains and automotive bodies, instrument panels, beams, transfer cases, steering components and radiator supports [1, 2]. The growing applications of Mg and its alloys in the automotive industries are originally driven by the policy of reducing vehicle weight for energy saving and lower environmental impacts [3]. Currently, Mg and its alloys have become more popular since their increasing utilizations as a candidate material for bioresorbable implants [4, 5]. With such growing demands, new challenges have, on the other hand, risen related to disposal of unused parts and a huge amount of waste made of such Mg-based materials [6]. Attempts to recycle these materials had nowadays become one of the preferred solutions to overcome those problems.

Actually, Mg and its alloys are hard to be recycled by remelting process, mainly because of their high reactivity with oxygen and susceptibility to fire-up below their melting temperature [7, 8]. In addition, contamination of Mg and its alloy scraps due to the previous product processing, such as coating and painting, also caused difficulty in acquiring high-quality die-casted ingots that could meet ASTM standard [6]. Once a remelting process was conducted for a painted or coated Mg scrap, a contaminated ingot would be achieved together with a large amount of dross and harmful gas emission. Therefore, careful pre-treatments should be carried out prior to recycling such Mg-based materials.

Basically, the recycling process of light metals consisted of the following steps: (1) comminution, (2) sorting, (3) de-coating and (4) remelting [9]. Initially, comminution is conducted to reduce the sizes and shape variations of the scrap prior to remelting, so that a higher melting rates and finally an ingot with higher bulk density can be achieved. The comminuted scrap is then sorted to separate it from the unwanted parts. This step is principally aimed to lower the impurity levels of the ingot obtained from remelting. In some cases, sorting cannot completely liberate the scrap from the materials that would be the sources of contaminations, such as paints and coating substrates sticking at the surface of the scrap. To tackle this problem, de-coating is therefore conducted to remove all these coating substrates prior to the remelting of the scrap.

So far, thermal de-coating is the commonly used technique for pre-treating the scrap before the remelting. In this treatment, the scrap is heated up to temperatures that allow thermal and chemical decompositions of the coating substrates, through which organic compounds that composed the outermost layer could be removed from the scrap surface through volatilization

[9]. The earlier works [10-13], for instance, showed the importance of thermal de-coating as a pre-treatment during the recycling of Mg- and Al-based materials. Despite simple, this thermal-based treatment could not eliminate inorganic compounds [12]. Besides, the gaseous products emitted from de-coating process and the resulting carbon might be harmful and contaminating the de-coated material [9]. Therefore, additional strategies should be taken to enhance cleanliness of the scrap material prior to remelting, e.g., by using chemical reagent de-coating. Although it was promising, chemical de-coating method is actually more complex than thermal de-coating and still rarely reported in open literature, causing difficulty in finding references for performing such technique for recycling Mg-based scrap.

In this research, the effects of chemical reagent de-coating on the ingot obtained from recycling Mg scrap were studied. A commercial paint removing liquid was preferred as the reagent for removing paint layers over the Mg scrap surface. The de-coated scrap was then remelted in a conventional furnace with NaCl powder as the fluxing layer poured over the top surface of the stacking scrap within the furnace. The resulting Mg ingot was then characterized in terms of its chemical compositions, density and microhardness.

2. Materials and Methods

In this research, the Mg-based scrap was prepared with three steps of pre-treatments prior to remelting, i.e., (1) scrap sorting, (2) comminution and (3) chemical de-coating and cleaning. Unlike to the recycling procedure proposed by Capuzzi and Timelli [9], the scrap was first sorted before the size reduction step was carried out to ease a hand-sorting and selection of such a scrap based on their markings and shapes further processes. A photograph of a sorted and isolated Mg-based scrap that would be recycled in this experiment is shown in Figure. 1(a).

The sorted Mg scrap was then subjected to manual comminution by hand-hammering to reduce and homogenize its size, such as shown in Figure. 1(b) and then placed in a lab-scale, 100 mm diameter crucible shown in Figure. 1(c) for a melting process. The size of the comminuted scraps were determined in terms of their circular equivalent diameter (D). For this purpose, a 2-dimensional (2D) image analysis of the scrap in Figure. 1(b) was conducted and the D value was determined by using Eq. (1):

$$D = (4A/\pi)^{1/2} \quad 1$$

where, A is the 2-dimensional area of the scrap, which could be determined by using image analysis. With this method, the average size of the scrap in this research was 7.96 ± 1.71 mm. As also seen in Figure. 1(b), several scraps were obviously painted and this would be introducing impurities on the recycled product. Therefore, a de-coating process was then carried out prior to the melting and casting of the Mg scrap.



Figure. 1. *The recycling process of the magnesium scrap in this research.*

Table 1. *Chemical compositions of the paint removal agent used in this research*

Elements	wt. %
Dichloromethane	<90
Parrafin	<2
Naphta (petroleum)	<5
Alcohol	<10
Ammonium hydroxide	<1

In this research, chemical de-coating was conducted by immersing the sorted and comminuted Mg scrap into a bath containing paint removal agent (VIP Paint Remover, PT. Avia Avian, Indonesia) for 30 min until all the coats and paints were removed from the scrap surface. Table 1 shows the chemical compositions of the paint removal agent used for the scrap de-coating process in this research. To increase the removal rates, a manual stirring by using a spoon was conducted after 30 min of scrap immersion in the paint removal agent. Once all the coats and paint had been removed from the surface, the scrap was cleaned up in flowing tap water and then dried at atmospheric temperature.

The melting process of the magnesium scrap in this research was carried out by using a custom-designed gas furnace, in which a crucible containing Mg scrap was placed and heated, such as shown in Figure. 1(d). To prevent the molten scrap from oxidation in the atmospheric environment, a shielding strategy was conducted by pouring fluxing NaCl powder (Bratachem, Indonesia) over the outermost part of the scrap. The melted magnesium was then casted at a temperature of ~680 °C and ground prior to characterizations, such as shown in Figure. 1(e) and (f), respectively.

The Mg-based scrap and its ingot forms obtained in this research were characterized in terms of their chemical compositions and compounds, microstructure, physical density and microhardness. Their chemical compositions were determined by using Metavision 1008i

Spectrometer (Metal Power Lab., India). Meanwhile, elemental analysis by using energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) were carried out to aid in determining compounds that were formed at the Mg-based scrap and its ingot forms. Microstructural observation of the Mg-based scrap and its ingot forms was carried out by using optical microscope (Olympus, Japan), with an etching pre-treatment by using a solution composed of 1 ml acetic acid and 150 ml ethanol diluted in 50 ml water. Finally, the densities and microhardness of all the specimens were measured by using Electronic Density Meter (LiYi, China) and Vickers microhardness tester (Buehler, USA), respectively.

3. Results and Discussion

In this research, a sorted Mg scrap had been successfully recycled through a remelting process at a temperature of ~ 700 °C. A salt flux layer was created by pouring NaCl powder over the top of the scrap and it could effectively reduce oxidation of the scrap and the amount of dross formed during the remelting process, such as seen in Figure. 1(e). In earlier work, Kimura et al. compared direct remelting of painted and chemically stripped Mg scrap using salt flux on laboratory scale [14]. They noticed generation of a large amount of dust and off gas during the remelting process as a result of decomposition of organic resin in the former case [14]. Meanwhile, Meskers et al. reported chemical interactions that occurred between the coating substrates and the Mg scrap, alloying elements and salt flux during the remelting process [10].

The interaction between the coating substrate with Mg resulted in metal loss due to the formation of magnesium oxide or solid (inter)metallic particles. The coating substrate could also dissolve to Mg liquid, which could eventually lead to the changes in metal composition and quality [10]. In this research, a cylindrical ingot having a diameter of 20 mm was achieved, as indicated in Figure. 1(f). This ingot was then cut, ground and polished to examine its structural integrity. As can be seen in Figure. 1(f), the resulting Mg ingot was obviously intact, having no indications of defects at its surface and interior.

Table 2. Chemical compositions of the Mg scrap and its ingot forms

Elements	wt. (%)			
	Scrap	Recycled without de-coating	Recycled with de-coating	AZ31B Mg alloy
Al	5.4955	>15.000	5.3341	2.0619
Cu	0.2865	>0.5000	0.4520	0.2257
Mn	0.1277	0.2127	0.1627	0.1800
Zn	2.4474	>2.5000	>2.5000	2.2997
Ca	<0.0100	<0.0100	<0.0100	<0.0100
Ag	0.0133	0.0335	0.0262	0.0097
Si	>0.2500	>0.2500	>0.2500	>0.2500
Fe	>0.0250	>0.0250	>0.0250	>0.0250
Ni	0.0027	0.0083	0.0030	0.0218
Be	<0.0080	<0.0080	<0.0080	<0.0080
Cd	0.0092	0.0105	0.0092	0.0098
Sn	0.0684	0.0635	0.0687	0.0528
Sr	<0.0005	<0.0005	<0.0005	<0.0005
Ce	>0.0200	>0.0200	>0.0200	>0.0200
La	>0.0250	>0.0250	>0.0250	>0.0250
Mg	91.2019	76.8123	90.3585	94.8019

The chemical compositions of the Mg scrap and its ingot forms with and without the de-coating process in this study are shown in Table 2. For comparison, the compositions of a plate made of AZ31B Mg alloy used in the previous studies [15, 16] were also presented in this table. As seen in Table 2, both the Mg scrap and its ingot forms demonstrated the presence of Al and Zn as their major elements. It is also noticed from this spectroscopic data that the amount of Mg and Zn contents of the Mg scrap were comparable to those of AZ31B Mg alloy, i.e., around 91 – 95 wt.% and ~2.2 – 2.4 wt%, respectively. Meanwhile, the Al content of the scrap was slightly higher, i.e., ~5.5 wt.%, than that of the reference alloy, i.e., ~2.1 wt.%. The importance of de-coating process conducted in this study was demonstrated by the lower contents of Al, Cu and Mn at the de-coated ingot; which might correspond to the presence of coating or paint substrates covering the Mg scrap. With such a de-coating step, all these paint or coating layers could be removed, resulting in the increased Mg content in the ingot. This finding confirmed the work reported by Wang et al. [12] which demonstrated that chemical reagent de-coating was more effective in removing coatings over the scrap material than the thermal assisted de-coating treatment. The earlier work of Meskers et al. [10] reported the use of thermal decomposition at temperatures between 200 and 450 °C for removing paint layers over the scrap surface. According to their work, the organic resin that built up the paint layers decomposed at this temperature range in argon or air atmosphere. However, the non-volatilized material, for instance pigments, fillers and certain coating substrates could not be removed and remained exist over the scrap surface, leaving residues in the form of TiO₂, CaO, BaSO₄, SiO₂ and Fe₂O₃.

Figure. 2 shows a series of microstructural images of Mg scrap, its ingot forms and AZ31B Mg alloy. As can be seen in this Figure, the microstructures of all these materials were apparently similar, showing typical granular grain of Mg-Al-Zn alloy [7]. The microstructure of ingot with and without de-coating in this research are actually hard to be distinguished.

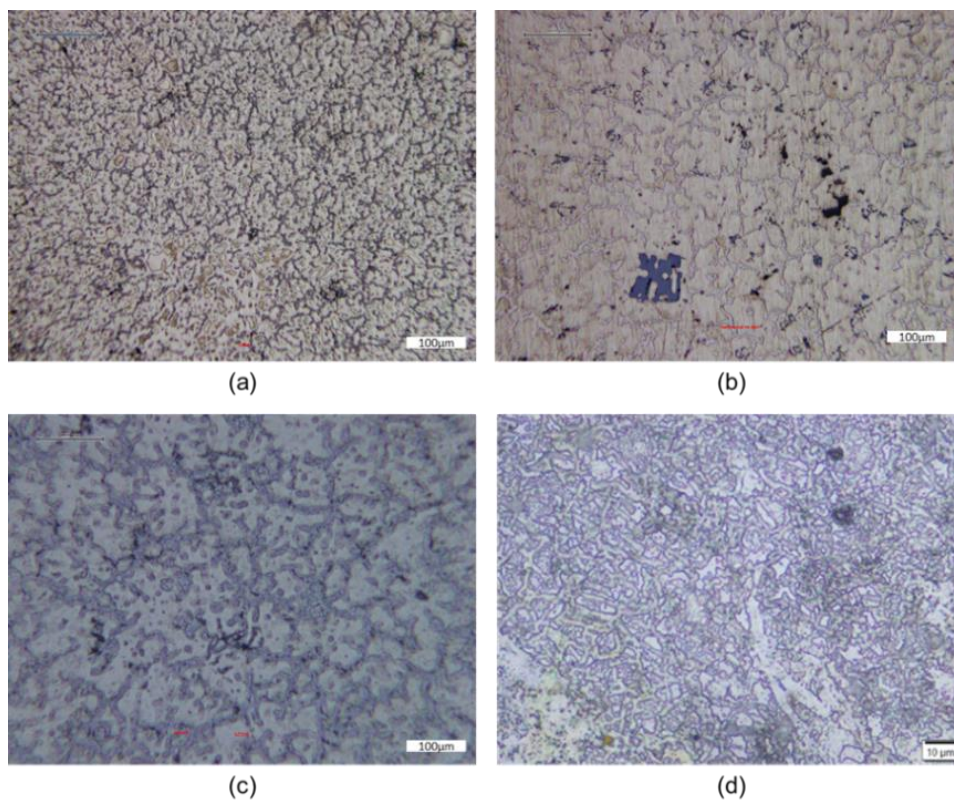


Figure. 2. Microstructures of (a) Mg scrap, (b) non de-coated ingot, (c) de-coated ingot and (d) AZ31B Mg alloy

The result of SEM-EDS analysis shown in Figure. 3 confirmed the presence of Al and Zn as the major components of the recycled Mg scrap in this research. Figure. 3(a) presents the backscattered electron image of the microstructure of de-coated ingot, in which distinguished bright and dark regions could be clearly seen indicating the Mg-Al-Zn and Mg-Al phases of this ingot, as revealed from the EDS spectra in Figures. 3(b) and (c), respectively.

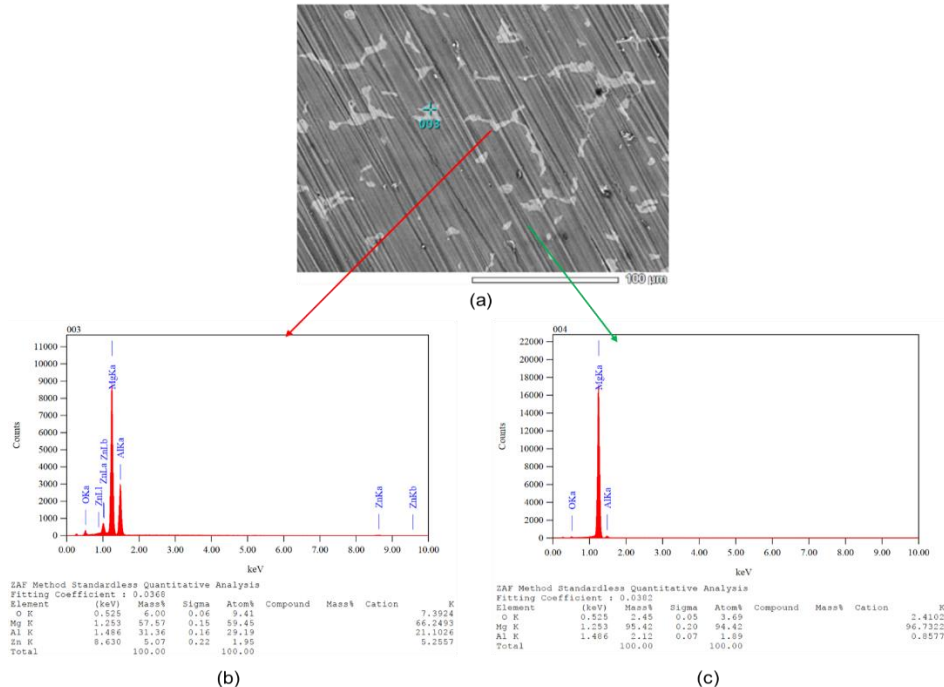


Figure. 3. The electron-microscopic images and EDS spectra of the de-coated Mg ingot

The XRD spectra in Figure. 4 obviously shows a scrap and ingots composed of Mg and Al contents, similar to those indicated by the reference AZ31B alloy. As can be seen in this Figure, all the spectra showed the peaks corresponding to the presence of Mg and Mg₁₇Al₁₂ phases. The peaks indicating the Mg phase within the scrap and the reference alloy appeared at $2\theta = 165^\circ$, but a similar peak was also seen for the scrap at $2\theta = 262^\circ$. As noted from Figures. 4(a) and (b), both the non de-coated and de-coated ingots all showed the presence of these two phases. This finding was confirmed by the work of Dudek et al. who showed the presence of α -Mg and β -Mg₁₇(Al, Zn)₁₂ phase within a recycled AZ91 Mg alloy scrap [7].

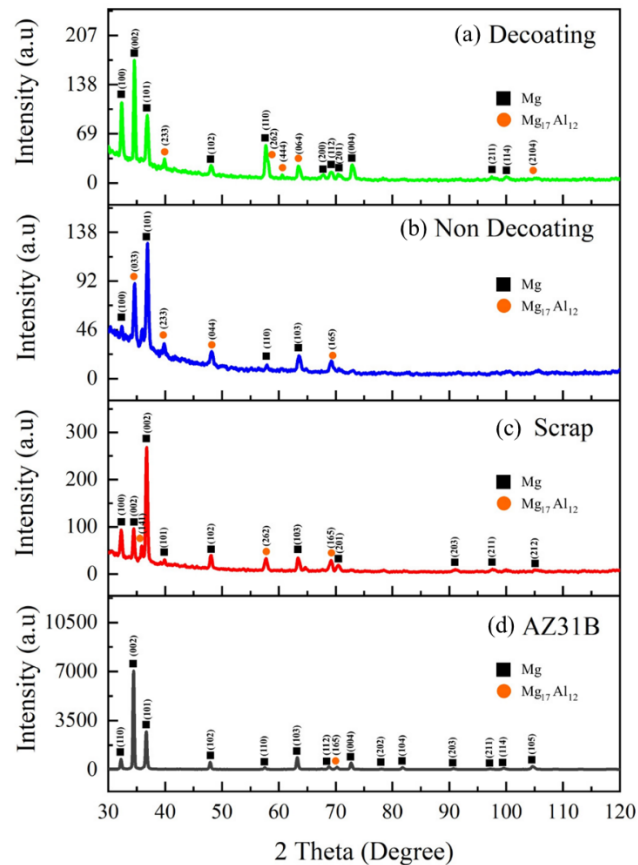


Figure 4. XRD spectra of the Mg-based scrap, its ingot forms and AZ31B Mg alloy

The densities of the Mg scrap and its ingot forms are shown in Figure. 5, together with that of a reference specimen made from a commercial AZ31B Mg alloy. As seen from this Figure, the densities of the Mg scrap and its ingot processed without de-coating were obviously heavier than that pre-treated with de-coating. The weight addition at the Mg scrap might correspond to the presence of impurities derived from paints and coating substrates that dissolved into the molten Mg during the remelting process. It is also important to note that the density of the de-coated ingot obtained from this research was comparable to that of the referenced Mg alloy material; confirming the formation of ingot having major components of Mg, Al and Zn.

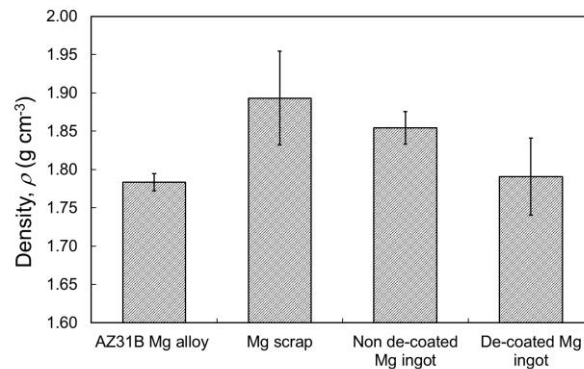


Figure 5. The density of Mg-based scrap, its ingot forms and AZ31B alloy used in this research

In addition to the ingot density, the result of microhardness measurement confirmed the main compositions of the de-coated ingot which consisted of Mg, Al and Zn. As shown in Figure. 6, the hardness of the de-coated ingot was also comparable to that of the reference AZ31B Mg alloy. Meanwhile, the Mg scrap and the non de-coated ingot were slightly harder than the de-coated ingot and the reference alloy.

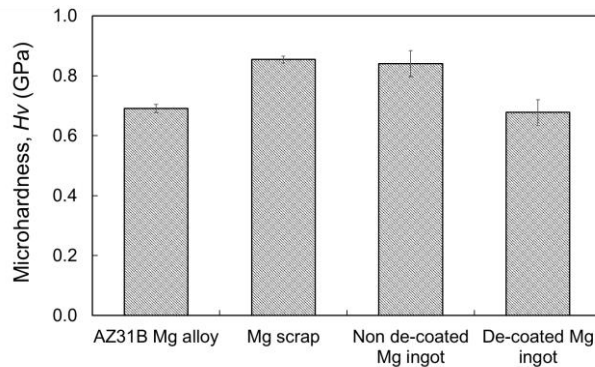


Figure. 6. The hardness of Mg scrap, its ingot forms and AZ31B Mg alloy

4. Conclusion

In this research, the effects of chemical reagent de-coating on the compositions and properties of ingot obtained from remelting Mg scrap were studied. On the basis of the experimental results obtained in this study, it is confirmed that the scrap and ingot were composed mainly by Al and Zn. Meanwhile, chemical de-coating process with paint removal agent could effectively reduce the impurities in the casted Mg ingot and yielded a casted material that possessed density and hardness close to the Al-Zn based Mg alloy. With this findings, it is also confirmed that the commercial paint removal such as that used in this research could effectively improve the quality of Mg ingot obtained from a scrap recycling process. This technique might be promising to be applied in foundry and metal recycling industries as well as contributing in the sustainability of light metallic materials such as magnesium.

4.1 Acknowledgments

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